The Hydrogen Bond

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The Hydrogen Bond

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W. H. FREEMAN AND COMPANY
SAN FRANCISCO AND LONDON

Trade distributor: Reinhold Publishing Corporation, New York, N. Y.

LIBRARY OF CONGRESS CATALOGUE CARD NUMBER: 59-7482

PRINTED IN THE UNITED STATES OF AMERICA (C2)

TO OUR FATHERS

Who lacked college degrees

But not the vision and will to guarantee ours.

PREFACE

The hydrogen bond has been of great interest to chemists over the last three decades, and has stimulated a large and growing volume of study. A number of symposia have been conducted; the most recent, the 1957 Ljubljana Symposium on the Hydrogen Bond, attracted scientists from all over the world. Yet there has been no comprehensive and critical review to unify the mass of literature on this topic. The need for such a review is amplified by the breadth of recent applications of the hydrogen bond, particularly in biochemical problems. We hope this book will fill that need and accelerate the growth of understanding of this chemical interaction.

We have written *The Hydrogen Bond* with emphasis upon the physical and chemical facts and with three primary goals in mind. The first is to compile and summarize these experimental facts, thus furnishing a basis for prediction and interpretation of hydrogen bond behavior in substances not yet studied. The second is to present a critical discussion of the present state of the theory of this bond and its effects on physical and chemical behaviors. The third is to present a bibliography (comprehensive through 1956) which will aid workers in locating relevant studies.

We have not attempted to delve into the many interesting applications of hydrogen bonding systems. Chapter 11 offers only a brief survey of some applications, to indicate the wide range of possibilities. Even in Chapter 10 (which treats proteins) attention is largely focused on one phase—the role of the hydrogen bond in fixing protein structures.

Naturally our judgment has entered in deciding the relative weights to be given various topics. Furthermore, we offer critical discussions to supplement the factual record. Thus, we have tried to aid the worker new in this field while retaining the depth required by specialists. Though mathematical detail has been omitted, we have striven for precise statement of conceptual material.

The subject matter of *The Hydrogen Bond* contains many interesting questions which are as yet unanswered. The effort which has gone into this book will be well justified if its readers are stimulated to study these challenging problems.

We would like to acknowledge the advice and encouragement we have received from all of our colleagues. Specific parts of the manuscript were read by Drs. E. D. Becker, R. E. Connick, F. C. Goodrich, F. E. Harris, P. S. Magee, T. Miyazawa, C. T. O'Konski, W. G. Schneider, D. H. Templeton, and J. R. Thomas, and their criticisms were valuable.

We thank Mr. Roger Hayward for his artful treatment of the figures—and his originality in suggesting some of them.

We appreciate the many valuable stenographic and photo-copying services made available by California Research Corporation, Richmond, as well as the aid received from their Technical Information Center in procuring some of the bibliographic material.

Finally, we must praise the untiring and conscientious secretarial work of Mrs. Wilma Whittlesey whose spark of cheer was not extinguished by many rough drafts.

May 1959

GEORGE C. PIMENTEL

AUBREY L. McCLELLAN

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Dimroth ring
chelate ring
proton bond

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$\mathrm{A{-}H} \longleftarrow \mathrm{B}$

$\mathrm{A{-}H} \cdots /\mathrm{B}$

$\mathrm{A} \cdots \mathrm{H}_b \cdots \mathrm{B}$

${}_{\mathrm{A}}\mathrm{H} \cdots \mathrm{B}$

$\mathrm{AH} \cdots \mathrm{B}$

$\mathrm{A(H} \cdots \mathrm{B)}$

German	*wasserstoffbindung*
	wasserstoffbrücke
French	*liaison hydrogène*
	pont hydrogène
Dutch	*waterstofbruggen*
Spanish	*hidrogéno puente*
Italian	*legame a idrogeno*
Russian	водородная связь
Japanese	水素結合

CHAPTER 1

Introduction

Water . . . shows tendencies both to add and give up hydrogen, which are nearly balanced. Then . . . a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together. . . . Indeed the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation.

Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak "bond."[a]

W. M. LATIMER and W. H. RODEBUSH *University of California, Berkeley, 1920.*

It is fitting to open a treatise on the hydrogen bond with this remarkably accurate description of the structure of water, given almost four decades ago by Latimer and Rodebush (1201). It is an amazing fact that every word of their description remains acceptable in the contexture of chemical knowledge today. But the true historical importance of this statement derives from its pioneering invasion of a frontier of chemistry that even today presents uncertain footing to the chemist. This is the borderland between chemical bonds and the weaker and less specific interactions that cause every known substance

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[a] From *J. Am. Chem. Soc.* **42**, 1419–33 (1920).

to liquefy if the temperature is sufficiently low. To provide a basis for consideration of the H bond,[a] these two extremes should be examined.

1.1 Types of Bonds

1.1.1 Chemical Bonds. A molecule is an aggregate of atoms in a distinct three dimensional arrangement. Such aggregates, which are conveniently considered as entities, are held together by chemical bonds in a number and pattern described by the molecular formula. Widely applicable and simple rules of valence predict the molecular formulae to be found in nature. The fragmentation or major rearrangement of such an aggregate involves energy quantities of the order of tens of kilocalories.

1.1.2 van der Waals Interactions. All such aggregates of atoms can be brought to a sufficiently low temperature to effect a change to a condensed (liquid) phase. This condensation indicates additional attractive interactions among the molecules. These attractive interactions involve much smaller energy quantities, usually in the range of a few tenths of a kilocalorie. The transition from gas to liquid is readily reversible, and many of the properties of the molecular aggregates are virtually unchanged. The lack of specificity, the difference in energy, and the ease of reversibility make convenient a differentiation of such interactions from chemical bonds. These weaker attractive forces are called van der Waals forces.

1.1.3 Association and the Hydrogen Bond. Between these extremes there are interactions of intermediate energies which produce clusters of the molecular aggregates. Since these clusters conform in many respects to the criteria identifying molecules, the interactions holding them together might again be classified as chemical bonds. Indeed, they *are* chemical bonds, but the relative weakness of the bonds gives them distinctive properties that warrant a distinguishing name. Hence these clusters are called "complexes," and the process of forming them is called "association." The most striking property distinguishing most complexes from most molecules is the rapid reversibility of the association under normal laboratory conditions.

The H bond is such an "associative interaction": the energy of

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[a] Hereafter we shall use the abbreviation H, for hydrogen, in "H bond" and related terms such as "H bonded," "H bonding." However we do not wish to propagate the abbreviation in substitute for the usual term "hydrogen bond." To emphasize this we have uniformly used the article "a" with the abbreviation as a reminder that the expression "a H bond" is to be vocalized as "a hydrogen bond."

breaking a H bond is of the order of a few kilocalories; clusters of molecules are held together in specific orientations and often in well defined numbers; the equilibria among the clusters and their component molecular parts are rapid and reversible.

1.2 The Occurrence and Definition of the Hydrogen Bond

1.2.1 Historical Background. Many years ago scientists recognized that special theories were necessary to explain the behavior of associated compounds (1497). Empirically they found that association was more likely among molecules containing certain functional groups than among others. For example, alcohols and phenols formed associated complexes readily, whereas hydrocarbons did not. A particularly tenacious interaction was recognized in molecules with hydrogen-containing functional groups. But before the cause of such association was discerned, there were some early proposals in which hydrogen was assigned the unusual bonding position we now associate with the H bond. In 1903 Alfred Werner proposed that an ammonium salt has a configuration in which a proton lies between the ammonia molecule and the ion, linking the two (2158). He symbolized the interaction $(H_3N \cdots H)X$. Several years later Moore and Winmill concurred with Werner in proposing a H bonded structure of undissociated trimethyl ammonium hydroxide, thus accounting for its slight dissociation as compared to tetramethyl ammonium hydroxide (1444). They display a figure representing a structure of $(CH_3)_3NHOH$ in which a hydrogen atom is placed between the oxygen atom and the nitrogen atom. The bonds connecting these three atoms are considered as differing, which is indicated by a heavier line drawn between the H and O.

Quite independently, and only three years after Werner's proposal, Oddo and Puxeddu proposed *intra*molecular H bonded configurations for some azo derivatives of eugenol (1536). Seven years later Pfeiffer made a similar proposal of an *intra*molecular "*inner Komplexsalzbindung*" between the hydroxyl and carbonyl functional groups in 1-hydroxyanthraquinone (1624).

Then in 1920 two young men working in the laboratory of G. N. Lewis recognized the cause of the association of water, the cause of its unique chemical and physical properties. W. M. Latimer and W. H. Rodebush had the genius to recognize the H bond and the audacity to propose it, in departure from the well substantiated octet rules of valence[a] (1201). The impact of their proposal was intensified by its lucidity and its accuracy, and by the importance of the chemistry of water.

From these early beginnings welled a rising number of studies of H bonding. As the common occurrence and importance of this weak bond has become apparent, the volume of work using the concept of a "shared" proton has grown tremendously and at an increasing rate. Figure 1-1 shows in curve A the growth over approximately the last twenty-five years of the scientific literature abstracted in *Chemical Abstracts*, and in curve B the rising percentage of those publications which concern or invoke H bonding. Over the last decade, though the rate of scientific publication has more than doubled, the percentage of articles mentioning H bonding has approximately quadrupled. In order to treat the subject adequately it was necessary to consider over 3,000 papers in the literature study that formed the basis for this work.

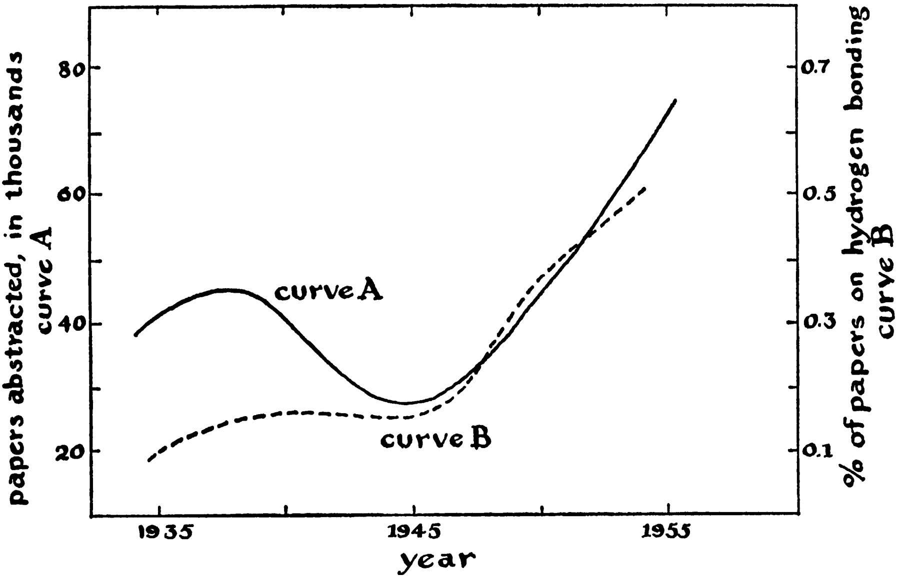

FIGURE 1-1 Growth of chemical literature and hydrogen bonding literature.

1.2.2 Occurrence of Hydrogen Bonds. The mass of literature with

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[a] Indeed, among the personal papers of Wendell M. Latimer is recorded the remark that the first response of G. N. Lewis to the manuscript of the now-famous Latimer and Rodebush paper was to suggest the deletion of the H bond proposal because of its contradiction of these rules.

which working scientists are presently struggling reveals the variety of conditions under which H bonding can occur. It is clear that the interaction involves two functional groups in the same or different molecules. One of these groups must serve as a proton donor (an acidic group) and the other as an electron donor (a basic group). Most commonly the proton is donated by a carboxyl, hydroxyl, amine, or amide group. The hydrogen from S—H or C—H can take part in hydrogen bridges, but generally such bonds are weaker. Also the proton attached to a halogen can be active in association, and the properties of HF depend strongly on H bonding. Finally, and less well known, there are the H bonds formed by protons joined to Se, P, and other atoms. The usual electron contributing parts of the molecule are oxygen in carbonyls, ethers, and hydroxyls; nitrogen in amines and in *N*-heterocyclic compounds; and halogen atoms in particular molecular environments.

1.2.3 Intermolecular Hydrogen Bonds. The widest general class of H bonding involves association of two molecules of the same or different substances. The resulting H bonded complexes are not limited to dimeric linkages. Multiply bonded arrangements occur in liquid water and in liquid HF, and they are common in alcohols, phenols, amides, proteins, polypeptides, and polyhydroxyorganic and inorganic materials. Intermolecular H bonds may produce chains, rings, or three dimensional networks. In crystalline solids they may occur in chains, rings, three dimensional networks, or even in spirals.

1.2.4 Intramolecular Hydrogen Bonds. The other broad class contains those substances in which the H bonds are formed between groups within a single molecule. This process was first called "chelation," (after the Greek *chele*, claw) because in some molecules the closing of a ring by H bonding is a pincer-like action resembling the closing of a crab's claw. A large part of this picturesque model is lost in proteins and in other large molecules that have *intra*molecular H bonds, so the more general term "*intra*molecular H bonding" is usual. Also, chelation now has common usage in reference to interactions with a metallic atom. However, we will use "chelate" and "*intra*molecular H bonding" interchangeably, and specify "metal chelate" when such substances are discussed.

1.2.5 Definition of the Hydrogen Bond. Because there are certain advantages and disadvantages in framing a precise definition of the H bond, as discussed in Chapter 6, justification of the particular definition used here will be postponed until then. Yet, it would be unwise to begin discussion of the H bond without giving some idea of the bounds of the topic in the eyes of the authors.

There is no universally accepted definition. Some definitions of the H bond are based on a single operational criterion (such as an infrared[a] spectral shift), others on a listing of suitable functional groups, and still others on a mathematical or physical picture of H bond formation. We will use the term "H bond" to refer to an interaction that fits the following operational definition:

A H bond exists between a functional group A—H and an atom or a group of atoms B in the same or a different molecule when

(a) there is evidence of bond formation (association or chelation),

(b) there is evidence that this new bond linking A—H and B specifically involves the hydrogen atom already bonded to A.

Paraphrasing this definition, we have required that there be some evidence of bond formation (either by forming larger molecular aggregates or by restricting a molecular configuration to maintain proximity of two groups) and also that there be some evidence that a specific hydrogen atom is intimately involved. It is convenient to separate parts (a) and (b) because there are many physical measurements that provide information relative to (a) but only a few substantiating (b). It is specifically criterion (b) that differentiates the H bond from other types of associative interaction.

1.3 Properties of Hydrogen Bonded Substances

The formation of a H bond in a solution or compound modifies a great many physical and a few chemical properties. Usually the properties are changed sufficiently to require special treatment for associated materials in any correlation of behavior. These changes are not surprising in light of the fact that H bonding may alter the mass, size, shape, and arrangement of atoms, as well as the electronic structure of the functional groups. The most important, or most commonly observed, physical property modifications are frequency shifts of IR and Raman bands, altered freezing and boiling points, solubility differences as a result of H bonding between solvent and solute, deviations from ideal gas and solution laws, changed dielectric properties and electrical conductivities, and proton magnetic resonance shifts. A large number of other properties are affected in some cases (normally those cases in which the strongest association bonds are present), and many

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[a] Infrared is abbreviated IR throughout this book.

of them have been used to study association. Some of these less important properties are liquid and vapor density, molar volume, parachor, viscosity, electronic spectra, and both heat and sound velocities.

The various effects might be clarified by discussing briefly the changes in the molecule which are responsible for the changes in observed characteristics. For example, the spectral changes indicate altered electron arrangements and positions of atoms in the neighborhood of the

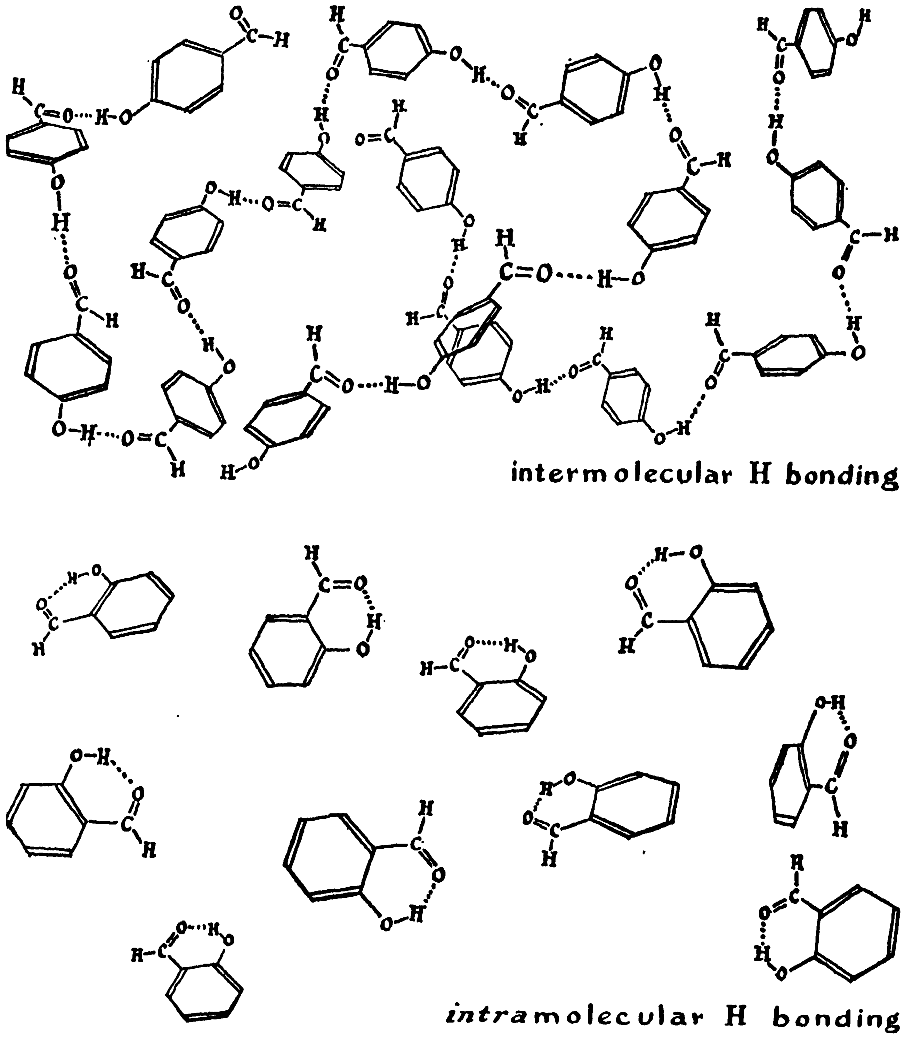

FIGURE 1-2 Comparison of the structure of associated chains and chelated molecules.

donor groups. The result is a stretching vibration of lower frequency and bending vibrations of higher frequencies. Several new vibrational modes are introduced. These are low frequency motions and have been reliably identified in only a few cases.

Hydrogen bonds can form *within* molecules as well as between molecules. Very different structures result, as pictured in Fig. 1-2. Of course, the properties of a substance depend strongly on whether the molecules exist as discrete, chelated individuals or are linked in long, possibly entwined chains. For example, pure compounds that form intermolecular H bonds have high freezing and boiling points because of the strong intermolecular forces. This effect is reduced or lost if the H bonding groups are so placed in the molecule as to permit *intra*molecular H bonds. Thus, the boiling points of *p*-chlorophenol, *o*-chlorophenol, and chlorobenzene are, respectively, 217°C, 175°C, and 132°C. The difference between the *para* and *ortho* compounds indicates how the effect of intermolecular H bonding is partially lost when *intra*molecular H bonding is possible.

Again, in solubility measurements, chelating molecules contrast in behavior to similar but nonchelating molecules. Chelated substances are generally more soluble in nondonor solvents. Intermolecular H bonded compounds are more soluble in an electron donating solvent that can interrupt the intermolecular bonds but still satisfy the H bonding tendency of the material.

Deviations from ideal gas and solution laws are caused principally by the increased molecular weight resulting when one complex unit is formed from more than one molecule. Electrical properties are un-

TABLE 1-I Comparison of Melting Point, Boiling Point, and Heat of Vaporization for Some Simple Substances

SUBSTANCE	MELTING POINT (°K)	BOILING POINT (°K)	HEAT OF VAPORIZATION AT THE BOILING POINT (KCAL/MOLE)
H_2O	273	373	9.72
H_2S	190	212	4.50
HF	181	292	7.20
HCl	161	189	3.87
NH_3	195	240	5.57
CH_4	89	112	2.21

usual for H bonded substances because the dipoles are affected by the positions of the hydrogen atoms, and in many materials the dipoles are aligned in special, orderly arrangements by polymeric complexing.

Table 1-I shows some properties of similar compounds. For each pair of compounds the first forms strong H bonds, as reflected by the higher melting point, boiling point, and heat of vaporization.

1.4 Importance of the Hydrogen Bond

The theory of the H bond remains one of the frontiers of our knowledge of chemical bonding. H bonding compounds are one of the classes of chemical substances which involve weak bonds and display unusual valence properties (e.g., the polyhalogens, metal chelates, boranes, Al_2Cl_6). The extent to which these situations are similar cannot be stated until theoretical developments advance considerably.

Only a few examples are needed to illustrate the broad application of the principles of the H bond. The structures of many organic crystals and inorganic crystalline hydrates are determined by the H bond. Similarly, it fixes the structures of the proteins, as has been so forcefully emphasized by Pauling during the last decade. Among the rapidly opening fields of application of H bonding are adsorption, catalysis, enzyme activity, dyeing, and kinetics.

In fact, man himself is fabricated of H bonding substances. We feed, clothe, and house ourselves in H bonded materials. What is the key to the catholic importance of this chemical interaction in our environment? It is, no doubt, to be found in the H bonding properties of water since all of the physical and chemical properties of water are determined or influenced by H bonding. And this interaction pervades our chemistry simply because all living things evolved from and exist in an aqueous environment. It is hardly an exaggeration to say that in the chemistry of living systems the H bond is as important as the carbon-carbon bond.

CHAPTER 2

Methods of Detection: Nonspectroscopic Techniques

> *On the basis of . . . a proposed internal structure for water, the following properties of water . . . have been deduced . . .*
>
> *. . . the crystal structure of ice . . .*
> *. . . the x-ray diffraction curve for water . . .*
> *. . . the heats of solutions of ions . . .*
> *. . . the mobility of hydrogen and hydroxyl ions . . .*
> *. . . the density and density changes of water . . .*
> *. . . the unique position of water among molecular liquids . . .*
> *. . . the dielectric properties . . .*
> *. . . viscosities of dilute ionic solutions . . .*[a]
>
> J. D. BERNAL and R. H. FOWLER *University of Cambridge, 1933*

In 1933 Bernal and Fowler showed that many of the properties of water can be explained with the aid of a model containing much local order and structure (199). These pioneering workers did not name the intermolecular linkage in their proposed structure, but it is now recog-

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[a] From *J. Chem. Phys.* **1**, 515–48 (1933).

nized as the H bond.[a] The list of properties that are known to be influenced by this association has grown to include most of the physical properties of H bonding systems.

Hydrogen bonds were first detected through solubility studies (1497), and were quickly found by the many other "classical" methods available in the first quarter of the twentieth century. Vapor pressure and vapor density, molecular weight, dielectric constant, partition or distribution, molar volume, parachor, refractive index, electrical and thermal conductivity, and acoustic behavior are a few of the physical properties that reflect the presence of the H bond.

Beginning in the mid-thirties, the IR and Raman spectroscopic techniques achieved major importance. Still later, neutron diffraction and nuclear magnetic resonance measurements became available to describe the positions of hydrogen atoms, thus providing a valuable supplement to x-ray studies.)

To codify the results of the many kinds of measurements we have chosen a grossly chronological approach for Chapters 2, 3, and 4, each of which treats certain methods of detection. Nonspectroscopic methods are grouped in this chapter, and the next two treat the newer techniques. In Chapter 2 we have chosen to make the main division by type of experiment: dielectric constant and dipole moment, vapor imperfections, solubility or partition coefficient, and so forth. This aids in illustrating the progress in each of these fields at the sacrifice of fragmenting the discussion of classes of compounds. Also, such division serves our aim of touching each major avenue of study without covering each substance exhaustively. There have been many reviews of H bonding systems and their nonspectral properties; those of Lassettre (1197), Hoyer (972), Hunter (1003), Davies (487), Lutskiĭ (1278), and Badger (99) are the most comprehensive.[b]

In this chapter the treatment of each topic proceeds from a brief introduction, through the methods and basic principles of detection, to a discussion of pure compounds, solutions, and mixtures. The study of *intra*molecular H bonding is taken up in Chapter 5, except for a few minor methods which hardly deserve treatment in two places.

The methods treated in Chapter 2 give only indirect information about the participation of the hydrogen atom in the H bond. In other

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[a] It is interesting that in their classic paper Bernal and Fowler pointedly avoided the term "H bond" in reference to water. Clearly, they were in doubt that the association of water should be called H bonding.

[b] Others are: 1737, 1165, 1738, 1005, 1736, 1530, 1903, 1002, 1123, 1120, 641, 818.

words, they provide information about criterion (a) in the definition of a H bond given in Section 1.2.5. Only by inference from the types of groups involved do they bear on criterion (b).

2.1 Dielectric Constant

2.1.1 Introduction. The use of electrical measurements has been fairly important in the study of H bond association. In the main, this is the result of three facts: (1) the experimental quantities are readily obtained; (2) dipole moments calculated from the measured quantities have directionally additive properties and therefore can often allow a choice between various possible structures; (3) dielectric dispersion studies permit separation of the several kinds of rearrangements that occur. The experimental determinations have increased in complexity as more extensive ranges of frequency are scanned in studying dielectric dispersion, as biological and polymeric substances become of interest, and as improved theories demand more accurate data. The advantage of the directional aspects of the dipole vector is somewhat nullified by extraneous effects of the solvent and of parts of the molecule not involved in H bonding.

The classical treatment of nonpolar dielectric materials is expressed by the Clausius-Mossotti equation. Polar materials in nonpolar solvents are better handled by Debye's modification, which allows for the permanent dipole of the molecule. Onsager made the next major step by taking into account the effect of the dipole on the surrounding medium, and finally Kirkwood treated the orientation of neighboring molecules in a more nearly exact manner. (See Table 2-I.) The use of these four theoretical expressions can be quickly narrowed. Because of their limitations to nonpolar liquids or solvents, the Clausius-Mossotti and Debye equations have little application to H bonded systems. Kirkwood's equation has great potential interest, but in the present state of the theory of liquids the factor g is virtually an empirical constant. The equation has been applied in only a few cases.

The Onsager equation is the one most used for H bonded systems. For solutions, the experimentally determined dielectric constant is commonly plotted in terms of polarization (see Table 2-I) against concentration. Extrapolation to infinite dilution gives P_∞ and hence the dipole moment. The last steps require knowledge of the electronic (P_E) and atomic (P_A) polarizations. The value of P_E is usually found from refractive index values, and P_A (fortunately small) is estimated or

TABLE 2-I Comparison of Equations Relating Dielectric Constant and Dipole Moment

NAME OF EQUATION	DATE PUBLISHED	EQUATION	USEFUL FOR
Molar polarization		$P = \frac{M}{d}\frac{(\epsilon - 1)}{(\epsilon + 2)}$	—
Clausius-Mossotti	1850–1880	$\alpha_o = \frac{3M}{4\pi Nd}\frac{(\epsilon - 1)}{(\epsilon + 2)}$	Nonpolar gases and liquids
Debye	1912	$\mu_o = \frac{9kTM}{4\pi Nd}\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right)$	Polar gases Polar gases in nonpolar solvents (dilute)
Onsager	1936	$\mu_o = \frac{9kTM}{4\pi Nd}\frac{(2\epsilon + \epsilon_\infty)(\epsilon + 2)}{3\epsilon(\epsilon_\infty + 2)}\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right)$	Polar liquids
Kirkwood	1939	$g\mu_o = \frac{9kTM}{4\pi Nd}\frac{3(2\epsilon + \epsilon_\infty)}{(\epsilon_\infty + 2)(2\epsilon + 1)}\left[\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right]$	Polar liquids

α_o = polarizability

μ_o = permanent dipole moment

ϵ = dielectric constant

ϵ_∞ = dielectric constant at infinitely high frequency

M = molecular weight

N = Avogadro's number

d = density

k = Boltzmann's constant

T = temperature (°K)

g = a constant (for given substance, temperature, concentration) accounting for restricted rotation of neighboring molecules.

neglected. Smyth (1906) describes the method and the alternative Hedestrand method in which ϵ and density are plotted against concentration. From the slopes and intercepts of these lines, P_∞ is calculated and, as before, yields μ. The Hedestrand procedure has the advantages of linear extrapolations and lower sensitivity to contamination. Smyth summarizes by saying that solution values are usually more accurate, and they may differ by as much as 10 percent from gas dipole moments. These developments can be followed in works on dielectric properties, such as that of Brown (305), which highlights the physical and mathematical aspects, and that of Smyth (1906), which stresses chemical behavior. Smyth also describes (in his Chapter VI) the measurements and some of the precautions necessary. Latimer (1200) published a review specifically dealing with dielectric constants of H bonded materials. There are also available several compilations of data (2160, 2).

We will discuss dielectric effects in H bonded substances in two broad categories: structure determination, and dispersion measurement. The first includes configurations, the solvent effect, and association between the solute and the solvent. The second touches on relaxation times, ferroelectricity, and the structure of complexes.

2.1.2 Structure Determination. It is not possible to make a simple statement about the effect of H bonding on dielectric constant or dipole moment. The following generalizations are valid.

1. Dielectric constant and dipole moment do not increase together. (See Table 2-II.)
2. High values of ϵ are usually found in intermolecularly H bonded substances in which noncyclic association occurs.
3. Low values of ϵ are usually found in *intra*molecularly H bonded substances. (*Intra*molecular H bonds are discussed in Chapter 5.)
4. The arrangement of atoms within a molecule and, with less confidence, of molecules in a polymeric unit can be determined by comparing the measured dipole moment with values calculated by the vectorial addition of bond dipole moments for various arrangements.
5. H bond formation between the components of a solution are inferred in the same fashion as in number 4.

Table 2-II illustrates the first three points. Compare the ϵ and μ values of the first eight compounds. Whereas ϵ varies over about a sixteenfold range, μ does not change by a factor of four. Contrast these H bonded compounds with those at the bottom of the table to confirm

the high ϵ values in associated substances (nitrobenzene is a conspicuous exception).

TABLE 2-II H Bond Type, Dielectric Constant, and Dipole Moment for Some Simple Compounds

			μ (DEBYE[b])	
SUBSTANCE	H BOND TYPE	ϵ (20°C)[a]	BENZENE SOLUTION (20–30°C)	VAPOR
HCN	Intermolecular, polymeric	95	2.65	2.93
Formamide		84	3.37	3.22
H_2O		80	1.76	1.84
CH_3OH		33	1.68	1.69
NH_3		15.5	1.40	1.52
Pyridine		12.5	2.2	—
Phenol		9.9 (48°C)	1.70	—
Ethylamine		6.3	1.38	0.99
Acetic acid	Cyclic	6.4	0.86–2.0	1.73
o-Methoxyphenol	*Intra*molecular	11.7[c]	2.46	—
Salicylaldehyde		13.9	2.9	—
o-Chlorophenol		8.2 (19°C)[b]	1.3	—
Dioxane	None	2.2	0.4	0.3
Benzene		2.28	0	0
Heptane		1.9	0	0
Diethyl ether		4.3	1.27–1.7	1.17
Nitrobenzene		36.1	3.98	4.24

[a] Values from *International Critical Tables*, Vol. VI (1929).

[b] Values from Smyth (1906), LeFèvre (1206a), or Wesson (2160).

[c] Supercooled, less than 32°C.

There are, in general, two types of measurements. In the older and perhaps simpler method the capacitance of a condenser is determined when it is empty (or when it contains a standard substance) and when it is filled with the gas, liquid, solution, or solid. The various states require different sizes and types of condenser cells and measuring circuits, and errors arise from difficulties of maintaining uniform field on the condenser plates, balancing the bridge circuit and, especially for solids, filling the condenser uniformly. H bonding materials, however, present no unusual problems. This technique (most frequently applied in the 10^6–10^8 cps region) gives a single value, usually called the *static* or *low frequency* value of dielectric constant (and hence dipole moment). Nothing is learned about dielectric loss. It is the method typically used by chemists for molecular structure determination of organic molecules.

Dielectric measurement has been a useful aid in determining the structures of many organic compounds. For H bonding substances it has been less successful, except for some particular cases usually involving *intra*molecular H bonds.

The lack of a clear answer for intermolecular interaction may be illustrated by acetic acid or, more generally, the fatty acids. It is normally assumed (usually from the electron diffraction work on gaseous acetic acid dimers and the magnitude of ΔH of formation) that fatty acids in solution or pure liquid form a planar, cyclic, H bonded dimer. This planar form should have zero dipole moment, and the nonzero experimental value (0.86–2.0 D) has been explained as the result of an atomic polarization (1208 among others). Another possibility is that a portion of the dimeric units are noncyclic, with only one H bond. Other arrangements can be suggested. Chains of molecules may be present, as found for formic acid by IR spectroscopy (373). There is no reason to be certain that in the liquid a cyclic dimer is planar; it might assume, on the average, some bent shape as a result of molecular collisions. Hobbs and others (1353, 1652, 1352, 938) considered and rejected the last possibility for acids on the basis that the carboxyl moment is nearly at right angles to the H bonds. Bending the dimer then has little effect on the resulting moment if the moment angle is calculated in the usual vectorial way from values for *unassociated* molecules. Of course there remains the possibility that H bond formation changes the angle, as is suggested by the enhanced moments measured in solutions (see Table 2-IV), but this question is not yet resolved (additional discussion is presented on pp. 22–26). These same authors ruled out higher polymeric forms, but there is also disagreement here (1272), at least for the gas phase. In spite of the many references to the cyclic case, its existence has not been rigorously proved as the only species in the liquid state or in concentrated solutions (see Section 9.4.1 for another discussion of the structure of solid acids). Refer to LeFèvre and Vine's summary (1208) of early work on acids, and their conclusions that the *apparent* moment of the double molecule of trichloroacetic acid is 1.1 D. The possible contribution of self-ionization to the dipole moment of acids is mentioned in Section 8.3.5.

Water is probably the outstanding example of a compound for which a high dielectric constant is attributed to the presence of H bonding. No doubt an important contributing factor is the relatively high degree of order that H bonds produce in ice and liquid water. This order affects many physical properties and prevents water from displaying the simple behavior of its analogues lower in the periodic table, H_2S, H_2Se, and H_2Te. Dorsey's book (544) gives an authoritative review but is now rather out of date.

The anticipated importance of H bonds to the dielectric constant can be followed in the various theoretical calculations for water at several temperatures. Table 2-III collects several sets of values, and Fig. 2-1 illustrates the temperature variation. The figure shows that some theoretical treatments give both the correct magnitude and temperature variation (854, 877). Others fail to reproduce one or both of these characteristics.

TABLE 2-III Comparison of Dielectric Constants of Water Based on Several Theoretical Treatments

t (°C)	ϵ (OBSERVED) (2209)	ϵ (CALCULATED)				
		OSTER AND KIRKWOOD (1557)	POPLE (1659)	HAGGIS, HASTED, AND BUCHANAN (854)	HARRIS AND ALDER (877)	HARRIS[a] (875)
0	88.0	84.2	71.9	89.0	90.7	83.7
25	78.5	78.2	63.8	78.3	79.9	74.0
62	66.1	72.5	53.0	65.5[b]	65.7	60.2
83	59.9	67.5	47.8	59.0[b]	59.6	54.8

[a] Six percent "fluctuation" correction.

[b] Interpolated.

The calculated values are from treatments developed since Bernal and Fowler's qualitative description (199). Those authors gave a hypothetical picture of water as having one of three "lattices," depending on the temperature. Below 4°C it is tetrahedrally H bonded in a somewhat irregular tridymite-like structure; from 4°C to about 200°C it is tetrahedrally H bonded in an irregular quartz-like lattice, and above 200°C it is a close-packed, normal liquid without appreciable H bond-

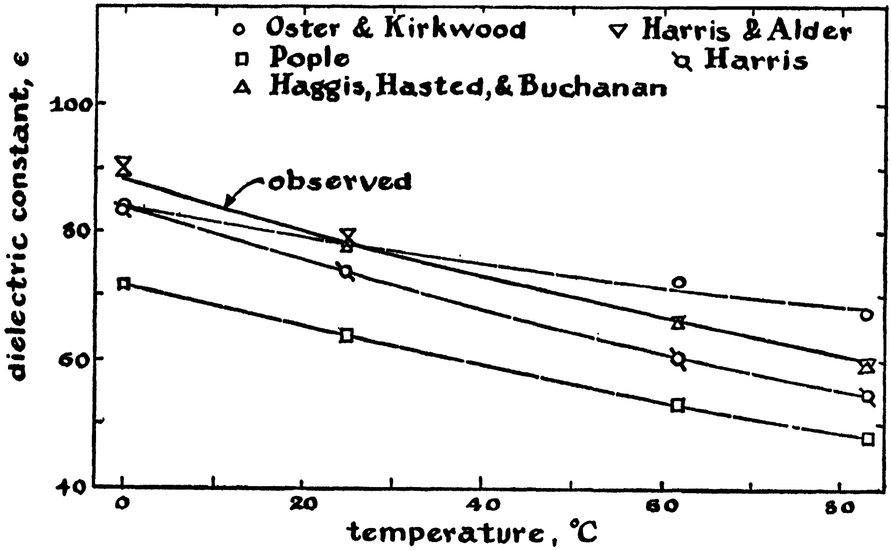

FIGURE 2-1 Comparison of experimental and calculated temperature variation of the dielectric constant of water.

ing. According to Bernal and Fowler, these types blend continuously into one another, and the lattices are only imperfectly formed.

They then explained (in a descriptive fashion only) the dielectric constant as the result of the reorientation of indefinite liquid "crystals" in the applied field. Within the crystals the H bonds are more or less regularly oriented in such a manner that the bond dipoles do not cancel. A large dielectric constant results. The temperature variation of ϵ is attributed to changes in the relative amount of the three lattice types present.

Oster and Kirkwood (1557) assume the tetrahedrally H bonded model for water. They assume free rotation about rigid, directed H bonds and take into account only the first shell of nearest neighbors [using four and five members of the first shell from Morgan and Warren's x-ray work (1447)]. Pople (1659) took a different tack—postulating bendable H bonds that could rotate and calculating the effect of the first three shells of neighboring molecules. The result was poor for magnitude but gave an improved temperature dependence. The next group of workers [Haggis *et al.* (854)] used a probability method to allow for some water molecules having no H bonds to other molecules, some having one H bond, others two, and so on, to those having four. Otherwise, their model was like Oster and Kirkwood's. Later, Harris and Alder

(877) used Pople's model but refined the dielectric equation to account for polarization resulting from distortion of the molecule in the field. Finally, Harris (875) allowed for fluctuations in the dipole moment of individual molecules.

This example shows that a consideration of H bonding is mandatory in explaining the electrical properties of a highly associated material. Further, it illustrates that specific details of the nature of the H bonds and spatial arrangements of the H bonds might be deduced from dielectrical data. Of course, the agreement of calculated values with experiment does not prove the uniqueness of the model.

At present the generally accepted picture for liquid water can be described as a three dimensional, multi-connected net of reasonably ordered molecules attached by a varying number of H bonds which are somewhat distortable. Grant (821) uses the expression "one constantly changing, branched polymer" to describe water. Heavy water (D_2O) differs from this picture only in details (877).

Hydrogen peroxide also has a high dielectric constant, but not so great as water (73 for H_2O_2 at 20°C). Gross and Taylor (834) concluded that H_2O_2 may be less H bonded than H_2O because of its two equivalent nonplanar, bent forms which can be easily interconverted by rotation about the O–O axis. Because of this structure, the molecules do not fit such a compact "lattice."

The dielectric properties of most other associated compounds are presumed to depend in a similar manner on H bonding, however, the details have not been worked out to the same extent. An example is the important class of organic hydroxyl compounds—alcohols and phenols. They are similar to water, but the replacement of one hydrogen by a large non-H bonding group appreciably disrupts the order that can be achieved. Zacharisen (2229) proposed the H bond chain arrangement shown in Fig. 2-2 to explain the x-ray diffraction peaks of liquid alcohols. This was supported by Pierce and MacMillan (1631) and Harvey (885). Oster and Kirkwood (1557) used the same model and applied the same general theory that was used for water but made the further stipulation that there were no H bonds between chains. Harris and co-workers (878) deduced from dielectric constant values at pressures up to 200 atmospheres (at 25–50°C) that in some liquid alcohols the chains are rather short. For example, in *t*-butanol the average chain probably contains fewer than five molecules. For alcohols with less steric hindrance (ethanol) an infinite chain length model fits the data.

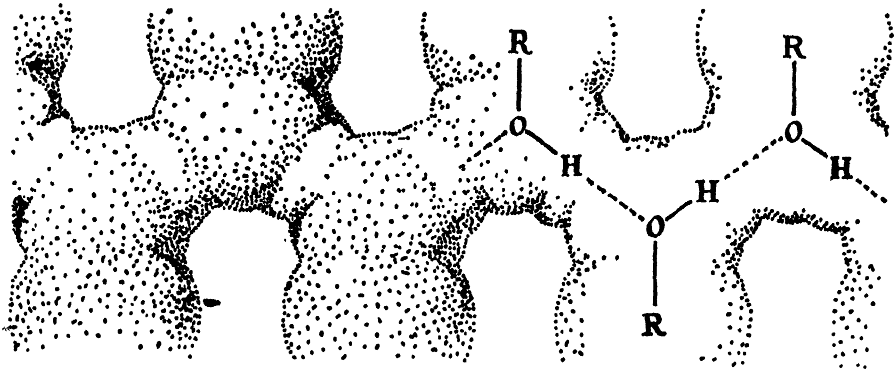

FIGURE 2-2 The H bond chain in alcohols.

Phenols also associate, but the benzene ring adds complicating factors. The ring provides some steric hindrance so that less extensive chain formation occurs. In some disubstituted benzenes, *intra*molecular H bonds may be formed. Both of these factors reduce intermolecular H bonding, and the dielectric constant is not raised.

Amides have structures that formally resemble acids, and H bonded ring dimers could form. Dielectric measurements show that only in special instances do these cyclic structures exist to any significant extent. Worsham and Hobbs (2197) interpreted their experiments on *N*-substituted benzamides to show that the —CONH— group is planar with the O and H in the *trans* arrangement. As a consequence, H bonded chains similar to alcohols result, and the dielectric constant is high.

Other workers (997) studied aliphatic lactams and concluded that the amide group is *trans* if the molecule is sufficiently flexible to adopt that configuration. For compounds of the type shown in Fig. 2-3 the dielectric constants suggest that members with *n* between 5 and 9 have *cis* amide groups, and hence cyclic dimers are formed. If *n* is greater than 9 (tested up to *n* = 19) the amide linkage is *trans*, and chain polymers result.

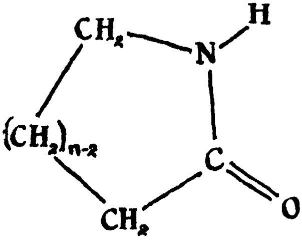

FIGURE 2-3 Schematic structure of aliphatic lactams.

Work of Davies and Thomas (503) casts doubt on the generalization that *trans* amides form linear polymers and *cis* amides form cyclic dimers. They have found that both trichloroacetamide and its *N*-methyl derivative form cyclic dimers. As Davies notes, the type of association is determined by the relative values of several free energies which can be changed by structural factors other than *cis-trans* character.

Baker and Yager (118) published an interesting discussion of the dielectric properties of some solid polyamides. They explained the variation of dielectric constant and dielectric loss in terms of the extent and perfection of the H bond network. Both quantities are high in samples for which the network is postulated to be poor either from awkward spacing of the amide groups or from misalignments due to quenching. Further, both of these dielectric properties increase rapidly with temperature, a behavior Baker and Yager relate to oscillation of hydrogen atoms between two minimum positions in the H bond. Other loss mechanisms also become important at high temperatures at which the H bonds are disrupted and their ordering influence is lost. In additional experiments Baker and Yager showed that powerful H bonding agents (H_2O) which interfere with the H bond network give dielectric behavior similar to that obtained at high temperature. This general equivalence of H bond breaking from chemical or thermal means is typical and is found by many experimental methods.

Before leaving the subject of structural influence of H bonds and the concomitant effect on dielectric constant, we should mention two more important inorganic examples: HF and HCN. In each case dielectric data give high dielectric constants (83.6 and 158.1, at 0°C, respectively), presumed to indicate association in extended linear chains (400, 191, 415).

2.1.3 Association between Solute and Solvent. Many studies have been made in which the variation of dielectric constant, dipole moment, or molar polarization is explained in terms of the association between molecules of solute or between solvent and dissolved material. Glasstone (777) used this technique to make one of the first suggestions of H bonding involving a C—H hydrogen atom ($CHCl_3$-acetone). According to Tomecko and Hatcher (2026), chain length and degree of association of acetone and fatty acids were found by polarization measurements and Raman spectra. The complexing between simple ethers and water (580), and between benzene and alcohols or halogenated materials (1690), has been reported. Few and Smith, and Smith and Walshaw (649, 648, 1902, 1901, 1904) investigated amines (largely aromatic) and concluded that mesomerism increases H bonding with dioxane. The same increase in dipole moment as a result of mesomer formation was reported for five-membered rings (oxazolidones and cyclic amides) (665). Other workers (1483) agree on the presence of H bonds between aniline and dioxane. Similar interaction has been observed for pyrrole and dioxane (1335). Oster (1556) describes the application of the Onsager-Kirkwood equation to polar molecules in nonpolar solvents.

The representative data compiled in Table 2-IV serve to demonstrate the changed moments when H bonding occurs. Compare the data in each row. The general behavior on passing from gas to CCl_4 and through benzene to dioxane reveals the presence of H bonding. Only a small change in μ is caused by a nonplanar solvent, a "solvent effect" to be discussed later. The dipole moment rises slightly in benzene solution and considerably more in dioxane. This suggests that the change is proportional to the electron donating ability of these bases. These effects are not observed for unassociated compounds, as illustrated by dimethylaniline.

TABLE 2-IV The Effect of H Bonding on Dipole Moment

SUBSTANCE	DIPOLE MOMENT (Debyes at 30°C)					REFS.
	Gas	Dissolved in				
		CCl_4	C_6H_6	Dioxane	$\mu_{\text{Dioxane}} - \mu_{\text{Gas}}$	
HBr	0.78	0.93	1.08	2.85	2.07	2151
HCl	1.03	1.06	1.25	2.12	1.09	2151
Phenol	—	1.45	1.52	2.29[a] (ether)	~0.8	1819
Formamide	3.22	—	3.37	3.86	0.64	150
Formic acid	1.51	—	—	2.07	0.56	2184a
HF	1.91	2.0	1.91	2.34	0.43	2151
Aniline	1.48	1.46	1.51	1.75	0.27	646
Dimethylaniline	1.61[b]	—	1.61	1.66	0.05	1901
H_2O	1.84	1.89[c]	1.83	1.89	0.05	2151
HCN	2.93	—	2.59	—	—	1906
CH_3OH	1.69	—	1.66	—	—	1906

[a] 139; [b] 649; [c] 1819.

Incidentally, though there are many measurements of dipole moments, only a small number of solvents is in general use. Furthermore, systematic studies such as those of Hobbs (2151), Mecke (1292), and Few and Smith (646) are not numerous.

The differences listed in the next to last column of Table 2-IV are interesting. The compounds have been listed in order of decreasing $\Delta\mu$, and it is startling to find water at the bottom of this list. Assuming that $\Delta\mu$ is indicative of the strength of the H bond, it is implied that water is a poor acid. This conclusion is supported to some extent by the IR data cited in Table 3-III, although inconsistencies are present. On the other hand, the order observed in both Table 2-IV and Table 3-III is not in accord with acid strength as indicated by the dissociation constant. It may be that neither $\Delta\mu$ nor $\Delta\nu_s$ is a direct measure of H bonding capability.

The "solvent effect" of CCl_4 mentioned earlier was demonstrated by Müller in a series of papers (1462, 1461, 1460). He found that dipole moment values measured in solution are different from values for gases. He also showed that the value depends on the solvent. Smyth (1906, pp. 39–51) gives a brief summary of the theories of Higasi, Franck, and Conner and Smyth. In a general way, the phenomenon is attributed to the electrical effect of a solute molecule on surrounding solvent molecules. The solution dipole moment will *exceed* μ_{gas} if the solute molecule is ellipsoidal in shape and the axis of the dipole moment coincides with or is close to the long symmetry axis of the molecule. Many substances fit this description. (For interpretive reasons this is called a "negative solvent effect.") For some molecules the dipole axis is along the short axis, and the solution dipole moment is *lower* than μ_{gas}.

In H bonding studies the amount of solvent effect to be expected in a "normal" solvent is estimated, and the additional part of $\Delta\mu$ is assigned as the H bonding effect. Some of the recent work is by Few and Smith (646), Mecke (1292), and others (469, 1482, 1901). There is unavoidably an overlap between the effect that can be ascribed to nonspecific electrical interaction as with CCl_4 or hexane, and H bonding between solute and solvent. We include benzene in the latter category because other work shows that its interactions fit our definition (see Section 6.4).

Some general comments on solution work are worth noting. Not all investigators have understood the H bonding possibilities of some solvents, particularly benzene and sometimes dioxane. The benzene ring was mentioned as a proton acceptor many years ago (1400), but this feature has not been generally recognized. Other workers emphasize this point and make similar remarks for the H bonding ability of dioxane (58, 1984, 649, 647, 646, 469). Spectral data (see Section 3.3.5) support this conclusion and point to the need to use more nearly inert solvents. Often the argument is advanced that the "dissolving power" of such solvents is needed to attain workable concentrations. Unfortunately the ease of study is obtained with a sacrifice in ease of interpretation. Dioxane and benzene are *not* inert to proton donating materials.

Related to this is the tendency for many workers to choose complicated systems for study. Solvents with known associating tendencies and sometimes even mixtures of these are used. Imagine the conflicting interactions in a system made up of a fatty acid dissolved in a pyridine-ether mixture.

Dielectric constant determinations can give H bonding equilibrium constants (1652, 997). Only a few values have been obtained, and they are presented in Chapter 7 and Appendix C. A particularly interesting research is described by Sutton and co-workers (518, 998). They pre-

TABLE 2-V Dipole Moment and Equilibrium Constant for Some H Bonded Complexes (at 25°C)

ACID	μ (Debye)		$\Delta\mu$ (Debye)	K (l/mole)	BASE
	ACID	COMPLEX			
Complexes					
β-Naphthol	1.53	3.80	1.41	230	Trimethylamine[a] ($\mu = 0.86$)
p-Chlorophenol	2.22	4.30	1.22	200	
α-Naphthol	1.41	3.41	1.14	110	
Phenol	1.53	3.24	0.85	86	
o-Cresol	1.41	3.02	0.75	70	
p-Cresol	1.57	3.13	0.70	65	
Indole	2.05	2.99	0.08	9	
Phenol[b]	1.36	1.86	0.12	15	Dioxane ($\mu = 0.4$)
Acid Dimers[c]					
Formic acid	[0.0][d]	1.06	1.06	126	
Acetic		0.94	0.94	370	
Propionic		0.88	0.88	392	
Butyric		0.93	0.93	428	
Trimethylacetic		0.92	0.92	690	
Benzoic		1.13	1.13	190	
Chloroacetic		1.97	1.97	102	

[a] In cyclohexane; [b] In heptane (1481); [c] 1652; [d] Expected for planar form.

sent a somewhat novel solution–vapor partition method and an interesting correlation between dipole moment data and H bond equilibria. They measured complex formation between a series of phenols (in cyclohexane) and trimethylamine. The excess dipole moment for the complex over the sum of phenol and amine, called $\Delta\mu$, is shown in the upper section of Table 2-V, with other data below. These workers found a proportionality between $(\Delta\mu)^2$ and K. This is shown in Fig. 2-4, where the data of Table 2-V are plotted. It is interesting that these quantities do not follow the ionization constants of the acids.

Figure 2-4 includes other work cast in the $(\Delta\mu)^2$-K form. As shown in Table 2-V, dipole moment values and equilibrium constants for dimerization of several carboxylic acids are available. Assuming these dimers are rigid planar, nonionized rings, the μ dimer value would be expected to be zero. Hence the experimental μ itself is analogous to the quantity $\Delta\mu$. The very different relationship to K is seen in Fig. 2-4.

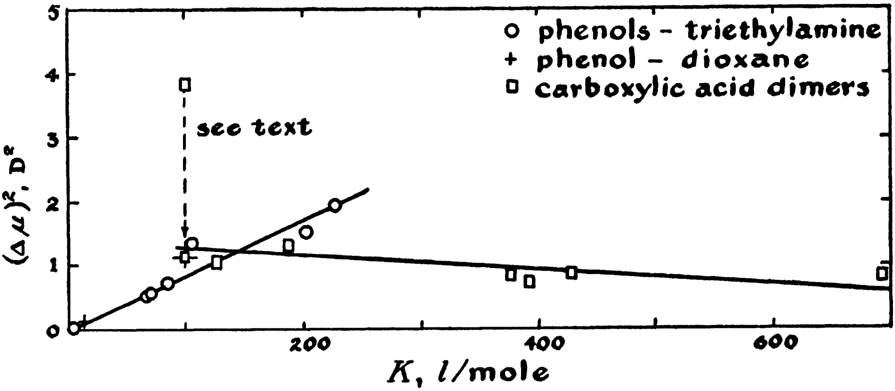

FIGURE 2-4 The relation between the square of excess dipole moment $(\Delta\mu)^2$, and K (25°C).

The monotonic relations between $\Delta\mu$ and K invite interpretation in terms of thermodynamic quantities. The enhanced dipole moment might be expected to be determined by the enthalpy of formation of the H bond. Such a dependence would be cast in terms of K as

$$\Delta F = -RT \ln K = \Delta H + T\Delta S$$

If, then, $\Delta\mu$ is related to ΔH, it will be revealed by a simple dependence of $\Delta\mu$ on $\log K$. Empirically there is a direct relation, as shown in Fig. 2-5, between $(\Delta\mu)^{\frac{1}{2}}$ and $\log K$. While this has no more obvious explanation than the linearity of Fig. 2-4, it condones discussion of $\Delta\mu$ in terms of the strength of H bond formation.

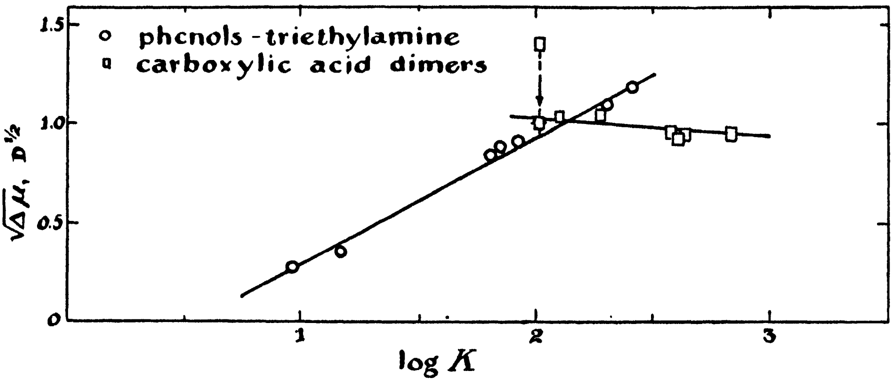

FIGURE 2-5 The relation between the square root of excess dipole moment, $\sqrt{\Delta\mu}$, and log K (25°C).

For the phenol complexes the positive slope seen in Fig. 2-5 indicates that a stronger H bond implies a higher induced dipole moment. For the carboxylic acids the behavior is quite different: the negative slope implies that $\Delta\mu$ decreases as H bond strength increases. This can be simply explained as a measure of departure from planarity of the cyclic H bonded structure. Any departure from planarity can result in a net dipole moment, but such nonplanar configurations become less likely as the H bond strength increases.

The wide divergence of chloroacetic acid from the general line for acids also can be rationalized. As a result of rotation about the C—C bond, the C—Cl dipole will contribute to $\Delta\mu$ since on the average it will not be in the H bonded plane. Using Eyring's method (1906, p. 235) the average value of the two C—Cl dipoles in a dimer is 0.91 D. Subtracting this from $\Delta\mu$ gives the adjusted point shown in Figs. 2-4 and 2-5, now in accord with the other data.

Further information comes from Sutton's research with additional assumptions. For the phenol-amine complex Sutton computed the relative bond character of the H bond—75 to 85 percent ionic and 25 to 15 percent covalent—on the basis of the calculated dipole moment direction corrected for induced moments. These figures are in general agreement with other estimates based on electrostatic models. The tenuous nature of the argument must be kept in mind.

2.1.4 Dielectric Dispersion. The second general dielectric method is the measurement of dispersion or loss. Basically, this involves determining the dielectric constant over a range of frequencies. Current experimental techniques permit the study of liquid samples in the microwave and short radio wavelength region, where dispersion behavior can be related to molecular properties. For highly viscous substances the dielectric dispersion is displaced toward the longer radio wavelength region. Frequencies from 1 cps to 10^{11} cps have been used, but few investigations have covered this entire range. Often a wide frequency range is not needed because the sample shows relaxation behavior only in a limited frequency region. Instrumental improvements are being made to extend coverage toward both ends of the scale.

Data usually are expressed in terms of ϵ' and ϵ'', the charging current and loss current. These quantities define a complex dielectric constant, ϵ^*

$$\epsilon^* = \epsilon' - i\epsilon''$$

Smyth (1906) gives the equations that Debye and others developed to express ϵ' and ϵ'' in terms of measured quantities. The Debye equations are

$$\epsilon' = \epsilon_\infty + \frac{\epsilon - \epsilon_\infty}{1 + \omega^2\tau^2}$$

$$\epsilon'' = \frac{(\epsilon - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}$$

where

ϵ and ϵ_∞ are as defined in Table 2-I

ω = angular frequency = (2π) (frequency in cps)

τ = relaxation time = time for polarization to become $(1/e)$th of its starting value.

The data are displayed in two forms. A plot of ϵ' and ϵ'' against frequency gives a curve such as the solid line in Fig. 2-6(a) if there is a single relaxation time. In the Cole-Cole plot ϵ'' is plotted directly against ϵ', as shown in Fig. 2-6(b) (1906).

Distributions of relaxation times produce shapes similar to the broken lines in Figs. 2-6(a) and (b). The curves labeled I result from a broad distribution, and those labeled II from mixtures of more or less discrete relaxation times. Type II curves are found less often than type I. The best known examples of type II are in alcohols, but the interpretation does not necessarily involve H bond rearrangements. Aspherical molecules, for example, may show a range of relaxation times and give curves of type I. This is true for *n*-octyl bromide (1906, pp. 58, 104).

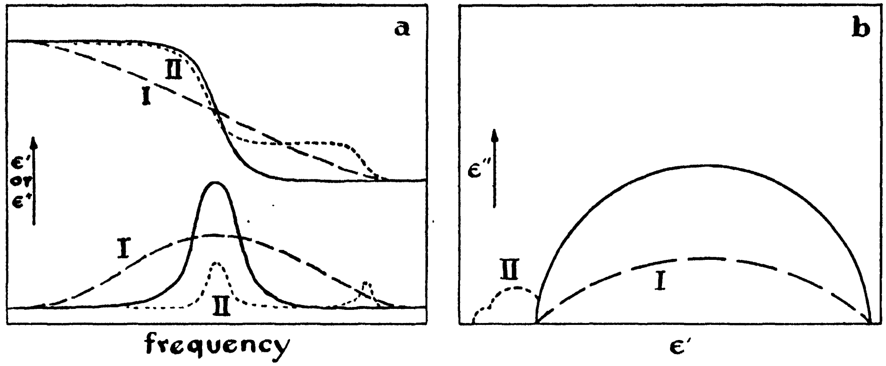

FIGURE 2-6 Schematic diagram of ϵ' and ϵ''. (a) Plotted according to the Debye equations. (b) Plotted according to Cole and Cole. Solid lines, a single relaxation time; broken lines, distributions of relaxation times.

Since either type of distribution can be present without association, dielectric loss measurements do not provide a diagnosis of H bonding. Nevertheless, dispersion behavior often can be explained in terms of rearrangements dependent on H bonding. Type I curves may result from the various molecular sizes and shapes of the H bonded polymers. Type II curves may occur when a H bond equilibrium has a relaxation time considerably different from the orientation time giving the main "peak." This happens, for example, in supercooled liquid *n*-propanol (416). Consequently, this tool deserves more detailed attention.

In general, dispersion phenomena occur when the response of a system lags behind the exciting force. In dielectric substances such lag indicates that a finite time period accompanies some type of rearrangement within the molecule. This rearrangement time is measured by τ, the relaxation time defined earlier. When a high frequency current is used, its frequency may exceed the rate at which the arrangement can adjust itself. As the lag develops, phase differences occur between exciting and response forces, and energy is dissipated in thermal motions. As Smyth mentions, in his interesting account of the accepted general physical picture (1906, pp. 52–54), there are different times required for various kinds of rearrangements as given in Table 2-VI. If a wide frequency range is available, this technique offers the possibility of distinguishing these processes. Works devoted to dielectrics (726) cover the subject thoroughly, and Davies (482) has reviewed chemical applications.

As a specific example of the study of dielectric relaxation in H bonding systems, the work of Meakins, Dryden, and co-workers is notable.

TABLE 2-VI Time Required for Various Molecular Rearrangement Processes

Electronic	10^{-15} sec
Atomic	10^{-12} to 10^{-14}
Molecular gas	10^{-12}
Molecular liquid	10^{-10} to 10^{-11}
Molecular viscous liquids	10^{-6}
Molecular solids and extremely viscous liquids	10^{-2} to 10^{2}

These workers made an extended study of solid alcohols of various structures and complexity.[a] They concluded that *n*-primary and secondary alcohols have long H bonded chains of OH groups running through the crystal, that the dielectric absorption is caused by rotation of OH groups or a proton transfer, and that the molecular structure, particularly around the OH group, is an important factor (865). Furthermore, these studies were made on pressed disc samples, and Meakins *et al.* concluded that the orientations of the crystals within the pressed disc samples were important. (Other drawbacks of pressed disc studies are mentioned in Section 3.2.2.) The structural effects are largely steric: *t*-butanol, triphenyl carbinol, and 2,4,6-tri-*t*-butylphenol show simple Debye curves, no doubt because the OH group is buried by surrounding groups and does not H bond into long chains.

Figure 2-7 shows space filling and conventional representations of methanol, *t*-butanol, and the tri-*t*-butylphenol. The O—H group of the last is clearly buried by the neighboring *t*-butyl groups. In *t*-butanol the interference is less pronounced, and for methanol it is essentially nonexistent. Other physical properties are, of course, also affected by such steric hindrance. One of the reports (1374) shows the effect of the position of the hydroxyl group along the eicosane chain. Daniels (472) proposed that there are interruptions in the H bonded chains present in long chain alcohols and that thermally induced changes in these centers of disorder are an important part of the polarization process. Meakins' group also studied H bonding in phenol (1369), quinol (554), aliphatic esters (555), and clathrate compounds of methanol and quinol (553).

Smyth (523) studied some systems of two solid phases, such as tetradecyl or hexadecyl alcohol and the corresponding mercaptans in dotriacontane. Mercaptans do not show long chains of H bonded

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[a] 1371–1374, 866, 552, 865.

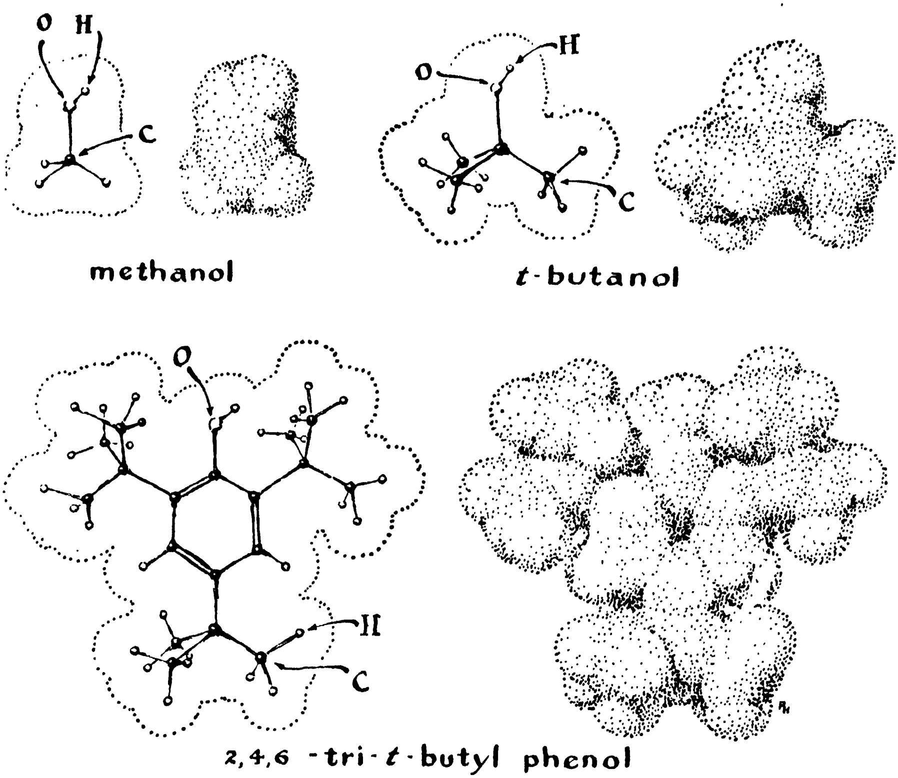

FIGURE 2-7 Comparison of the steric hinderance in some hydroxyl compounds.

S—H groups, presumably another manifestation of the relative weakness of H bonds in this group. Sack (1768) has developed a theory of high dielectric losses in terms of the number of states of the molecule. Other solid organic materials that have been studied less extensively include cyclohexanol (1515, 1128, 793), in which the H bonding apparently differs in various crystal phases; camphor and some related materials (793); and palmitamide (1075).

In addition to the more usual application to solids, dielectric relaxation or dispersion measurements are also used on solutions (and pure liquids). Cook (425) related the relaxation mechanism in water-dioxane mixtures to the rupture of H bonds. Hasted and co-workers (890) found that water-dioxane mixtures had longer relaxation times as the dioxane proportion increased or the temperature was lowered. Both trends are explained by formation of a H bonded complex. Yasumi (2219) found similar effects when large amounts of hexane were mixed with alcohol—in this case interruption of the H bonds is indicated.

2.1.5 Conductance. The mobilities and conductances of $H^+(H_3O^+)$ and OH^- ions are much greater than those of other ions. Several treatments considering H bonding are available (see, for example, 199, 1955, 2185, 1076, 423). The work of Conway, Bockris, and Linton (423) is particularly comprehensive in reviewing past treatments and the various difficulties encountered in each. They list six observations about H_3O^+ which must be explained: (1) increased mobility at high pressure, (2) low apparent heat of activation, (3) decrease in this heat with increased temperature, (4) the mobility ratio of $H_3O^+ : D_3O^+$, (5) lowered conductance when small quantities of water are added to alcohols, and (6) lowered mobility in alcohols as hydrocarbon chain length increases. They conclude, after considering several possible transfer mechanisms, that rotation of the water molecule is the rate controlling process for placing protons in the correct position (along a H bond axis) for transfer. Actual transfer along the H bond is by means of relatively fast, quantum-mechanical tunneling. (See 582 for experimental measurement of the fast transfer rate.) With this picture they are able to account for the six experimental facts.

In liquid ammonia the conductance is normal because there are very few ions (NH_4^+ or NH_2^-). This implies a lower tunneling rate, and the calculated value is in agreement—it is smaller than for water by a factor of 10^4.

H bonds influence the conductance mechanism in other systems. Pollock and Ubbelohde (1655) demonstrate two points for solid organic acids. Conductance is high for crystals having a "cooperative assemblage of H bonds," and almost a hundred times greater than it is in the solids with closed pairs of H bonds. Also, the interruption of the continuous chain (for example, by water of crystallization) decreases the conductance. These workers conclude that the H bond chain makes a good path for movement of protons. Preliminary work on some salts ($KHSO_4$, $NaHSO_4$, etc.) indicates that similar factors may be present there (1739). See Section 8.3.6 for a theoretical discussion. Wang (2136, 2137) showed by tracer methods on several isotopic species of water that diffusion is a molecular process that does not involve transfer along H bond networks as in electrical conductance. H bonds must be broken to free the molecule, but the process is similar to viscous flow. Chang and Wilke (365) studied some other H bonding systems and give an empirical equation which correlates diffusional behavior. The principal effect of intermolecular H bonding is to produce a high temperature coefficient of diffusion.

2.1.6 Ferroelectric Behavior. Ferroelectric substances are those which have a stable, permanent polarization. They are of interest here because H bonding is one of the important ordering mechanisms responsible for permanent polarization.

Dekker (515) lists four groups of ferroelectrics—three may be H bonded. However, there is not unanimous agreement about the importance of H bonding. Pepinsky reviewed neutron diffraction evidence concerning H bond contributions (1).

Mason (1355) determined the elastic, dielectric, and piezoelectric constants of potassium and ammonium dihydrogen phosphate. He concluded that there are two distinct sets of H bonds in the ammonium salt—one set (N—H to O of PO_4) is influential in thermal and specific heat anomalies, and the other set (part of the H_2PO_4 groups) affects the dielectric and piezoelectric properties. As mentioned earlier, a H bond reorientation can be too slow to follow a high frequency field. Mason quotes Yager's finding that the dielectric constant of Rochelle salt does not show the behavior shown in Fig. 2-8 when a frequency of $2.5 \cdot 10^{10}$ cps is used. An almost constant value of 8 D was found.

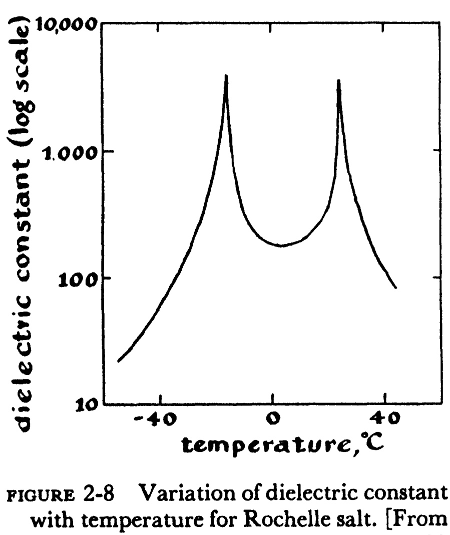

FIGURE 2-8 Variation of dielectric constant with temperature for Rochelle salt. [From Hablützel, *Helv. Phys. Acta.* **12**, 489 (1939).]

Figure 2-8 illustrates the unusual dielectric constant in the ferroelectric temperature region of Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$) (1463) which, with its analogues, has been studied by many workers (305). Ubbelohde and Woodward (2070), and Akao and Sasaki (13, 12) have dealt specifically with H bonding in Rochelle salt.

Other examples are the dibasic phosphates, arsenates, mixed sulfates, and similar compounds—KH_2PO_4, $NH_4H_2AsO_4$, $Ag_2H_3IO_6$, $(NH_4)_3Al(SO_4)_2 \cdot 6H_2O$, and $(NH_4)_2SO_4$. (See 305 for a general treatment of ferroelectrics.)

2.2 Pressure-Volume-Temperature

Hydrogen bonded materials show much greater deviations from the perfect gas laws than do nonassociated substances. Convenient measures of the extent of deviation are the virial coefficients B, C, D, etc., in the generalized gas law equation

$$\frac{PV}{nRT} = 1 + B\left(\frac{n}{V}\right) + C\left(\frac{n}{V}\right)^2 + D\left(\frac{n}{V}\right)^3 + \cdots$$

Here, B is called the second virial coefficient, C the third, and so on. The largest and most widely studied is B. At temperatures well below the critical value, second virial coefficients are generally negative, showing the attractive forces between molecules of a real gas as compared with a perfect gas. For H bondable gases, B is even larger in the negative direction (at the same corresponding state), reflecting additional attraction between molecules. Table 2-VII gives some values and compares them with values from Berthelot's equation. The interpretation of the difference for the H bonding compounds is illustrated by the work of Lambert and co-workers, who used experimental and Berthelot's B to obtain H bond enthalpy for a large number of compounds (1183, 1185, 681, 1182). They determined B from vapor pressure data at a series of temperatures and took Berthelot's B as representing all the molecular imperfections except the dimerization. The difference (or the part due to dimerization) was expressed as a function of the equilibrium constant.[a]

TABLE 2-VII Comparison of Second Virial Coefficient (B) for Some Simple Gases

SUBSTANCE	°C	B (ml/mole)	
		EXPERIMENTAL	BERTHELOT EQUATION[a]
C_2H_6	40	−50	−50
CH_3OH	60	−1220	−550
CH_3Cl	38	−401	−380
H_2O	40	−976	−421

[a] 1183.

$$B_{\text{obs}} - B_{\text{Berthelot}} = -RTK$$

---

[a] We have written this equation using an association constant K. Lambert's K is for dissociation.

By a combination of this and the Berthelot equation, values of the equilibrium constant were found at several temperatures, and the dimerization enthalpy found from the usual log K *vs.* $1/T$ plot.

Perhaps the best grasp of H bond effect on gases can be gained from Fig. 2-9, which is taken from Lambert (1182). Here, both the temperature and composition effect can be seen. Using the approximation that B for equimolar mixtures should be the average of B's for the pure components, the heights of the maxima above the average give a qualitative measure of H bonding.

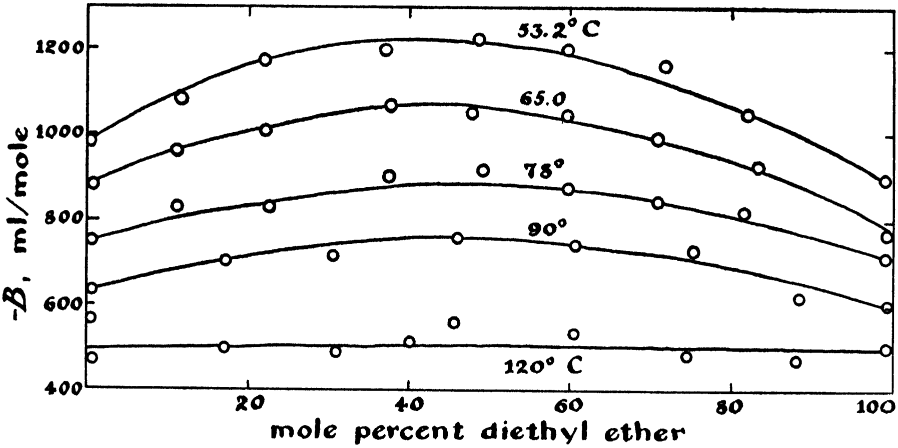

FIGURE 2-9 Second virial coefficient of chloroform-diethyl ether mixtures at several temperatures. [From Lambert, *Disc. Faraday Soc.* **15,** 226 (1953).]

This technique does not diagnose H bonds. When it is applied to such compounds as CO_2, esters, and acetaldehyde, "dimerization" constants are found of the same order of magnitude as for water, alcohols, and amines. However, when H bonds are known to be present, it can give reasonable values. The thermodynamic properties of H bonds are discussed fully in Chapter 7.

Rowlinson (1753) objected to the interpretation placed on the calculated B and used Stockmayer's (1957) statistical mechanical formulation. Several assumptions are required about the partition functions of the dimerization, but reasonable results are obtained for H bond enthalpies.

Another approach (1149, 2156) has been to avoid Berthelot's equation, but to express the H bonding in terms of appropriate equilibria and derive the relations between the equilibrium constants and the experimentally determined equation for *B* as a function of temperature. The final steps are the same as above.

Vapor density data, another form of *P-V-T* measurement, can be used to calculate "apparent molecular weight" (1272), "association factors" (1011), or "degree of association" (1305). Again, this is a means of connecting equilibrium constants to temperature.

These methods require accurate *P-V-T* data over a fair range of temperature for molecules whose critical constants are known or for which some thermodynamic values have been measured. It is not surprising that only a few of the more common materials have been studied.

A related method is typified by Pitzer and Weltner's paper on methanol (2156). They used heat capacity expressions corresponding to the virial equation to calculate virial coefficients. They use the calculated fourth virial coefficient to argue that H bonded tetramers are present. A corresponding interpretation of *B* is not given.

2.3 Melting Point

Melting and boiling points are usually raised by intermolecular H bonds, often to a marked degree. The high boiling point of water is probably the most commonly cited evidence of H bonding. Table 2-VIII gives some comparisons for associated substances, and Chapter 5 treats *intra*molecular cases (Section 5.3.4). See Section 2.4.6 for some discussion of cryoscopy—a special aspect of melting point behavior.

In the inorganic pair, the higher molecular weight of H_2S should make its transition temperatures the higher. For the organic molecules we have provided some comparisons at the same formula weight and some at twice the formula weight. The second is a better fit, particularly for the boiling point. This rough rule seems to hold even though there is ample evidence of higher polymers, for example, in ethanol at room temperature. Table 2-VIII presents only the grossest kind of comparison. The Martinets (1346) present a great many more data and discuss both inter- and *intra*molecular H bond effect on boiling point.

An example of the use of H bonding to vary melting point is given by Champetier's discussion of polyamides (345, 362). He compared the melting point with the number of H bonds per 100 chain atoms. His results can be summarized in a schematic fashion, as in Fig. 2-10. The H bonded materials have higher melting points than the polymethylene, *and* the melting point increases with the relative number of

TABLE 2-VIII Comparison of Melting and Boiling Points of Intermolecular H Bonded Materials with Similar Sized Compounds

COMPOUND	MELTING POINT (°K)	BOILING POINT (°K)
H_2O	273	373
H_2S	190	211
Acetic acid	290	391
*Iso*butane	128	263
p-Xylene	286	411
Ethanol	156	351
Dimethyl ether	135	249
Propane	83	231
Hexane	179	342
Methylamine	181	267
Ethane	101	185
n-Butane	138	273

H bonds. The references to "even-even" and "odd-odd" in the figure indicate whether both the diacid and diamine used in the polymerization had an even or an odd number of carbon atoms. The spread among the polyamides therefore shows the benefit of optimum use of the H bondable groups. In the "odd-odd" cases, maximum H bonding is not achieved, and the melting point is low. Section 11.3.1 discusses

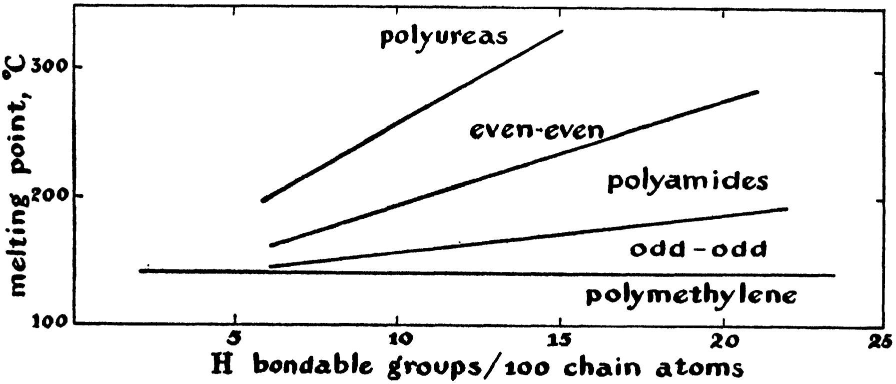

FIGURE 2-10 The relation between melting point and fraction of H bonds in some polymers.

this point in connection with applications. (See also 1134 for similar relations.) Trifan (2032a) suggests that while this may be a convenient way to describe melting point variation, it does not agree with his spectral data. At room temperature he finds essentially 100 percent H bonding of all N—H and C=O groups, and even at 300°C there is 85–90 percent of maximum possible bonding. Possibly the polyamide chains are not in such regular arrangement as assumed.

Liquid crystals can be considered as "partly melted" solids. Although the fluidity indicates destruction of the three dimensional order, optical behavior shows the retention of structure. Many of the compounds which form these mesophases have H bondable groups (e.g., cholesterols, polypeptides). Robinson (1731, 1735) discovered the effect in polypeptides and commented briefly about the structure responsible.

2.4 Additional Methods: Liquids and Solutions

Pure liquids and solutions have probably received a major portion of the experimental effort devoted to the nonspectroscopic methods of detection. The liquid phase is susceptible to simple techniques and is the naturally occurring state for many substances. The principal methods of study are vapor pressure measurements, cryoscopy, solubility, and partition studies. To a lesser degree parachor, refractive index, thermal and acoustic conductivity, osmotic pressure, and magnetic susceptibility measurements have been applied to H bonded materials. Unfortunately, the difficulty of giving an adequate description of the liquid state sometimes produces problems of interpretation.

One common measure of H bonding in solutions is of the kind already described for gases, in which the properties are compared with values calculated from ideal laws. Deviations from such relations as Raoult's Law can be caused by H bonding and other factors—differences in internal pressure, polarity, or molecular size of components. Hildebrand's warning against assigning *all* the discrepancy to a single factor should be kept in mind. On the other hand, H bonding undoubtedly causes an important fraction of the deviation in many cases.

2.4.1 Vapor Pressure, Boiling Points, and Azeotropes. Turning to solutions, the interaction or interference between molecules is revealed in plots of composition *vs.* vapor pressure or boiling point. Deviation from ideal behavior produces curves with maxima or minima. More specifically, positive deviations may give maximum points in vapor pressure curves, minimum boiling points, and minimum azeotropes, if the difference between component boiling points is small enough relative to the deviation, or if the difference in solubility parameter δ is large enough. The reverse is true for negative deviations. Mixtures of H bonded substances can show either positive or negative deviations from Raoult's Law, depending on the relative strength of H bonding between like molecules in each component and that between unlike molecules. For example, acetone-chloroform forms a maximum azeotrope, whereas acetone-water has been reported as showing a slight minimum, or no azeotropic behavior at all (959). In the first case, there are no H bonds present in the pure components and H bonds are formed in the mixture. This gives a negative Raoult's deviation and maximum azeotrope. In the second instance, association in the water causes a competition. Apparently the change from a water-water H bond to a water-acetone bond creates little net change, and essentially no deviation results. Intermolecular forces are reviewed by Rowlinson, and the influence of H bonds on solution properties is discussed (1751, p. 187).

Ewell, Harrison, and Berg (627) devised a compact classification based on the H bonding ability of generic classes of organic compounds. It allows qualitative prediction of the formation (or absence) of azeotropes and their types and, as our later sections and chapters show, it is useful for correlating other properties. Table 2-IX defines a classification scheme based heavily on their idea.[a] This classification will be used throughout this book.

Table 2-X describes the changes in H bonding on mixing and the type of deviation, along with some examples taken from Horsley's extensive tabulation of azeotropes (959).

Table 2-XI shows the fairly good predictive power of the classification when applied to 182 binary solutions.

Agreement with Raoult's Law is not a sufficient condition for ideality —though it is a necessary one (627). Occasionally a mixture capable of H bonding will form a pseudo-ideal system which obeys the equation. Pyridine-ethanol is an example (227) which must include H bonding, both in association of the alcohol and between the two components. The observed ideal behavior surely results from a fortuitous cancellation of effects.

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[a] Our scheme is the same except their Classes I and II have been combined in our Class AB, and our symbols are chosen to be mnemonic.

TABLE 2-IX Classification of Compounds by H Bonding Type

CLASS OF COMPOUND	MOLECULE CONTAINS		EXAMPLES
	PROTON DONOR GROUPS (Acid)	ELECTRON DONOR GROUPS (Base)	
A	Yes	No	Mainly halogenated compounds with enough halogens to activate the hydrogens: $CHCl_3$, C_2HCl_5, etc.; and possibly C_2H_2 protons
B	No	Yes	Ketones, aldehydes, ethers, tertiary amines, esters, olefins
AB	Yes	Yes	H_2O, alcohols, carboxylic acids, primary and secondary amines
N	No	No	Saturated hydrocarbons, CS_2, CCl_4

2.4.2 Solubility. H bonding plays several roles in determining solubility, just as it influenced the vapor pressure curves and azeotropic behavior. Actually, the same classification can be used for solubility. Thus, in the same order as in Table 2-X, the six types of mixtures would be expected to have mutual solubilities that were: (1) low, (2) high, (3) intermediate, depending on relative strength of bonds broken and formed, (4 and 5) intermediate, (6) not determined by H bonds; variable depending on polarity and dispersion forces.

The general effect of H bonding on solubility can be expressed by these statements:

1. Unassociated substances which have H bondable groups (classes A and B) tend to be soluble in a solvent that can supply the other partner in an H bond interaction.
2. Association between molecules of one component of a mixture (Class AB), tends to cause low solubility in solvents of Class N, while in other classes solubility may be high or low. High solubility results if the solute-solvent interaction is strong relative to mutual attraction. Low solubility results from the reverse relation.
3. *Intra*molecular H bonded compounds do not behave like AB species, despite their having both acidic and basic groups. They may behave either as Class N or Class B, and tend to show "normal" behavior.

TABLE 2-X The Effect of Mixing H Bonded Liquids on Boiling Point

CLASSES MIXED	DEVIATION FROM RAOULT'S LAW	CHANGE IN H BONDING ON MIXING	EXAMPLES[a]
1. AB + N	Always +	H bonds broken *only*	Butyric acid + *o*, *m*, or *p*-xylene (min), hexanol + 2,7-dimethyloctane (min)
2. B + A	Always −	H bonds formed *only*	Acetone + chloroform (max), pentachloroethane + cyclohexanone (max), butane oxide + chloroform (max)
3. AB + A	Nearly always +	H bonds broken and formed—breaking usually more important	Methanol + chloroform (min), pentachloroethane + butyric acid (min), 1,1,2,2-tetrachloromethane + glycol (min)
4. AB + AB	Usually +	H bonds broken and formed	Ethanol + water (min), water + hydrazine (max), water + formic acid (max), water + allyl alcohol (min)
5. AB + B	Usually +	H bonds broken and formed	Dioxane + water (min), formic acid + dioxane (max), methanol + acetone (min), 2-butanone + butylamine (min), acetic acid + pyridine (max), methylamine + 1,3-butadiene (min), methanol + ethyl formate (min), methanol + benzene (min)
6. B + B A + A N + N A + N B + N	Quasi-ideal, + deviation if any	No H bonds involved	Acetone + *n*-hexane (min), benzene + methylcyclopentane (min), propyl ether + triethylamine (min), methyl mercaptan + butane (min), 2-butanone + benzene (min)

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[a] From 959 and 627.

TABLE 2-XI Comparison of Predicted and Actual Binary Azeotropic Behavior

Within each horizontal box in the four center columns, the top line shows the predicted behavior; next is the number of cases found *as predicted;* last is the number of cases *opposite* to the prediction.

	AZEOTROPIC BEHAVIOR WITH COMPONENT 2 OF				
COMPONENT 1	CLASS A	CLASS B	CLASS AB	CLASS N	RATING RATIO[b]
H_2O	min	Usually min	min or NA[a]	min	
Class AB	11	39	29	6	85/92 = 0.92
	0	3	4	0	
Formic acid	min	Usually min	min or NA	min	
Class AB	6	10	0	23	39/47 = 0.83
	0	6	2	0	
$CHCl_3$	min or NA	max	min	min or NA	
Class A	0	10	3	5	18/25 = 0.72
	0	5	1	1	
Acetone	max	min or NA	Usually min	min or NA	
Class B	1	5	2	5	13/18 = 0.72
	1	0	4	0	

[a] NA = nonazeotropic.

[b] The rating ratio is the number correctly predicted divided by the total considered.

Before presenting examples, we should remark that the subject of solubility of nonelectrolytes has been treated in detail by Hildebrand and Scott (921). They discuss (in their Chapter XI) the various "chemical" and "physical" theories of the interactions, such as H bonding, that are responsible for extreme deviations from regular behavior. Both approaches can provide equations to fit experimental data. The first does so by relating equilibrium constants and activity coefficients for assumed reactions, and the second by the use of varying values of the energy of interaction and empirical factors for the effective volume of solute and solvent molecules. They conclude with the observation, still valid, that no satisfactory theoretical treatment is available.

The thermodynamic functions of mixing two substances, *a* and *b*, are conveniently expressed in terms of the difference in solubility parameters ($\delta_a - \delta_b$). The applicability of this treatment is limited to systems for which the interaction between *a* and *b* molecules is the geometric mean of the separate interactions among *a* molecules and among *b* molecules. This is rarely true for H bonding liquids.

As simple examples, consider diethyl ether and chloroform. These compounds are miscible with each other, but their solubilities in water are not high (7.5 percent for ether, less than 1 percent for $CHCl_3$). They cannot "compete" with the strong H bonding in water. On the other hand, each is miscible with ethanol—a Class AB substance that is not so thoroughly H bonded as water. Ferguson (642) argues that the low solubilities of various ethers in water (as compared to those of the isomeric alcohols) show there is a steric shielding factor (see Fig. 2-7). He cites the high solubility of dioxane, and explains it as lack of shielding—dimethyl ether also has high solubility in water. Certainly H bonding is not the only factor. For example, compare acetone, butanone, and 2-pentanone. The first is miscible, the second dissolves 35 g/100 ml H_2O, and the last is only slightly soluble. On the other hand, steric hindrance is not a comprehensive explanation. Note the work of Hoerr *et al.* (940) in which the solubility of 2-nonadecanone is found to be less than or about equal to that of 10-nonadecanone in several solvents—H bonding and non-H bonding. Boucher and Skau (250) have published an extensive set of solubility charts.

The formation of H bonds by C—H hydrogen is not as well accepted as formation by O—H and N—H. In Chapter 6 evidence for this and other doubtful cases is collected. Included there is the extensive work of Zellhoefer, Marvel, and Copley[a] on the solubility of partially chlorinated hydrocarbons. They concluded:

1. The proton of the C—H group can H bond, at least when "activated" by halogens.
2. Ethers, aldehydes, ketones, and trialkylamines as bases form the strongest H bonds and are the best solvents for compounds containing labile hydrogens.
3. Acids, alcohols, amides, and oximes form strong complexes among solvent molecules, and, as a result, are not good solvents.

These results are typical of the generalizations we have given earlier.

The solubilities of polymeric materials and complicated compounds can often be predicted on the basis of the behavior of simpler com-

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[a] The first paper was 2234a and the fifteenth 1350.

pounds. Valentine (2085) correlated the solvent power of about twenty phenols for cross-linked polyamide (nylon 66) with H bonding ability. Becker and Stahmann (183) showed how copolymerization produced mixed polypeptides of greater water solubility than that of polymers of either compound. Steric misalignment in the copolymer leads to fewer *intra*molecular H bonds and leaves bondable groups available for association with the solvent. (See also 1774.)

Since H bonding equilibria are very dependent on temperature, it is probable that the temperature coefficient of solubility is a relatively high negative number for solutions that depend on H bonds. It is known that pairs of H bondable substances often have large negative heats of mixing, a condition for decreased solubility at higher temperature (131a, 1996). (See our Section 2.4.4, plus Fig. 3-7 and the accompanying discussion.)

Another solubility phenomenon that may depend partly on H bonding is consolute temperature or critical solution temperature formation in mixtures that have a composition region in which they are immiscible. The region narrows as the temperature is changed. Above an *upper* consolute temperature, or below a *lower* consolute temperature, the components are miscible over the entire composition range. Figure 2-11 shows such loops for 2,4- and 2,5-dimethylpyridine in water, as reported by Andon and Cox (45a). Other pyridine-water systems are considered by the same workers in later papers (see 453 and references given there). The upper values can be explained by the theory of regular solutions, but lower values are more difficult to treat since a large

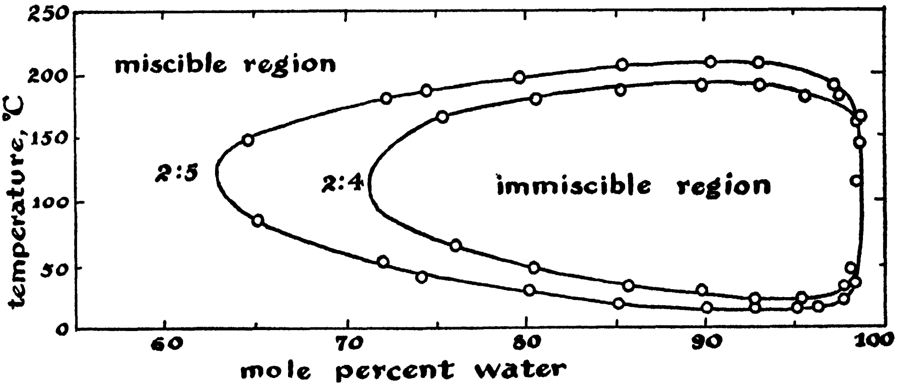

FIGURE 2-11 Closed solubility loops for some dimethyl pyridines in water. [From Andon and Cox, *J. Chem. Soc.* 1952, 4601–6.]

negative excess entropy change and small negative enthalpy are required. Eyring (932) suggested H bonds in a delicate balance with van der Waals forces as the responsible factor. More recently, Copp and Everett (441) discussed the thermodynamics and structural factors necessary for critical solution behavior, and concluded that a necessary condition for lower values is components which can "associate." (See also 131a and 440.)

H bonding is, of course, an important type of complexing, and the H bondable substances dominate the list of substances known to form lower critical solutions. They are most commonly Class AB (H_2O, alcohols, glycols) with Class B (amines, ketones, ethers) mixtures. (See also 939.) Andon, Cox, and Herington (48) conclude that H bonding and ionization have a role in producing lower consolute temperatures. The value of the upper critical temperature is raised and that of the lower critical temperature is lowered by replacement of H_2O by D_2O. Furthermore, the region of immiscibility is increased (46). D_2O is thought to form stronger associative bonds than does H_2O, and the immiscibility might be so explained. The effect of pressure is not well documented, but Cox and Cretcher (451a) refer to the methylethylketone-water system as having a closed loop at high pressure. This might be expected, provided the system very nearly forms a loop at atmospheric pressure.

2.4.3 Ionization. There is an empirical correlation between ionization and dimerization constants of carboxylic acids. In general the two increase together. A comparison of these properties is shown in Fig. 2-12, taken from Allen and Caldin (25). Tamres and his colleagues (1996) studied aliphatic amines and pyridines more closely and related pK_a and heat of mixing with $CHCl_3$. Their data are replotted in Fig. 2-13, which shows clearly that no single relation exists to correlate ionization and H bonding. Separate empirical curves are necessary to allow for structural effects as well as general chemical type, since, for example, pyridines do not fit the same equation that aliphatic amines do.

2.4.4 Heat of Mixing. When H bonds are formed in a mixture, the heat of mixing is a larger negative number than it is for noninteracting components. Just as for the solubility case, a somewhat qualified statement is necessary for those mixtures in which the equilibria already existing in one component are upset and new ones are formed when the second member is added. Then ΔH of mixing can be higher or lower than for unassociated solutions. The data from one of the most extensive studies (1313), which were reported without discussion of the cause of the effects, permit the construction of Table 2-XII. This table also includes a comparison of the actual trends with those predicted from Table 2-X.

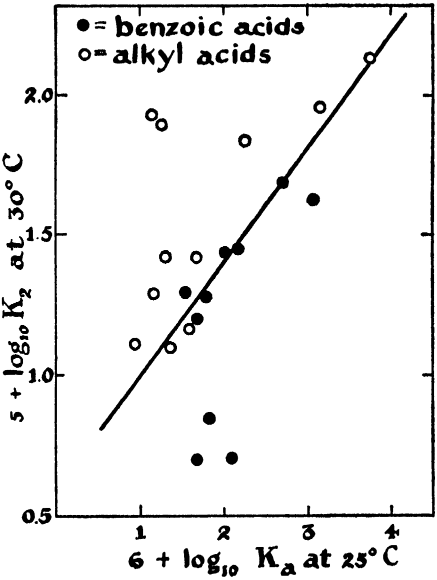

FIGURE 2-12 The relation between dimerization constant (K_2) and ionization constant (K_a) for some carboxylic acids. [From Allen and Caldin, *Quart. Revs.* (*London*) *7*, 255–78 (1953).]

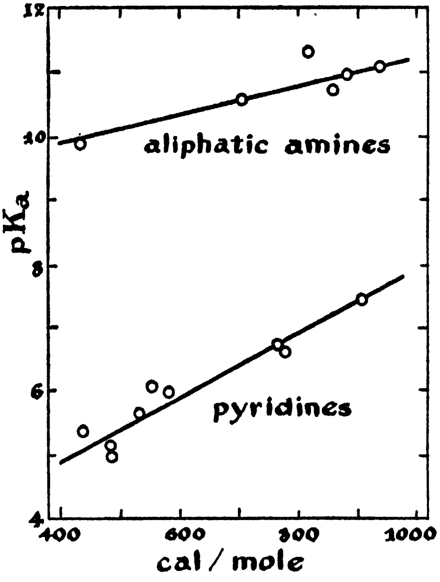

FIGURE 2-13 Comparison of heat of mixing (amines and $CHCl_3$) with pK_a. [From Tamres, Searles, Leighly, and Mohrman, *J. Am. Chem. Soc.* **76**, 3983–5 (1954).]

In general, the predictions are good enough to be useful, and for the first two types listed, which involve only making or breaking H bonds, the predictive success is high.

2.4.5 Partition. Another phenomenon related to solubility and also affected by H bonding is the partition or distribution of a substance between two liquids. The subject is quite extensive, having grown particularly in recent years as chromatography has been developed for analysis and separation. Several books (961, 2149) and Craig's reviews (456, 457) give good starting points for the reader interested in the general theory and applications. Some aspects of H bonds in chromatography are discussed in our Chapter 11. Davies and Hallem (481) have reviewed the determination of association by distribution.

The partition coefficient, *k*, is the ratio of equilibrium concentrations

TABLE 2-XII Heat of Mixing as Related to H Bonding Type

CLASSES MIXED	TEMPERATURE CHANGE		
	PREDICTED FROM TABLE 2-X	EXPERIMENTAL[a]	
		FALL	RISE
1. AB + N	Fall	87M[b]	0
2. B + A	Rise	10	56L
3. AB + A 4. AB + AB 5. AB + B	Usually fall	98	42
6. B + B A + A N + N A + N B + N	No effect or fall	215S	116S

[a] Number of pairs of mixtures.

[b] M = medium, L = large, S = small average effect for each mixture type.

necessary to produce equal chemical potential of the solute in the two liquids. Hence the effect of H bonding on the coefficient ratio is understandable in terms of the discussion of H bonding and solubility (Section 2.4.2). For example, the ratio will be high if H bonding enhances the solubility in the numerator of k.

As a practical matter, there are several limiting features that have restricted the method's usefulness. Among these are association of the third component with either or both solvents, the change in mutual solubility of the solvents which the solute may cause, and ionization in one or both solvents. As a result, reliable quantitative interpretations are possible for only the simplest systems. We shall be content to describe the qualitative aspects of the part which H bonding takes.

It is well established that k varies among different solvent combinations in a way generally predictable from solute solubility in the solvents. Table 2-XIII shows k values for partition of the first few members of the fatty acid series between various organic solvent-water combinations. High k values reflect relatively large concentration in the aqueous layer, and low values concentration in the organic phase.

The values of k in CCl_4 establish a norm for an organic solvent with

TABLE 2-XIII Partition Coefficients (k) of Some Fatty Acids in Various Organic Solvent-Water Systems[a]

$$k = \frac{\text{acid conc. (in water)}}{\text{acid conc. (in organic solvent)}}$$

$t = 25 \pm 2°\text{C}$

ACID	ORGANIC SOLVENT AND H BONDING CLASS				
	BUTANOL AB	ETHYL ACETATE B	ETHER B	CCl_4 N	$CHCl_3$ A
Formic	1.2	1.7	3.1	—	—
Acetic	0.91	1.5	2.3	50	—
Propionic	0.36	0.45	0.67	1.8	5.6
Butyric	0.14	0.18	0.19	0.39	1.2

[a] Data from 1351a, except the CCl_4 values which are from 214a.

negligible acid or base character. Both ether and ethyl acetate form H bonds with the solutes, in agreement with the expected base strengths of these solvents. Butanol, acting as both an acid and a base, gives even lower *k*'s. The acid strength of chloroform appears to be too low to "compete" with the acids and water.

The role of H bonding can be illustrated still more forcefully by grouping solvent systems according to the classification described previously (Table 2-IX). Brown and Mathieson (297) suggested a similar classification. Table 2-XIV collects a large number of *k*'s for acetic acid (again in organic solvent-water systems), tabulated according to the H bonding type of the solvent molecule.

These *k* values show two trends—in a row across the table they increase (more acid in the water) as the organic solvent becomes less able to form H bonds. Down each column they grow larger as the organic phase has a smaller fraction of its atoms available for H bonds. The same trends can be expected if some other H bonding solvent replaced water.

In order to keep this section within manageable size, we have discussed partition of but one compound, acetic acid, but other classes of chemicals behave according to the same principles. Collander has presented several broad studies covering hundreds of compounds (419, 418, 417).

The quantitative understanding shown in Tables 2-XIII and 2-XIV can be used in controlling partition. For example, Pearson and Levine

TABLE 2-XIV Partition Coefficients of Acetic Acid in Various Organic Solvent-Water Systems[a]

$$k = \frac{\text{acid conc. (in water)}}{\text{acid conc. (in organic solvent)}}$$

$t = 15°\text{C}$, unless noted

NO. CARBON ATOMS	ORGANIC SOLVENT AND H BONDING CLASS									
	PHENOLS AB		ALCOHOLS AB		ESTERS B		ETHERS B		N[b]	
4	—		Butanol (26°C)[c]	0.91	Ethyl acetate (18°C)	1.1	Diethyl	2.0	—	
6	Phenol	0.71	Cyclohexanol	1.12	Butyl acetate	2.8	Di*iso*propyl (23°C)	3.8	Benzene (25°C)	25
7	Cresol	1.04	—		—		—		Toluene (25°C)	25
8	—		Octanol (20°C)[d]	2.04	Hexyl acetate	2.8	di-*n*-Butyl (23°C)	10	CCl_4	50

[a] Unmarked data from 571a.

[b] Compounds in this column not arranged according to number of carbon atoms.

[c] 1351a.

[d] 417.

(1603) have shown how solvent mixtures can be designed to combine the various solvent actions and produce a desired change in *k*.

There are inherent complications in partition studies. The presence of at least three components implies many possibilities for interactions. More important is the effect of the mutual solubilities of the two solvent phases. No two solvents are perfectly immiscible, and hence the data always refer to the partition of one component between two binary liquids. The effect of the usually small amount of dissolved solvent can be large. For example, a useful test for distinguishing *intra*molecular and intermolecular H bonding is the determination of the "dry" and "wet" melting points. The small amount of water that dissolves in the liquid phase has a pronounced effect on the melting point of intermolecularly H bonded substances. See Section 5.3.4 and Table 5-IV for examples and discussion of this effect.

2.4.6 Cryoscopy. Cryoscopy is the measurement of freezing point lowering by a solute to determine molecular weight. It has been applied extensively to the study of H bonding, in large part as a qualitative measure of the type and existence of association. Hunter and his school reported a long series of researches from 1937 to 1952, covering hundreds of examples dealing mostly with substituted amines and amides plus compounds with multiple nitrogen atoms.[a] Hunter's work is exemplified by Fig. 2-14. In general, H bonding materials have increasing apparent molecular weights as the concentration goes up, whereas constant molecular weight is found where no association occurs. In the specific case shown, the results indicate that polymers form when one or two hydrogen atoms remain on the nitrogen, but no association occurs if the nitrogen is fully substituted. A similar result came from dielectric work (1204).

Amides are by no means the only substances to be studied by freezing point depression. Phenols have received attention (507, 1743), as well as such widely varying substances as organophosphorus compounds (1136), pyrrole (1066), arylstibonic acid (527), and trimethylsilanol (169).

The cryoscopic method can be used to determine the equilibrium constants (*K*) of the association involved. This is illustrated by Barton and Kraus' work (144) on the dimerization constants of some carboxylic acids. Their value of *K* for benzoic acid in benzene fits well on the ln *K vs.* $1/T$ line determined by Wall's isopiestic data (2134, 2133) and

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[a] 372, 371, 370, 369, 895, 1009, 1012, 1008, 894, 897, 955, 1011, 325. See also 636, 1437, 2100, 1576, 2073, 1023, 1171.

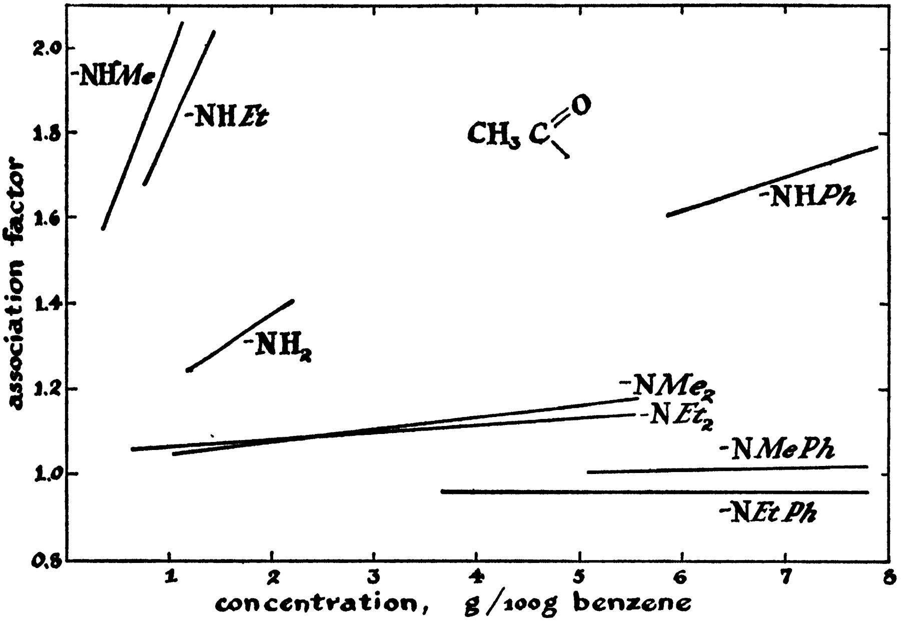

FIGURE 2-14 Cryoscopic evidence for H bonding of acetamides in benzene solution. [From Chaplin and Hunter, *J. Chem. Soc.* **1937**, 1114–8.]

gives $-\Delta H$ of association as 8.4 kcal/mole. In another example, Allen and Caldin (26) used the change in boiling point at three pressures to obtain *K* and thermodynamic properties of various aromatic carboxylic acids. The $-\Delta H$ values are between 4.0 kcal/mole and 4.6 kcal/mole. These *K* values, and those mentioned below, are treated in Chapter 7 along with those determined by other methods.

There are several formulae (222, 565, 1198) for this purpose, and a paper by White and Kilpatrick (2170) is an excellent example of their application. For eight fairly complex organic compounds[a] containing N—H groups, three methods of calculating *K* were applied and the type and extent of equilibria determined. Table XIII of that paper is a challenge to further work in this field. All the compounds listed have N—H groups and other nitrogen atoms capable of acting as proton acceptors, yet three of them hardly associate at all, two others form linear polymers, and the remaining three seem to have cyclic dimers or a mixture of linear dimers and cyclic trimers. Calculated

---

[a] 2-*n*-Butylbenzimidazole, benzotriazole, *N*,*N'*-diphenylguanidine, *N*,*N'*-diphenylformamidine, 3,5-dimethylpyrazole, diazoaminobenzene, benzaldehyde phenylhydrazine, *N*-phenyl-*N'*-*p*-tolylacetamidine.

values of the equilibrium constants are about the same by the three theories—usually agreeing fairly well for monomer-dimer or monomer-trimer formation. The higher order constants vary more.

As a final example, Scheele and Hartmann's paper (1808) on sulfonamides illustrates the use of several cryoscopic solvents (with the concomitant changes in boiling point) to give sufficient temperature range so that ΔH can be determined from the ln *K vs.* $1/T$ plot. Their work showed that dimers form for the amides with just one hydrogen on the nitrogen. If more than one H bonding site exists per molecule, chain formation and cross-linking can occur. The enthalpy for the N—H···O bonds is in the range 1.9–3.7 kcal/mole for various *N*-diphenylsulfonamides.

There are many other physicochemical properties that show the presence of H bonds. They are of lesser importance, mainly because of difficulties of quantitative interpretation. We shall cover, in brief, some of these less commonly used methods of investigating H bonding.

The first column of Table 2-XV lists these properties and some additive functions that have been used; the middle column gives the

TABLE 2-XV Effect of H Bonding on Some Physicochemical Properties of Liquids

PROPERTY	BEHAVIOR OF INTERMOLECULAR H BONDED COMPOUND RELATIVE TO NON-H BONDED[a]	REFS.
Molar volume	Lower	
Density	Higher	
Molar refraction	See discussion 2.4.9	
Molar polarization	Higher	
Thermal expansion	Lower (slightly)	
Thermal conductivity	Higher	1144 1571
Acoustic conductivity	Higher	1027
Viscosity	Much higher	
Surface tension	Higher	
Self diffusion	Lower	
Parachor	Lower	
Diamagnetic susceptibility	(Increases with concentration)	54[b]

[a] See Chapter 5 for a discussion of *intra*molecular H bonding and a more extensive table of this type (Table 5-I).

[b] See, however, 55.

general direction of deviation caused by intermolecular H bonding; the final column lists references to reviews or articles of broad coverage on that topic.

The relations shown in Table 2-XV do not always apply to solutions or gas mixtures. As mentioned before, the presence of more than one component may greatly complicate the interpretation because of the possible association in each component as well as intermolecular attraction between them. As temperature and concentration change, these two types of attraction are present in changing degrees; the present state of knowledge does not permit a reliable prediction of the final effect on a physical property.

2.4.7 Molar Volume-Density. In general, H bonds increase density and lower molar volume; this behavior reflects the unusually short interatomic distances of the H bond. The data in Table 2-XVI are illustrative. The first three pairs indicate that each of the H bonding compounds has a molar volume about 10 percent lower than comparably sized nonassociated substances. One of the examples in the fourth group, *N*,*N'*-dimethylacetamide, suggests that the low molar volumes of the amides are not wholly due to H bonding. This draws attention to the fact that density and molar volume are affected by structural factors other than H bonding, as a glance at the API tables of physical properties will show.

The last two groups of compounds in Table 2-XVI illustrate the same trend for inorganic molecules. They follow the same pattern as the organic compounds. The values for water are especially interesting since they indicate water has a close packed arrangement of molecules. This statement is contrary to the usual reference to the "open" structure of ice. Two important qualifications on the usual statement are necessary. First, ice has an open structure *relative to liquid water*, but it is still quite close packed relative to a nonassociated substance. Second, the unusual decrease in density when water is frozen is misleading. It is unique in water and, in fact, occurs only for the low pressure (naturally occurring) form, ice I, but not for the higher pressure forms, all of which are more dense than water at the same conditions (1746; 544, p. 395–398).

The overall, generally small, effect of pressure to increase H bond formation can be understood as a molar volume change. It is another fulfillment of LeChatelier's principle—H bonds reduce the space occupied by the molecules so their formation is enhanced by a process

TABLE 2-XVI Density and Molar Volume of H Bonded Compounds Compared to Nonassociated Substances of Similar Size[a]

COMPOUND	MOLECULAR WEIGHT	DENSITY, 20°C, (g/cc)	MOLAR VOLUME (cc/mole)
Phenol	94	1.071 (25°C)	87.5
Anisole	108	0.990 (22°C)	109.2
Propanol	60	0.804	74.8
Methyl ethyl ether	60	0.697	86.0
Propionic acid	74	0.992	74.5
Methyl acetate	74	0.933	79.4
n-Butyramide	87	1.032	84.2
N-Ethylacetamide	87	0.942	92.3
N,*N'*-Dimethylacetamide	87	0.943	92.3
N-Methylpropionamide	87	0.930 (25°C)[b]	93.5
2-Methylpentane	86	0.654	132
H_2O	18	0.99987 (0°C)[c]	18.0
NH_3	17	0.817 (−79°C)[c]	20.8
HF	20	0.988 (13.6°C)[c]	20.2
CH_4	16	0.47 (−184°C)[c,d]	34.0
H_2O_2	34	1.71 (−0.43°C)[c]	19.9
H_2S	34	1.22 (−194°C)[c,e]	27.9
SiH_4	32	0.68 (−185°C)[c]	45.8

[a] Data from *International Critical Tables*, McGraw-Hill Book Company, Inc., 1926, New York; or *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, 1956, Cleveland, Ohio, except as noted.

[b] *J. Am. Chem. Soc.* **59**, 109–11 (1937).

[c] At the melting point, except H_2S which melts at −83°C.

[d] *C.A.* **3**, 866.

[e] *C.A.* **26**, 2096.

producing less available space per molecule. More definitive is the thermodynamic relation

$$\left(\frac{\partial \Delta F}{\partial P}\right)_T = \Delta V_m = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T$$

This shows the direct relation of K and the change of molar volume.

In H bonded solutions, density is often greater than an arithmetic average value calculated from the components (2019). Here again, any general statement must be tempered by qualifying remarks based on the kind of association existing in the two components *before* mixing and that possible *after* combination. We might expect the density change to follow the same type of pattern as heat of mixing—density decreasing as H bonds are broken, and becoming larger as they are formed. Sometimes, of course, steric limitations prevent obeyance of this straightforward rule of thumb. This density change has been used to detect association. Bramley's work provides an early example of association as an explanation for property deviations in phenol solutions (263). See also Madsen (1314) (toluene + CH_3OH), Vansenko and Dubrovskiĭ (2104, 2105), (water + amide, mixtures of amides), and Taketa (1992, 1993), (pure oxy-acids). In the usual study several physicochemical properties are measured—density is one commonly included.

The work of Migal and Belotskiĭ (1402) furnishes a good example of the difficulties that can arise. Their extensive and careful work shows only slight indications of interactions detected by density or surface tension measurements of ethanol-aniline, whereas their viscosity and refractive index data do not show complex formation at all. In the ethanol-$CHCl_3$ system none of their tests shows interaction.

Gibson and Loeffler (752) treated solutions of ionic salts in glycol and water, and concluded that H bonds (and changes in them) have a major effect on contraction during mixing and thermal expansion in aqueous solutions.

2.4.8 Parachor. The parachor is the best known of a group of additive functions related to molecular volume and based usually on some easily measurable quantities. Parachor is almost the only one of these which has been applied to H bonding, but similar findings would probably hold for others. There is some question about the theoretical basis for the parachor (1707), and perhaps it should be considered an essentially empirical relation.

Hydrogen bonding pure liquids and solutions yield experimental parachor values lower than nonassociated liquids. For example, the observed parachors of pure formic and acetic acids are 93 and 131 (calculated 102 and 141) (999). Similarly, Shukla and Bhagwat found a minimum in the parachor–concentration curve for pyridine mixed with a variety of alcohols (1868).[a] Shukla and Bhagwat make the pertinent point that a fixed group parachor value for H bonding cannot be expected because various H bonds are different and give differ-

[a] See also 751, 750, 60, 208–210, 2034.

ent "lowering" of parachor. As yet, no extensive, systematic study has been reported.

Sidgwick and Bayliss (1875) studied *o*-substituted phenols and noted that the experimental parachor is lower than that calculated from the atomic values. They assigned this lowering to the formation of a chelate ring, and derived a parachor value for this structural arrangement. With changing temperature, internally H bonded compounds reveal no change in parachor, in contrast to the increase usually found for intermolecularly associated isomers (315).

The parachor does not appear to be a particularly useful index of H bonding. The quantities making it up are all affected by H bonding; surface tension in particular is extremely sensitive to impurities.

2.4.9 Molar Refraction-Refractive Index. Molar refraction $[R]$ is related to molar volume (V_m) and refractive index (n) by the equation:

$$[R] = \frac{V_m(n^2 - 1)}{n^2 + 2}$$

Since both molar volume and refractive index are influenced by the actual molecular species present in a solution, molar refraction has some potential value for studying association equilibria. Giles and co-workers (65–68) correlated the method with dielectric constant measurements, and have been the most active users of refractive index for studying compound formation. Reference 68 reviews earlier work (which is sketchy) and lists about forty systems (mostly oxygen containing compounds) that were studied. References 65–67 deal with amide, amine, and azo compounds, plus esters and additional work on alcohols, aldehydes, ketones, and carbohydrates. The method is simple; the refractive index of a series of mixtures of varying composition but constant concentration in a solvent is measured. Compound formation is shown by a change in the slope of the *n vs.* mole fraction plot, such as in Fig. 2-15.

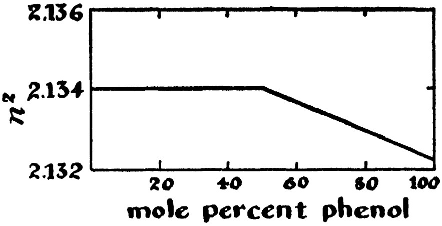

FIGURE 2-15 Refractive index of phenol-dimethyl formamide solutions (in CCl_4) showing 1:1 compound formation. [From Arshid *et al.*, *J. Chem. Soc.* **1955**, 67–79.]

One disturbing factor about this research is the extensive use of H bonding materials (water, dioxane, diethyl ether, benzene, ethanol, acetone, aniline, and ethylene glycol) as solvents, with occasional use of CCl_4 and "light petroleum." Unfortunately, many of the cases in which no complex was detected are in CCl_4 or one of the poorer proton acceptors (benzene or toluene). On the other hand, not all water and dioxane solutions showed compound formation. A firmer basis for the proof of these complexes would result if the only possibility for H bonding were between the two solutes. Probably the only clearcut conclusion to be drawn from this work is that changes in index of refraction *have* been observed, verifying the possibilities of the method.

Batsanov and his group report (237, 151, 153) a molar refraction increase for H bonded inorganic solids. They first compare $[R]$ of potassium and ammonium halides and find that the NH_4 salt has, on the average, a refraction larger by 1.60 cc. Then they find the refraction difference in various K and NH_4 compounds. Any difference larger than 1.60 cc is said to be "excess refraction" due to H bonding, and this quantity is divided by the number of H bonds postulated for the compound. In this way, they derive $[R]$ of several types of H bonds: N—H···O (0.17–0.50 cc), O—H···O (0.13–0.24 cc), N—H···F (0.27 cc), N—H···N (0.96 cc), and N—H···Cl (0.08 cc). The method is also applied to salt hydrates and some H bonding found among the molecules of hydration. These values have not been tested for an extensive list of compounds, nor has the use of these H bond $[R]$ values in organic substances been verified yet.

2.4.10 Thermal Conductivity and Thermal Expansion. Thermal conductivity of liquids (and gases to some extent) is still an empirical subject in any but the broadest sense. Kowalczyk (1144) reviewed the subject and the equations which relate thermal conductivity to viscosity, molar volume, melting point, and sound conductivity. Sakiadis and Coates (1776, 1777) tabulate values for a number of compounds and present correlation functions for thermal and sound conduction.

Associated compounds conduct heat better than do non-H bonded substances, and Table 2-XVII illustrates some trends and magnitudes. The alcohol series probably reflects the interference of longer hydrocarbon chains and the increasing difficulty of rotation for larger molecules. Water is compared with CS_2 because compounds nearer its molecular weight (e.g., methane) are gases at 30°C.

Palmer (1571) made special use of H bonding in his explanation of the conductivity of alcohols and glycols. Two contributions by H bonds are visualized; one is an orientation of the molecules along the path of heat flow, and the other is the addition of another mechanism for heat transfer. Hydrogen bonds break at the hot side of the tempera-

TABLE 2-XVII Thermal Conductivity Coefficient for Intermolecular H Bonded Liquids

COMPOUND	$k \cdot 10^6$ at 30°C (cal-cm²/sec-°C)	TYPE OF H BONDING
n-Butanol	365	Intermolecular
Diethyl ether	329	None
Pentane	322	None
Methanol	500	Intermolecular
Ethanol	410	Intermolecular
n-Propanol	380	Intermolecular
n-Hexanol	386	Intermolecular
Aniline	412	Intermolecular
Toluene	364	None
Water	1480	Intermolecular
CS_2	382	None

ture gradient (absorbing heat) and reform, after migration or rotation, at the cold side of the gradient. The mechanism is similar to that for electrical conduction (see Section 2.1.5), but he has not worked it out in detail. Intermolecular H bonds are expected to facilitate this passage of heat, and the **k** values are high (see water and the alcohol series). Chelation interferes with this mechanism, and the few data available show lower **k**'s for these substances. Palmer calculates, by assuming that any increase of **k** over the value for the corresponding hydrocarbon is due to the presence of H bonds, that H bonds carry the following fractions of the heat conducted: for water, 0.80; for methanol, 0.32; and for longer chain alcohols, a decreasing fraction.

Hydrogen bonding must also play an important part in determining the temperature coefficient of heat conductivity, which is positive for water and glycerols, negative for alcohols, and more negative for unassociated substances. Typical average values[a] of $\Delta \mathbf{k}/\Delta T$ are: water, $+10 \cdot 10^{-7}$; *iso*-pentanol, $-1 \cdot 10^{-7}$; and toluene, $-6 \cdot 10^{-7}$. The temperature coefficient for water is positive between 0°C and 120°C and then becomes negative up to the critical temperature.

Filippov (653, see *C.A.* **49,** 15430h; 652, see *C.A.* **50,** 8276g) studied many of the same compounds that Palmer did, as well as mixtures which might be expected to associate. In general, he found that the

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[a] Data from Bridgeman and Smith, as quoted by Smith (1900a); Units of **k** as in Table 2-XVII.

presence of H bondable groups (OH, NH_2, NO_2) increases **k** in the pure liquids. In solutions (mainly alcohols, esters, and ketones), he concludes that the data can be expressed by the same empirical equation used for "normal" liquid mixtures. This is a curious result and deserves further checking. Sakiadis and Coates (1776) published tables of additive group values (similar to those for molar refractivities or parachor) for acoustic and heat flow. No provision is made for H bonding, but calculated values are in good agreement with experiment (within 2–4 percent). In each correlation, the value for —OH is considerably lower than for other groups—perhaps a H bond contribution is concealed there. It is generally observed that H bonded gases show a relatively rapid increase in conductivity as temperature goes down or pressure goes up. Since these changes in conditions are known to increase H bonding, this behavior suggests that H bonds are important carriers of heat.

In studying vapor association, Lambert (1184), Vines (2119, 192, 193), and Foz Gazulla (687, 686) have been most active. The last author, working with Schafer (1804; see also *C.A.* 37, 4943, 5294), derived an equation relating conductivity to the heat of dimerization and the dimerization constant. The final equation has three limitations: it is rather complicated, it is limited to dimerization, and it is based on a modified perfect gas law. Vines (2119) gives examples of this method and calculates $-\Delta H$ for methanol as 4.2 kcal/mole, in agreement with other values discussed in Chapter 7. A rather high value for the enthalpy of association of HF gas (6.8 kcal/mole) was found by another method based on heat conductivity (694).

2.4.11 Acoustic Conductivity and Adiabatic Compressibility. Acoustic conductivity is usually increased by intermolecular H bonding (860, 1958, 2002). Kittel (1114a) describes the interrelation of translational and vibrational energies and how they are transmitted. Kittel uses Eyring's model of the liquid state to give the following general picture of conductivity. The molecule itself is a low resistance path for sound (or heat) flow because the molecular vibrations effect "instantaneous" transfer of any incoming energy to all of its parts. The space between molecules is a barrier to transfer. In H bonded aggregates of molecules, there are fewer "spaces." On this basis, *intra*molecular H bonding would have little effect on conductivity, which is in agreement with experience (1776). (Table 2-XVIII gives a few values of acoustic conductivity in some H bonded liquids.) This same model also explains why conductivity in H bonded liquids increases with pressure and decreases with temperature.

H bonding is not the sole factor in conducting acoustic vibrations. For example, tetralin (1465 m/sec) and dioxane (1378 m/sec) conduct the acoustic waves better than does ethanol.

TABLE 2-XVIII Acoustic Conductivity in Some H Bonded Liquids

LIQUID	T (°C)	u^a (m/sec)	REFS.
Water	22.5	2008	1897
Ethanol	23.5	1207	1578
Ethylene glycol	24.0	1721	
Aniline	24.0	1682	
Pyridine	24.0	1448	
Cyclohexanol	23.5	1622	
Cyclohexanone	23.5	1441	
Cyclohexane	23.0	1257	
Water-ethanol	20	~1200	1192
Phenol-CCl_4 (0–13 mole %)	20	940–970	1397

[a] Acoustic velocity.

In addition to affecting transmission, H bonds can take part in acoustic absorption. Hall (860) explained the absorption of water as being partly caused by molecular rearrangement lag. He visualized two energy states and found that ΔF for transition between them was 0.5 kcal/mole and, on the strength of Ewell and Eyring's viscosity study (626), concluded that the breakage of a H bond was the process occurring between the two states. Smith and Lawson (1897) support Hall's treatment to some extent, but demurred at the idea of H bond breakage. They find $-\Delta H$ to be 2.6 kcal/mole and propose that this represents the energy to bend a H bond. The question is still an open one.

Although there is yet no adequate theory for pure liquids, H bonding solutions have received attention. See the work of Maier and Mez (1321, 1397, 1322), Eppler (611), Larionov (1191–1193, 1528), and others (1958, 119, 1832, 1632). Solutions generally show a decrease in u with increasing temperature.

Acoustic vibrations also show relaxation behavior similar to that described under dielectric properties (Section 2.1). In some cases (glycerol), the relaxation times from the two types of measurement are of similar magnitude (1295). In any event, curves like those of Figs. 2-6(a) and 2-6(b) are obtained, and distributions of relaxation times are found. There is much less work in acoustics than in dielectrics. Furthermore, Lyon and Litovitz (1295) show why the process of alignment or molecular flow itself will produce a distribution whether or not any distribution results from H bonding. So care must be used in interpreting acoustic results. (See also 609.)

Adiabatic compressibility, β, is related to acoustic velocity in a liquid by the equation

$$\beta = \frac{1}{u^2 d}$$

where u = acoustic velocity, and d = density. Clearly, the behavior of β comes easily from this equation, since the effects of H bonding on both u and d are known and are in the same direction. H bonded materials are less compressible than their unassociated counterparts.

Jacobson (1027) published a clearly written review which has the additional advantage of dealing specifically with H bonding. He derives an algebraically simple, four constant equation to connect compressibility (or sonic velocity) with concentration. Most interesting is a factor, α, the fraction of H bonds between solute and solvent (water) relative to the number of H bonds present in solvent alone. He shows α to be about 0.20–0.30 for alcohols and acetone in water. However, it can equal 1, as it does in ethanol-methanol mixtures in which the interaction in each component is almost identical to that in the mixture. In this situation the best fit of the equation is obtained. If more or stronger H bonds are formed in the mixture than in the components, α can exceed unity. For example, Jacobson predicts $\alpha > 1$ in acetone-$CHCl_3$ solutions. See Fig. 2-16.

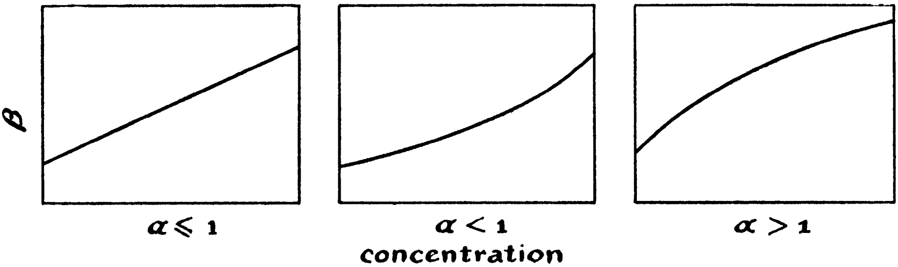


FIGURE 2-16 Schematic relation of compressibility with concentration for various types of mixtures.

Note that the same classification system used before for solubility, partition, and heat of mixing can serve as a rough guide here also. The correlation of curve shape is not completely dependable. For example, though some of Parshad's data (1577) fit Fig. 2-16, he reports curves such as that in (b) for ether-chloroform and ether-benzene even though the first would be expected to behave like acetone-chloroform and the second like CCl_4-ethyl acetate.

Other uses of ultrasonics to investigate H bonding are illustrated by a study of supercooled water (699) (which was interpreted as showing there was no ordering of the liquid in anticipation of freezing), the determination of the amount of "bound" water carried by sugar molecules (1417a), the detection of compound formation (1688), and the study of monomer-dimer equilibrium in (for example) acetic acid (699, 1180, 1181, 1632. See our Chapter 7).

2.4.12 Viscosity. Although viscosity measurements are not a particularly sensitive tool for detecting H bonds, the viscosity of associated substances is commonly higher than that of similar nonassociated compounds.

Figure 2-17 shows the variation of viscosity with molecular weight

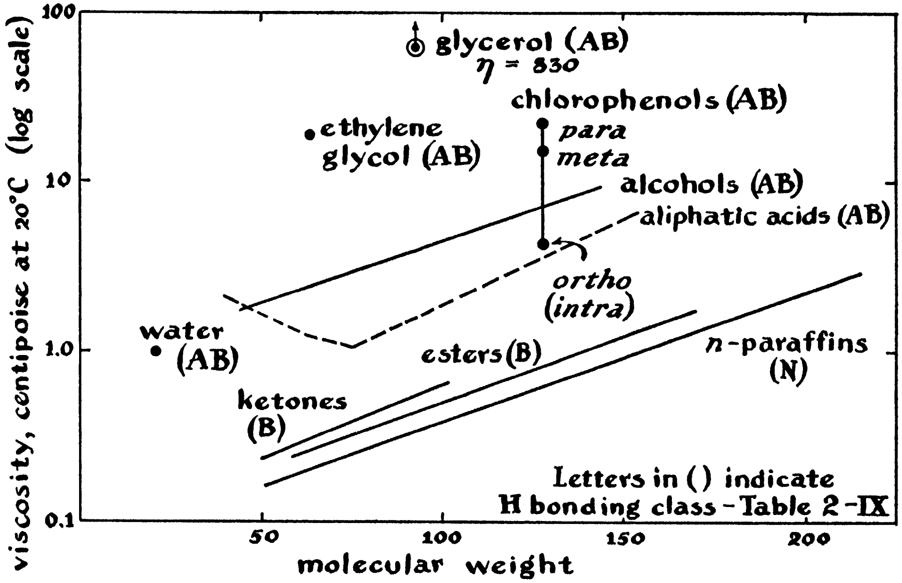


FIGURE 2-17 Comparison of viscosity (logarithmic scale) with molecular weight for H bonded and non-H bonded compounds. The acid line turns up at the left showing the anomalous behavior of acetic and formic acids. [From Kendall, *Chem. and Ind.* (*London*) **1944,** 211.]

as presented by Kendall (1097). Notice the influence of H bonding as shown by the higher viscosity for alcohols, acids, etc., and the individual points for water, glycerol, and chlorophenols. Compared to the non-H bonded esters, ketones, and paraffins, intermolecular H bonds greatly increase viscosity. Summarizing, as Kendall did, if the molecular weight is about 100, the viscosity (centipoise) will probably be in these ranges at 20°C:

	ALIPHATIC	AROMATIC
No H bonds	0.1–1.0	0.5–1.5
H bonds	1–5	2–20
Multiple H bonds	20–several hundred	—

The greater viscosity observed in associated liquids is reasonable in view of the increased size and reduced mobility of the H bonded complex.

Eyring applied his reaction rate theory to viscosity and specifically modified it for H bonded fluids (626). However, he used it just to explain in a general way the viscosity of associated liquids, since "the contributions . . . of van der Waals, dipole, and H bond forces, and especially of repulsive forces, are not known for any associated liquid." The state of affairs is not greatly different today.

Bondi (240) makes further use of the rate theory. He concludes that the H bonded polymers in alcohols require a large energy of activation for "hole formation" to explain why the viscosity is higher than that of a compound of equivalent molecular weight and similar structure. The presence of definite polymers (size not specified) is inferred from abrupt changes in the line relating thermodynamic properties of the activated state to temperature. The H bond adds complications in making radial distribution calculations when continuous association is possible (239). In the same book Alfrey and Gurnee (23a) describe how H bonds can help cause a distribution of relaxation times in viscoelastic materials as a result of their disruption and reformation.

Thomas presented an interesting paper (2021) relating H bonding and viscosity, and he was quick to point out the approximate nature of his treatment. He combined a modification of Andrade's viscosity equation with a relation between vapor pressure and latent heat of vaporization and still another function relating the heat of H bonding with the degree of association. From these he calculated an approximate heat of vaporization and compared it to a "nonassociated" value from a modified Trouton rule equation. The difference is called the "heat of H bonding at the boiling point." Clearly, only estimates can come from such a combination of empirical relations, and Thomas claims no more. It is interesting that he obtains average values of 5 kcal/mole for methanol through octanol, and 3.8 kcal/mole for branched chain alcohols.

Like other physical properties, the viscosity of a solution may have a complicated variation with composition, due to the possibility of H bonds among the solute and solvent molecules. See, for example, Madsen (1314), and Staveley and Taylor (1939).

Polymeric substances may show enhanced viscosity in H bonding solvents. Edelson and Fuoss (576) show that the greatly increased effect of water as a solvent (even compared to methanol) results from its bifunctional H bonding character which helps hold polyacrylate chains together.

In summary, H bonding definitely affects viscosity, increasing it in mixtures where H bonds occur. Drawing fundamental and quantitative information from viscosity measurements is obstructed by the same formidable complications that make any theoretical treatment of the liquid state a difficult task.

2.4.13 Surface Tension. No really definitive paper connecting surface tension to H bonding has appeared. The subject is difficult. As Hückel (978) points out, this may be a result of the sensitivity of the test to impurities—particularly water.

Lutskiĭ (1280, 1277, see *C.A.* **49**, 15324h) shows that *intra*molecularly H bonded substances have lower surface tensions than do the isomers that have interaction between molecules. For example, at 131°C the surface tensions of *o*-, *m*-, and *p*-methoxyphenol are 28.8, 33.6, and 34.2 dynes/cm. For the three dimethoxyphenols, the values are all 26 ± 0.5 dynes/cm. This same "*ortho* effect" on surface tension (as well as on viscosity, density, and boiling point) is illustrated with many types of compounds in the papers quoted.

Other studies include Taketa's series (1993, 1992) on oxyacids, from which he concludes that these compounds are polymerized via H bonds. Puchalik (1676) used surface tension (and other tests) to show that the interaction in ethanol-water mixtures is greater than in the pure alcohol. Early work on this system (2086) showed it to be abnormal "at medium concentration." As a final example, we mention some of the compounds such as the hydrated forms Glagoleva (775, 774) suggested for formic and acetic acids, and those Dunn and Polya presented for the interaction of acetamide and diacetamide (566).

Some work has been directed toward the surface film and association in it. Alexander (16, 17) studied acids, amides, and esters, and showed that H bonding, both within the layer and with the substrate, is important; it influences the formation and stability of the layer, and is a major factor in the area occupied by each molecule. Two dimensional solid films were obtained only when either long, close-packed chains of atoms were present or when H bonding was present. Such findings are clearly of interest in detergency work. These tests were made in the usual way with a water substrate. In fact, there are essentially no measurements on other liquids, so the H bonding ability of water may be an important part of the observed behavior.

Teĭtelbaum and co-workers (2012–2014) describe the use of the temperature coefficient of surface tension to study H bonding in mixtures. The curve of this coefficient against the concentration of one component normally shows a minimum, but for H bonding solutions it has a maximum. With this technique the group proposed hydrates of alcohols, ketones, and some miscellaneous compounds.

Interfacial tensions should also reflect H bonding in the liquids since association influences the equilibrium which must exist at the interface. Girifalco and Good (772) proposed a function (Φ) relating the free energy of adhesion between phases to the geometric average of the free energies of cohesion. According to their interpretation, Φ is less than 1 if there is no interaction between phases, and Φ is greater than 1 when H bonds (or other interactions) operate between the phases. In our notation of H bonding classes

$\Phi > 1$ for AB–AB, AB–A, AB–B, or A–B mixtures
$\Phi < 1$ for all others (see Table 2-X)

They find $\Phi \geqslant 1$ for water *vs.* alcohols, acids, aldehydes, ketones, ethers, and nitriles; $\Phi < 1$ for water *vs.* aliphatic, aromatic, and halogenated hydrocarbons (including benzene and $CHCl_3$, which we would place in class B). In general, good qualitative agreement is obtained, but the method requires more testing before it is very reliable for predicting surface or interfacial tensions. It also suffers the same criticism that is leveled at surface tension work—the sensitivity toward impurities is very high.

Sinfelt and Drickamer (1886a) found that the resistance to diffusion across an interface between a H bonding substance and a hydrocarbon was proportional to H bonding ability. Hindered molecular rotation in the interfacial layer is advanced as the explanation. This field is a potentially important one since it offers both fundamental knowledge about diffusion and possible improvements in extractive separations.

2.4.14 Diamagnetic Susceptibility. The change in diamagnetic susceptibility when H bonds form is not clear, but at most a rather small decrease occurs. Early exponents of a decrease as a result of H bond formation include Angus and Hill (salicylic acid, benzoic acid in various solvents, 54), Venkataramiah ($CHCl_3$-ether, 2112), and Anantakrishnan and Varadachari (alcohols, water, 43). The early work of Rumpf and Séguin seems to confirm this view (1758), but in later papers they conclude that H bonding has no direct effect on the molecular dimagnetic susceptibility (1756 and 1757). Milligan and Whitehurst review the controversy and interpret their own measurements of magnetic properties of H bonding substances (water, propanol, acetic acid) adsorbed on silica gel with the assumption that H bonding does decrease diamagnetism (1408). (See also 389, 654, 2113.)

With respect to a related measurement, Waring and Custer (2139) review the data on Verdet constants. The magneto-optic studies do not reveal distinctive effects of the H bond. Waring and Custer feel the negative results "serve as additional magnetochemical evidence that the H bond occurs as simple electrostatic attraction."

2.4.15 Miscellaneous Tests. A few other test methods will be mentioned but will not be developed. Brun (307) made an extensive review of the effect of H bonds on the electrical conductivity of binary liquid mixtures. Polarographic potentials, as related to association, were studied by Holleck, Marsen, and Exner (946). Osmotic pressure measurements can detect *intra*molecular H bonding (1943), and internal H bonds can also affect optical rotatory power (1899).

2.5 Summary

From the experience with the variety of methods described here, these conclusions are well established:

1. H bonds occur in all three phases of matter, though they are less common as temperature increases and so are infrequently found in gases.

2. H bonding can be detected more or less easily by practically any physicochemical test method. Tests applied to the liquid state, which are of most practical interest, suffer from knotty and incomplete theoretical treatment. At present, and not considering spectral studies,

dielectric measurements and gas imperfections are most frequently used and give the most information. Cryoscopic and solubility investigations rank next, and a host of other methods are of lesser importance.

3. Since H bonding is likely to affect any physicochemical property, each worker should be aware that this widespread influence may affect the systems of his interest.

4. The strength of the H bond is such that H bond equilibria are delicately balanced under normal laboratory conditions. Large changes in these equilibria can result from relatively moderate changes of common experimental variables, particularly solvents and temperature

5. There are few truly inert solvents, and extra study is sometimes needed to separate purely solvent H bonding from that being examined Of course, in some work, the solvent-solute interaction is the object.

6. The classification system (Table 2-IX) provides a straightforward and useful division of compounds by their H bonding function. It serves as a basis for qualitative predictions about mixtures which are in agreement with many experimental facts. It is more accurate in cases where H bonds are *only* made or broken. Where mixing changes existing, or adds new, H bond equilibria, the classification is helpful but has less predictive value.

CHAPTER 3

Methods of Detection: Infrared and Raman Spectroscopy

> *Since the absence of characteristic OH absorption is found to be closely correlated with the presence of the hydrogen bond . . . , it has been inductively concluded that the absence of such OH absorption constitutes a good criterion for the presence of a hydrogen bond.*
>
> G. E. HILBERT, O. R. WULF, S. B. HENDRICKS, and U. LIDDEL *Bureau of Chemistry and Soils, 1936*

TIME: *circa* 1935.

PLACE: The Bureau of Chemistry and Soils, U.S. Department of Agriculture.

SETTING: The days of IR spectrometers home–built from source to galvanometer; the days of spectra read through a telescope point by point.

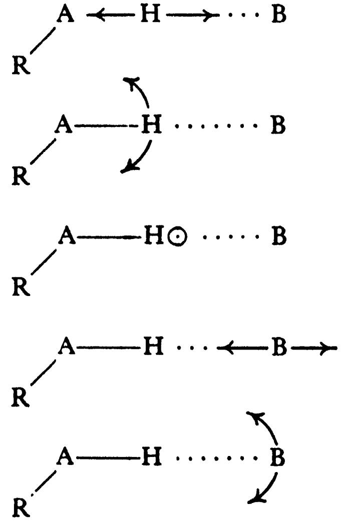
CAST: Four members of the small clique who are stealing the versatile IR method away from Physics and adapting it as an analytical tool for Chemistry.

Thus the stage is set for the opening line, quoted above. This announced the recognition of *the* most sensitive, *the* most characteristic, and *one of the* most informative manifestations of the H bond (919). From this start has grown the immense volume of work to be treated in this chapter. We shall begin by discussing the nature of the data obtained from IR spectra.

3.1 Introduction

Infrared and Raman spectra reveal the characteristic frequencies of molecular vibrations. Such frequencies are fixed by the masses of the vibrating atoms, the molecular geometry, and the restraining forces holding the atoms in their equilibrium positions in the molecule. Since the restraining forces (force constants) are simply related to chemical bond orders, vibrational spectra have been a lucrative source of information concerning chemical bonding and molecular structure. Consequently, it is fortunate and revealing that the vibrational spectra are significantly disturbed by H bond formation. The disturbances are so distinctive, in fact, that IR and Raman studies provide the most commonly used criteria for the presence of a H bond, criteria satisfying both parts (a) and (b) of the definition given in Section 1.2.5.

Vibrational modes which will be discussed are shown in Fig. 3-1. The arrows suggest the principal displacements involved in the oscillatory movements of the atoms. Note that symbols are assigned with the convention of an English letter subscript to identify vibrational



ν_s A—H stretch (3500–2500 cm^{-1}, 3–4μ)

ν_b R—A—H bend (in-plane) (1700–1000 cm^{-1}, 6–10μ)

ν_t R—A—H torsion [a] (out-of-plane) (900–300 cm^{-1}, 11–30μ)

ν_σ A · · · · B stretch (250–50 cm^{-1}, 40–200μ)

ν_β A—H · · · B bend (<50 cm^{-1}, $>200\mu$)

[a] The symbol ⊙ indicates a vibrational movement of the hydrogen atom perpendicular to the RAB plane.

FIGURE 3-1 Some vibrational modes of a H bonded complex.

modes that existed prior to formation of the H bond, and a Greek letter subscript to identify a vibrational mode created by the formation of the complex. Along with the description of the mode is a crude indication of the usual spectral region (in cm^{-1} and μ) for the absorption.

3.1.1 Early Work. The most prominent effect of H bonding on the vibrational spectrum is the shift of the absorption of the A—H stretching mode (ν_s) and its harmonics ($2\nu_s$, $3\nu_s$, . . .) to lower frequencies. This spectral change was first observed around 1930 for a number of compounds which form *intra*molecular H bonds: acetylacetone (Ellis, 602); benzoylacetone (Bawn, 174); salicylaldehyde and *o*-nitrophenol (Errera and Mollet, 617, 618). In 1932, R. Freymann noticed similar effects for alcohol solutions (716). In addition, he found that the intensity and frequency of ν_s of an alcohol are dependent on concentration and temperature, and attributed the behavior to molecular association. Simultaneously and independently, Hilbert, Wulf, Hendricks, and Liddel were conducting a systematic study of the IR spectra of many amines, alcohols, and phenols (1231, 2205). From it they generalized that the IR spectrum provides a criterion for detecting "chelation through hydrogen" (920, 919, 2206). The importance of this generalization was quickly recognized (e.g., Pauling, 1586), and during the next few years a large volume of corroborative evidence appeared [see, particularly, the work of Wulf and Liddel, R. Freymann and M. Freymann (summarized in 711), Buswell and Rodebush, Gordy, Ellis].

3.1.2 Importance of Infrared and Raman Techniques. Four facts which have stimulated most of the subsequent spectral studies of H bonds were soon established. Because of the sensitivity of the vibrational spectrum (ν_s in particular) to the H bond formation, IR spectroscopy provides:

(a) *a definitive criterion* for the detection of H bonds;
(b) *direct evidence of the role of the proton* in the association;
(c) *a quantitative index of the physical and chemical properties* of the H bonded systems;
(d) *a convenient tool* in a wide variety of H bond studies.

The most important experimental facts that characterize intermolecular H bonding systems are presented next in outline form. This outline does not include every topic in the chapter, but it does give references to some of the subsequent detailed discussions. Following the outline, there is a section dealing with experimental methods, another on the many studies of ν_s, and a third on the other vibrational modes. *Intra*molecular H bonding is taken up in Chapter 5.

3.1.3 Effect of the Hydrogen Bond on Vibrational Spectra.

A. Generality of Behavior: Similar spectral changes are observed for:

1. Organic and inorganic H bonded compounds
2. H bonded solids, liquids, solutions, and gases
3. IR and Raman spectra
4. H bonded complexes, polymers, and chelates

B. A—H Stretching Mode—ν_s:

1. *Frequency Shift.* The stretching mode and its harmonics are shifted to lower frequencies by H bond formation. In many systems these shifts, $\Delta\nu_s$, are of the order of 10 percent of ν_s (Section 3.3.5).

2. *Half-width.* The mode ν_s and its harmonics are broadened when a H bond is formed. The half-width, $\nu_{\frac{1}{2}}$, is approximately $\frac{3}{4}\Delta\nu_s$ (Sections 3.3.5, 3.3.8).

3. *Intensity Change*, $\Delta\mathbf{B}$.

a. *IR:* The integrated absorption coefficient of the fundamental ν_s increases many-fold when a H bond is formed, whereas the corresponding coefficients for the harmonics decrease slightly (Sections 3.3.5, 3.3.7).

b. *Raman:* The ν_s intensity behavior in the Raman spectrum is not well known since few quantitative measurements of Raman intensities are available.

4. *Temperature.* Both the frequency and intensity of ν_s may be altered radically by a temperature change of several degrees. (Section 3.3.1).

5. *Concentration.* Similarly, the frequency and intensity of ν_s are concentration dependent (Section 3.3.2).

6. *Solvent.* Again the absorption of ν_s may be altered either by an acidic or basic solvent (Section 3.3.3).

7. *Correlation of $\Delta\nu_s$ with Physical Properties.* The quantity $\Delta\nu_s$ is related to important chemical and physical properties of H bonding systems: H bond enthalpy, interatomic distances, chemical reactivity, ΔH of solution, base strength, etc. (Section 3.3.5).

C. RAH Bending Mode—ν_b:

1. $\Delta\nu_b$. The bending mode is shifted to a frequency above that of the molecule in the absence of H bonding. The relative magnitude of the shift of this mode ($\Delta\nu_b/\nu_b$) is usually smaller than that of the stretching mode (Section 3.4.1).

2. $\nu_{\frac{1}{2}}$ *and* **ΔB**. Again unlike ν_s, the bending mode ν_b displays no obvious spectacular changes in half-width and absorption coefficient. However, few definitive data are available (Section 3.4.1).

D. New Vibrational Modes: The formation of a H bond restricts certain rotational and translational degrees, and forms an equal number of new vibrational degrees of freedom.

1. *Torsional Modes.* Vibrations of a torsional type, characterized by restricted rotations around some bond, may be produced. The example with widest acceptance is the broad and intense absorption near 800 cm^{-1} by liquid water (Section 3.4.2).

2. *Stretching and Bending Modes.* The new stretching and bending modes are of extremely low frequency (possibly 20–200 cm^{-1}). Since these frequencies contribute heavily to the entropy of a H bond, they are of importance in H bond equilibrium constants. There are few reliable data because of the experimental difficulties inherent in this spectral region (Section 3.4.3).

E. Reviews: 1975, 1375, 1668, 1095, 817, 345a.

3.2 Experimental Methods

3.2.1 Infrared vs. Raman. These two spectroscopic techniques reveal the characteristic vibrational frequencies of a molecule. For most molecules, both the Raman and IR spectra are needed before the vibrational pattern can be understood fully. This is true because of the variation of absorption coefficients for different modes in the two spectra. This variation is particularly great for molecules possessing high symmetry. Then some of the vibrations may have absorption coefficients near zero in the IR spectrum, and others may have comparably low scattering coefficients in the Raman spectrum. In more rigorous language, molecular symmetry may give rise to selection rules. The selection rules for IR transitions are different from those for Raman transitions because the scattering coefficients depend upon different electrical properties. Infrared transitions require a dipole moment change associated with the vibrational displacements, whereas Raman transitions require a polarizability change. It follows that the two spectra may have few frequencies in common and both spectra are needed.

Unfortunately, Raman and IR spectra are not equally easy to obtain. Few Raman spectra have been recorded for gaseous samples because of the low intensity of Raman scattering by a gas. And a solid can be studied only if Rayleigh scattering is very low. Most often, Raman spectra are recorded for pure liquids and solutions, though even then the photographic technique is slow and inconvenient for quantitative intensity measurements. The experimental problems will be reduced considerably by the recording Raman spectrometers now becoming available.

On the other hand, the Raman technique has been utilized in studying the important low frequency vibrations. Few IR studies extend below 250 cm^{-1} because of the experimental difficulties of the far IR region.

3.2.2 Study of Pure Materials. Relatively little IR and practically no Raman study of the H bonding of gases has been reported. This shortage of data probably results from experimental and interpretive difficulties. For convenient IR spectral study of a substance in the gas phase its vapor pressure must be above a few millimeters of Hg at an accessible temperature. This pressure range is suitable for the study of the strongest H bonds—for example, the dimerization of the carboxylic acids ($-\Delta H = 14$ kcal/mole). Thus, at a total pressure of 25 mm, acetic acid gas is about 80 percent dimerized at 50°C and about 20 percent dimerized at 100°C (2008). However, $-\Delta H$ is more commonly 3–6 kcal/mole (alcohols, phenols, amides, etc.), and it is awkward to establish suitable conditions. And even under good conditions, interpretive difficulties stem from the overlapping of bands. This problem, familiar in the spectral study of H bonded substances, is aggravated for gases by the extreme band width of the rotational fine structure. Such interference is particularly troublesome for the low molecular weight compounds, the ones most readily studied as gases.

From the experimental point of view, the liquid state is most desirable for study by either Raman or IR, and many investigations of the H bonding of pure liquids have been reported. Unfortunately, there is a counteracting difficulty of interpretation—the uncertainty concerning the important species present. Most pure H bonding liquids contain a series of polymeric units with different characteristic frequencies and absorption coefficients. In the region of ν_s the band widths of the many H bonded species meld into a single broad band whose frequency is determined by the average over many species, each species with its own (unknown) band shape and absorption coefficient. Clearly, it is difficult to wrest more than qualitative information from such data.

This difficulty dictates a cautious approach to conclusions based on comparisons of liquid spectra. A single recent example brings this warning into focus. Finch and Lippincott have made careful measurements of frequencies and band intensities of ν_s for several alcohols over the temperature range 232–298°K (656, 657). These authors interpret the systematic temperature dependencies in terms of changes of force constants and absorption coefficients. Even though their contention is probably correct, that "the [spectral] shifts . . . cannot be explained solely on the basis of a shift in the monomer-dimer-polymer equilibrium," such an equilibrium shift must occur and undoubtedly contributes to the observed frequency and intensity changes. This factor of ambiguity certainly inhibits quantitative application of data of this type and detracts from the certainty of conclusions based upon them.

The study of pure solids also presents difficulties. Raman spectra can be obtained only for carefully grown crystals because of random scattering. Hence most studies of H bonding in solids are based on IR techniques. But there are problems here too.

Frequency shifts, intensity changes, and band splittings caused by crystal interactions complicate the interpretation of the vibrational spectrum of a crystal. These effects can sometimes be recognized, provided the crystal structure is well known. Even then the situation is not clear if there are two or more nonequivalent H bonds in the structure. As a partial solution to these problems, Hrostowski and Pimentel proposed a powerful tool for identifying crystal interactions—the use of dilute mixed crystals of the compound of interest in a crystal of its deuterated counterpart (975). In this technique any band splittings caused by intermolecular interactions are lost in the dilute crystal, whereas splittings caused by nonequivalent H bonds and band structure associated with *intra*molecular combination modes are retained. This method was first applied to a H bonded crystal by Hiebert and Hornig (918), who showed that the doublet observed in the IR spectrum of the HCl crystal is caused by crystal interactions.

There are several ways to obtain the IR spectrum of a solid, each with its peculiar problems. If single crystal studies are attempted, the preparation of sufficiently thin samples of known crystal orientation can be a major difficulty. If a solid is prepared by freezing quickly either a liquid or a gas, the sample must be annealed. Significant spectral changes usually occur during the annealing process, particularly in the region of ν_s, as has been observed for hydroxylamine (1505), hydrazoic acid (549), and ammonium azide (550). The equivalent of a powder spectrum can be obtained by the mull technique, but the C—H interference of a Nujol medium obscures a portion of the ν_s region. The pressed disc technique avoids this interference, but is susceptible to a more sinister fault. Farmer (631) observed that the KCl pressed disc spectra of six carboxylic acids, eight phenols, and two alcohols can be altered radically by changing the grinding technique. For example, he presents one spectrum (650–1600 cm^{-1}) of benzoic acid ground and pressed in KBr, and another of benzoic acid in KCl, prepared by a different grinding and preheating treatment. These spectra are so dissimilar that they would readily be accepted as evidence that different compounds were examined. How generally this will be observed for H bonding substances remains to be seen (630).

Despite all of these problems, the spectral study of H bonding in solids provides important information about H bonding, and it can be a useful guide in deducing crystal structures.

3.2.3 Study of Solutions. The great value of solutions for spectroscopic studies of H bonding lies in the possibility of controlling and determining the species present. At extreme dilution, intermolecular associations are eliminated or restricted to solvent-solute associations. At higher concentrations, intermolecular interactions become important but remain under control through the variables of temperature and concentration. In view of the importance of this type of work, we shall examine the method for pitfalls.

In a solution, the H bonding species present depend on the concentration, the temperature, and the solvent. Yet, at least one of these variables is unspecified in many published papers concerning H bonding. The uncertainty about temperature must be evaluated in terms of the occasional practice of thermostating IR spectrometers above 30°C, and the sensitivity of H bonding equilibria to temperature. If the solvent interacts either as a hydrogen donor or as a base, the situation is complicated by the disturbance of polymeric equilibria and the presence of associated species involving the solvent. For example, neither chloroform nor benzene is an inert solvent for H bonding compounds. The amide polymeric equilibria are distinctly altered in these solvents, as compared to CCl_4 solutions (e.g., see Fig. 3-3), and the IR spectra clearly indicate solvent-solute interaction (1117). A third major source of difficulty is in the solubility of water. Often solution experiments require solute concentrations below 10^{-2} M, at which traces of water can interfere. Many solvents can absorb enough water from the atmosphere to be detected in the IR spectrum and to hinder solution studies at extremely high dilution.

3.2.4 Matrix Isolation Technique. A novel approach to the IR investigation of H bonding has been developed by Pimentel and collaborators. In this method, the matrix isolation technique, a gaseous mixture of a H bonding substance in a large amount of inert gas (e.g., N_2) is quickly frozen at a temperature at which no diffusion can occur. The solid nitrogen forms a rigid matrix that isolates whatever species are present during the deposition. The unique advantage of the method is that the ν_s absorptions of H bonded species are narrow. The usual problem of overlapping bands is thus eliminated. Conventional low temperature apparatus is applicable, but careful temperature control is required to avoid diffusion in the matrix either during deposition or during spectral examination.

3.2.5 Practical Rules for Infrared and Raman Studies of Hydrogen Bonding.

1. Select solvent with attention to its H bonding properties.
2. Vary the concentration and determine the sensitivity of the spectrum to this variable. If possible, use a concentration sufficiently low to permit control of the intermolecular association.
3. Measure and control the cell temperature.
4. In publications reporting solution studies, specify the solvent, the temperature, and the concentration.
5. Raise the cell temperature 20–30°C to detect and identify H bonded species.
6. Use deuterium substitution to verify assignments.
7. Dry the solvent for studies at high dilution.
8. Remove alcohol (added as an antioxidant) from chloroform solvent.
9. Anneal solid samples, particularly if condensed from a gas.
10. For IR pressed disc spectra, check against mull spectra; vary grinding procedure.

3.3 The A—H Stretching Mode, ν_s

H bond formation has dramatically obvious and unusual effects on the IR and Raman spectra. The most prominent of the spectral changes occur in the region of ν_s near 3500 cm^{-1} (3μ). These changes have properly assumed the importance of qualitative criteria for H bond formation and quantitative indices of the H bond energy and of other physical properties. Hence, we shall examine the behavior of ν_s in detail.

3.3.1 Effect of Temperature. Spectacular reduction in the IR and and Raman intensity of the association band may accompany a temperature rise of 10–20°C. The IR spectra of benzyl alcohol in CCl_4, presented by Coggeshall and Saier (411), offer a striking and typical example, as shown in Fig. 3-2(a). This extreme sensitivity of ν_s to temperature changes reflects the following characteristics:

(a) H bonding systems involve monomeric and usually several polymeric species in rapid equilibrium;
(b) each polymer has a characteristic ν_s, and the higher the polymer the lower is ν_s;
(c) each polymer has a characteristic absorption coefficient **A**[a] at ν_s, and the higher the polymer the higher is **A**;
(d) since **A** may increase by as much as an order of magnitude on bond formation, a small shift of equilibrium produces a magnified spectral change.

This sensitivity of the IR and Raman spectra for both gases and liquids was one of the earliest observations of the spectral uniqueness of H bonding systems.[b] It has been used so frequently to verify the presence of H bonded species that many workers consider it to be the primary criterion of H bonding.[c] Of much greater importance is the spectral measurement of equilibrium constants at several temperatures. Such data permit calculation of the thermodynamic properties of H bond formation, ΔH, ΔS, and ΔF (see Section 7.3.1)[d].

It is generally accepted that the temperature effects reveal the shift of equilibria involving a variety of polymeric species, each with a characteristic ν_s and **A**. There is no question that this is a dominant factor in the behavior. Recently it has been suggested that there is another effect of temperature—that both the ν_s frequency and the absorption coefficient of *each* particular H bonded species may change with temperature. Finch and Lippincott draw this conclusion after

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[a] We shall use the symbol **A** for absorption coefficient and the symbol **B** for the experimentally measured integrated absorption of an IR band. Usually **B** differs from **A** because the low resolution of IR spectrometers causes apparent deviation from Beer's law. Various extrapolation methods are used to obtain **A** from **B**.

[b] A partial list of early studies: 716, 1651, 2181, 767, 616, 1485, 465, 272, 1870, 500.

[c] A partial list of studies: 1767, 2213, 1687, 409, 1345, 160, 161, 1332, 388, 1292, 1331, 411, 357, 497, 1509, 1490, 1694, 1860, 1218, 1242, 1793, 2011, 996, 2118, 1550, 1508, 757.

[d] A partial list of studies: 1328, 1377, 1292, 1375, 1866, 2048, 2049, 2047, 669, 483, 104, 494.

careful IR measurements showed that changes of the frequency (about 1 percent of ν_s) and integrated intensities (a factor of about $\frac{2}{3}$) occur for methanol, ethanol, four other alcohols, phenol, *o*-chlorophenol, and phenol in ether over the wide temperature range 180–335°K (656). They note that in a pure liquid alcohol all of the H bonded species are polymeric, and base their interpretation on the assumption that equilibrium shifts among the higher polymers could not account for all of the observed changes. This assumption needs further verification (see our Section 3.2.2).

Independently, Liddel and Becker have attacked the same problem (1229). For example, they examined the peak intensity and frequency of ν_s for monomeric methanol in CCl_4. They discovered that the intensity decreases by almost 36 percent if a dilute solution in CCl_4 (0.005 M) is warmed from 263°K (−10°C) to 323°K (+50°C) and the frequency increases about 6 cm^{-1} (+0.2 percent). No such changes are observed in the C—H stretching modes.[a] Since little dimeric or polymeric material is present, the change of absorption coefficient implies that the O—H group interacts with CCl_4 in a fashion that influences the intensity of the stretching mode and which is very temperature sensitive. The same absorbance behavior was reported by Hughes, Martin, and Coggeshall (996), and very much earlier by Davies and Sutherland (500), and by Fox and Martin (682), for dilute solutions of phenols in hexachlorobutadiene. Though it is not established that either CCl_4 or hexachlorobutadiene acts as a base, the work of these authors (1229, 996) is consistent with Finch and Lippincott's suggestion that the absorption coefficients of A—H stretching modes could be strongly temperature dependent in H bonded complexes. (See also 1073 in which this problem is discussed with reference to the carboxylic acids.) Clearly, such a variation in absorption coefficients would have serious impact on the spectroscopic measurements of thermodynamic properties.

3.3.2 Effect of Concentration.

The drastic spectral changes caused by temperature changes are caused also by variation of the concentration of a H bonding substance in an inert solvent. The similarity is evident in Fig. 3-2, where spectra of benzyl alcohol at several concentrations are presented [Fig. 3-2(b)] (407) together with the spectra at fixed concentration but at several temperatures [Fig. 3-2(a)]. The narrow band at 2.77μ (3610 cm^{-1}), due to O—H groups not participating in H bonds, dominates the lower frequency absorption in the

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[a] All data are corrected for density changes.

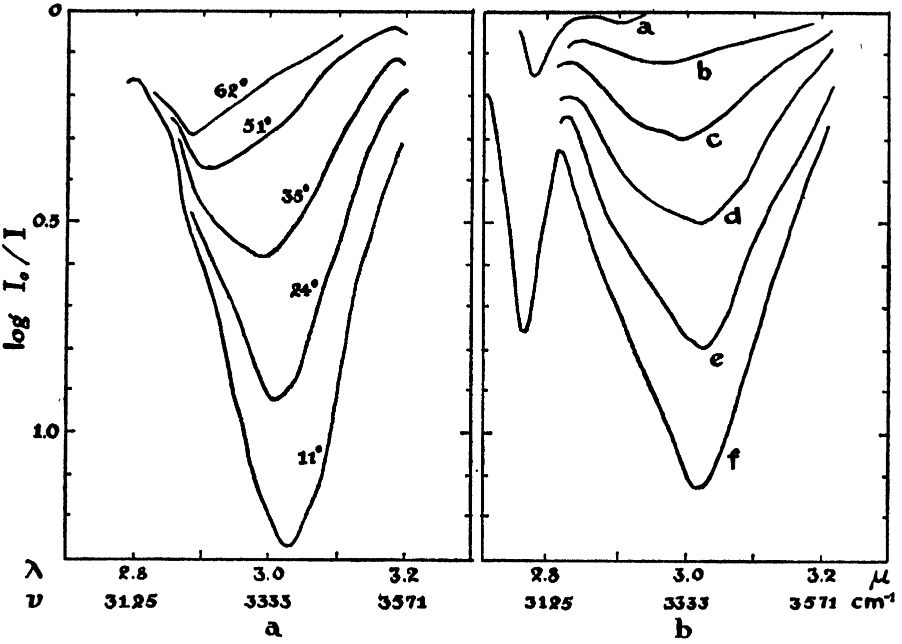

FIGURE 3-2 IR spectra of benzyl alcohol in CCl_4. (a) At various temperatures (11–62°C, 0.24 M). [From Coggeshall and Saier, *J. Am. Chem. Soc.* **73**, 5415 (1951).] (b) At various concentrations: *a*. 0.0486 M; *b*. 0.0972 M; *c*. 0.155 M; *d*. 0.194 M; *e*. 0.243 M; *f*. 0.278 M. [From Coggeshall, *J. Chem. Phys.* **18**, 980 (1950).]

most dilute solution. At high concentration, the broad band centered near 3.00μ ($3330\ cm^{-1}$), due to H bonded polymers, is by far the more intense feature. Exactly the same characteristics which account for the temperature behavior account for the concentration dependence. [Similar spectra for *N*-methylacetamide are presented by Davies *et al.* (492).]

Freymann first noticed this behavior in his IR studies of alcohols in CCl_4 (716). Within a few years it had been established that the changes were indicative and informative of the H bonding equilibria.[a] Of particular importance were the early contributions of Errera and Mollet, Kinsey and Ellis, Fox and Martin, and Buswell, Maycock, and Rodebush. Many of the numerous spectral studies of the concentration effect which have followed, particularly those leading to thermodynamic data, will be described later in this chapter.

Before leaving this topic we must note with regret the large number

[a] 1323, 616, 1107, 685, 102, 612, 615, 1106, 327, 331, 1330.

of published spectra of solutions of H bonding substances at unknown or unspecified concentrations. For reference and comparison purposes it is desirable to present a spectrum for a solution of high dilution (less than 0.02 M) in CCl_4, for a specified concentration, or for the pure liquid. Of course, the solution temperature should be stated.

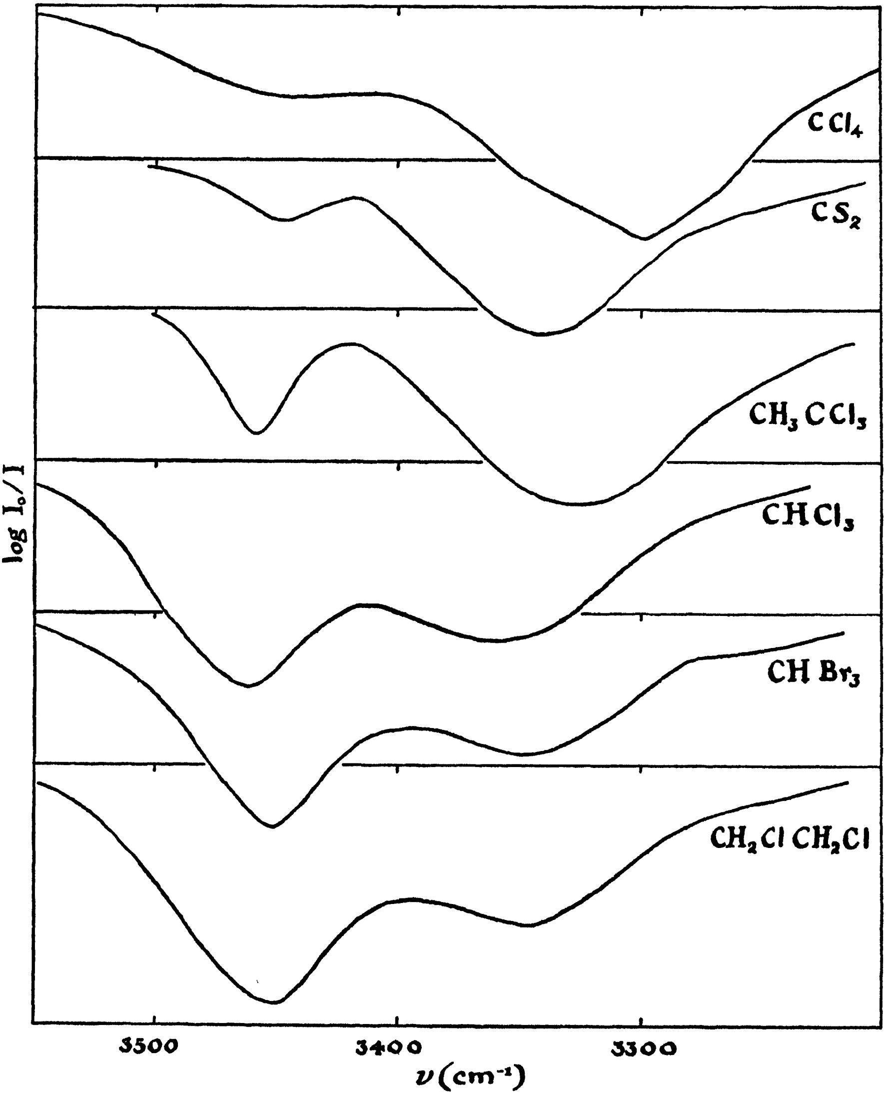

FIGURE 3-3 IR spectrum of *N*-methylacetamide in various solvents in the N—H stretching region: 0.4 M at 30°C. [Unpublished spectra of William A. Klemperer and George C. Pimentel.]

3.3.3 Effect of Solvent. The solvent is a third variable with extreme influence on the IR and Raman spectra of H bonding substances. Figure 3-3 shows the effect of solvent on the spectrum of *N*-methylacetamide. The changes indicate environmental influence on the distribution of monomeric and polymeric species. The solvent disturbances persist, however, even at such low concentrations that no polymeric species are present. This is evident in the spectra of Fig. 3-4, which shows the IR region near 3600 cm^{-1} for H_2O at low concentration in a variety of solvents. The superposition of the CCl_4 spectrum (dotted curves) shows that every spectral characteristic of the band is sensitive to the solvent: the structure and its spacing, the frequency, the band width, and the integrated intensity (i.e., the absorption coefficient). (See also 247, 385.)

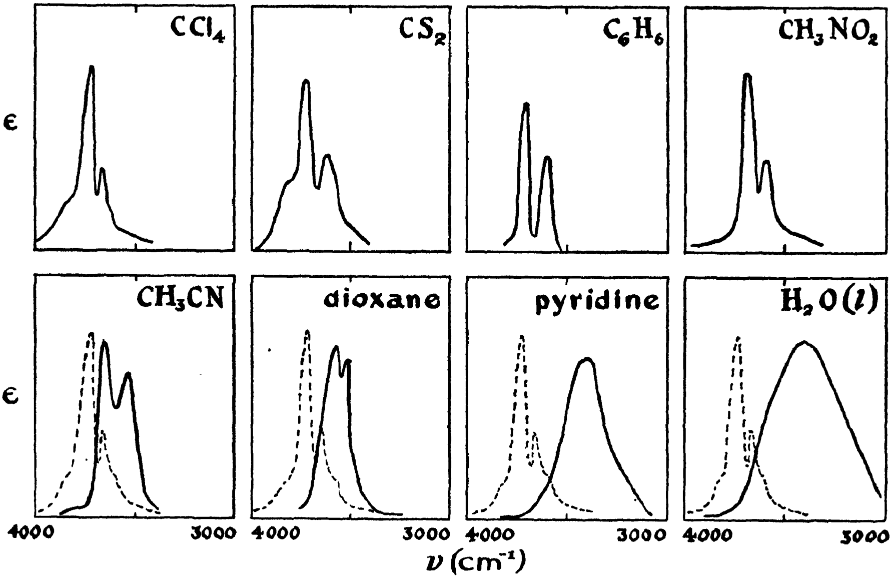

FIGURE 3-4 IR absorption of water in various solvents. Broken lines, H_2O in CCl_4. [From Greinacher, Lüttke, and Mecke, *Z. Elektrochem. Ber. dtsch. Bunsenges. physik. Chem.* **59**, 26 (1955), Verlag Chemie, Gmb H, Weinheim/Bergstr.]

It is clear that many solvents interact and produce new H bonding equilibria involving the solvent. These additional equilibria furnish an extraneous and interfering factor in a reference spectrum. On the other hand, a dilute solution of a proton donor in a basic solvent involves well defined species and avoids the usual complication of polymeric equilibria. Consequently, the spectral examination of such systems furnishes some of the most definitive information available on H bonding.

The recognition of the spectral influence of H bonding stimulated investigation of the effect of diluents in pure H bonding liquids, and then the systematic study of binary mixtures.[a] The extensive examinations carried out by Gordy and his co-workers were particularly important in establishing the generality of the H bond effect and determining what chemical substances have H bonding properties.[b] Although these early spectra were recorded with resolution and frequency accuracy that are low by present standards, they formed a substantial bulwark to the now accepted proposal that the shift in ν_s is a useful criterion of H bond formation and an index of base strength.

From a practical point of view, the possible solvent influence on the spectrum of a H bonding compound requires constant attention. For example, it is clear that the solvent characteristics of chloroform derive in part from its proton donor potentiality, permitting H bond formation. In proportion to the amount of H bonded complex, the spectrum of chloroform itself is drastically altered, the C—H stretching mode being many-fold more intense (980, 1259). Similarly, the proposal of using a CCl_4-triethylamine mixture as an IR transmitting solvent for organic acids has the same disadvantage (61). As found by Ard and Fontaine (61), the spectrum obtained in the mixed solvent is not characteristic of the monomeric acid molecule but of the H bonded complex between amine and acid in equilibrium with the monomeric acid. Of course the enhanced solubility of the acid in the mixture is a direct result of this H bonding. Thus, while $CHCl_3$ or a mixed solvent may be useful in achieving concentrations sufficient for spectral study, they yield spectra that cannot be compared to spectra obtained using any other solvent or the same solvent at a different temperature.

3.3.4 Effect of Pressure. A far less important effect is that of pressure, but it is worth noting this effect to emphasize that any displacement of the H bonding equilibria is evident in the IR and Raman spectra. This is evident in the IR spectra obtained by West for gaseous and liquid HCl up to the critical conditions (2161). More recently, Sluskin and Novak have studied the IR spectra of several alcohols in CCl_4 at pressures up to 3200 kg/cm^2 (1860). They found that raising the pressure 90–130 kg/cm^2 produces about the same equilibrium shift as lowering the temperature one degree. Thus the partial molar volume of

[a] See 807, 808, 715, 805, 2179, 684, 246, 612, 1106, 2168, 334, 333, 619, 360, 1786, 1330, 614.
[b] 797, 799–804, 809–815, 2180.

the alcohol in the H bonded polymer is lower than that of the monomer. (For more detailed discussion, see Section 2.4.7.) Fishman and Drickamer studied butanol in very dilute solution in various solvents at pressures up to 12,000 atm. (667). They find that the monomeric O—H stretching frequency shifts down, a result quite analogous to the temperature effect mentioned earlier (1229, 996).

The effects of the experimental variables—temperature, concentration, and pressure—on $\Delta\nu_s$ are contrasted qualitatively in Fig. 3-5. Changes in these variables cause shifts in the equilibria among the polymers, higher polymeric species resulting from lowering the temperature, raising the concentration, or raising the pressure. The frequency shifts indicate that the value of $\Delta\nu_s$ increases with increase in polymer size.

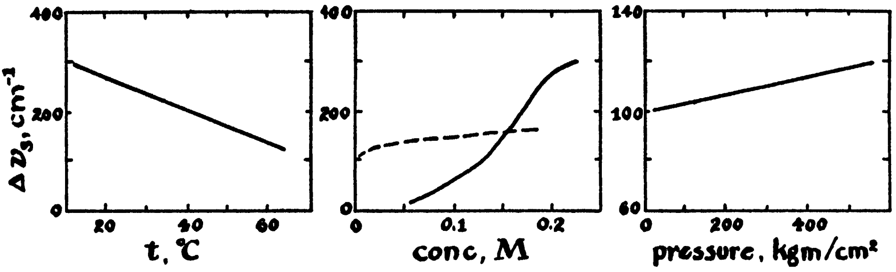

FIGURE 3-5 Frequency shift, $\Delta\nu_s$, caused by temperature, concentration, and pressure changes ($\Delta\nu_s$ measured relative to monomer). Solid lines, alcohols in CCl_4; broken line, amides in CCl_4.

3.3.5 Correlations of $\Delta\nu_s$ with Other Properties. With this introduction to the measurement of ν_s, we shall examine the important relationships which have been found between the physical properties of H bonded systems and $\Delta\nu_s$, the shift of ν_s brought about by the H bond interaction. Some of these relationships are summarized qualitatively in Fig. 3-6. These values of $\Delta\nu_s$ refer to a variety of systems, each with a well defined H bonded molecular species (in contrast to the $\Delta\nu_s$ data of Fig. 3-5, which refer to the superposition of absorptions of many different polymeric species of a single type of AB molecules). In Fig. 3-6 we see that $\Delta\nu_s$ is inversely related to the A$\cdots$B distance (R), and Hammett sigma function, whereas it is directly related to enthalpy of H bond formation, the A—H distance (r), and the two IR spectral properties, half-width and intensity.

$\Delta\nu_s$ and ΔH. The first and most important relation involving $\Delta\nu_s$ was proposed by Badger and Bauer in 1937 (101). It was restated by

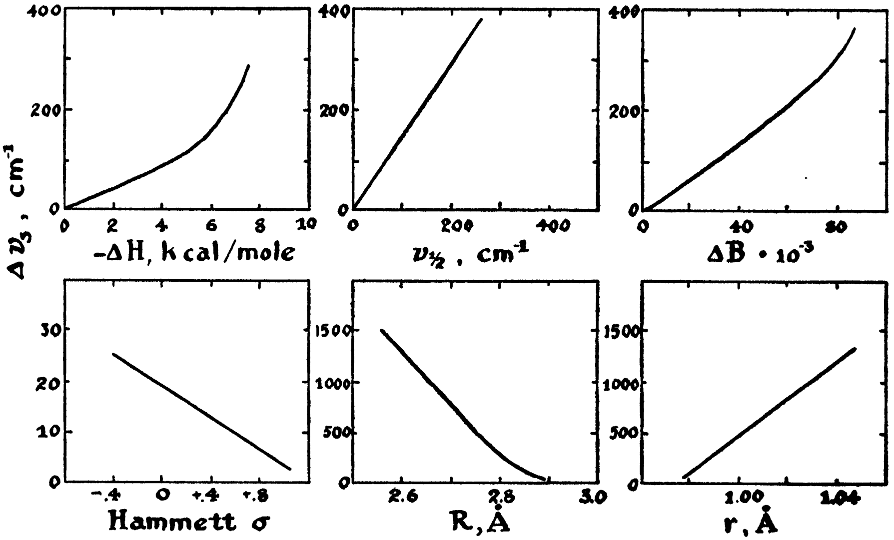

FIGURE 3-6 Correlations of frequency shift, $\Delta\nu_s$, and other properties of H bonding systems.

Badger (100): "There appears to be a relation between the energy of a hydrogen bond and the shift in frequency of the O—H bands." Badger noted that carboxylic acids did not seem to fit the postulated relation, and in the same year Herman expressed doubt that there exists a simple relation between $\Delta\nu_s/\nu_s$ and ΔH (908). Fox and Martin used the Morse curve to show that $\Delta\nu_s/\nu_s$ should be related to ΔH (684), but Davies found agreement with experimental data only within a factor of two (489). Nevertheless, there has been a general acceptance of the proposal that $\Delta\nu_s/\nu_s$ provides an index of ΔH of H bond formation.

Indirect evidence for this proposal is found in correlations between heats of mixing and frequency shifts. Systematic relationships have been noted between $\Delta\nu_s$ of methanol-*d* in a variety of bases and ΔH of solution of chloroform in these same bases, first by Gordy and Stanford (812) and later by Tamres and co-workers (1823, 1995, 1824, and 1996). Most of the data of Tamres *et al.* are shown in Fig. 3-7 together with their straight line correlations. These three distinct base types (aromatics, ethers, and nitrogen bases) display different intercepts, but the slopes are surprisingly similar.

Correlations with heat of mixing have the inherent disadvantage that the heat depends upon ΔH of complex formation through the equilibrium constant of complex formation. Thus the entropy of complex

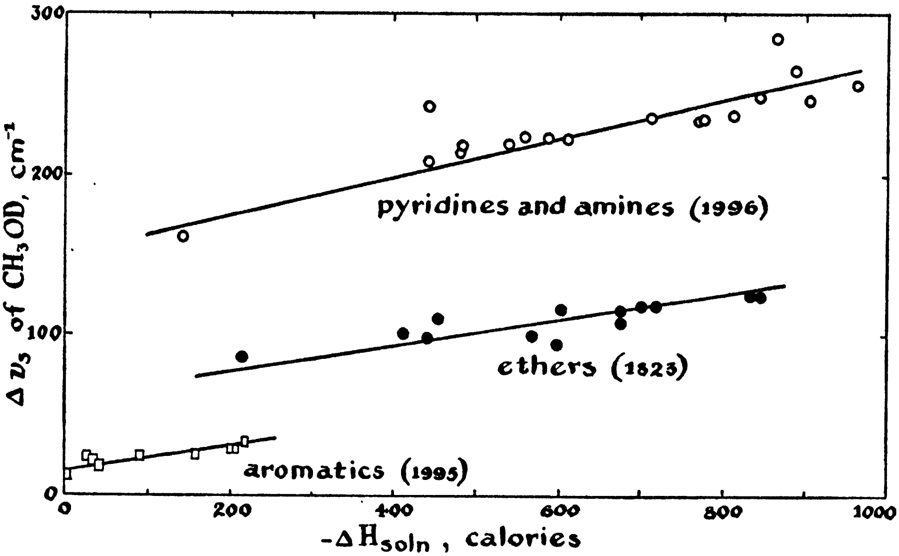

FIGURE 3-7 Heat of mixing *vs.* $\Delta\nu_s$. ΔH_{soln} = heat of mixing $\frac{1}{2}$ mole $CHCl_3$ with $\frac{1}{2}$ mole base; $\Delta\nu_s$ = shift of OD stretch for CH_3OD in same base.

formation influences the fraction of molecules present as complex. Presumably, more detailed substantiation has not been sought until recently because of the difficulties of determining ΔH of H bond formation (see Section 7.3.1). Some of the early estimates of ΔH were based on heats of sublimation. From the heat of sublimation is subtracted a guess as to that portion of the heat which should be attributed to van der Waals attraction. This van der Waals energy has been estimated by comparison with a structurally related compound without H bonding capabilities. The subtraction introduces uncertainty because the existence of H bonding implies unusually close distances of approach that would surely affect the van der Waals contribution. It is certainly necessary to look with caution on this type of estimate of H bond enthalpies. (See Section 7.5.1.)

Another factor that has inhibited the precise determination of H bond enthalpies of polymer forming compounds has been the uncertainty of the species present. Thus the determinations of the H bond enthalpy per mole in pure alcohol, as given by Mecke (1375), is of restricted value because of the variety of species present. On the other hand, solution determinations of ΔH have the advantage that van der Waals attractions play only a minor role. In an inert solvent, for example, little change is expected in the van der Waals attractions among the molecules if a H bond is formed. This advantage is bes realized in solution studies of H bonded complexes between a proto donor (of class A or AB) and a variety of bases (of class B). Here th measured enthalpies of formation of H bonded complexes refer to wel defined and readily determined species. For these systems Pimentel and Brown found ample reliable data to establish the dependence of $\Delta\nu$ on ΔH. Figure 3-8 shows the data for a single acid, phenol, interactin with a variety of bases. Unhappily the data do not substantiate th proposed relation of Badger, shown by the straight line in Fig. 3-8 Although a smooth curve can be drawn through the points applicabl to esters, it is not a linear relation. Furthermore, this smooth curve i not applicable to the data for other bases.

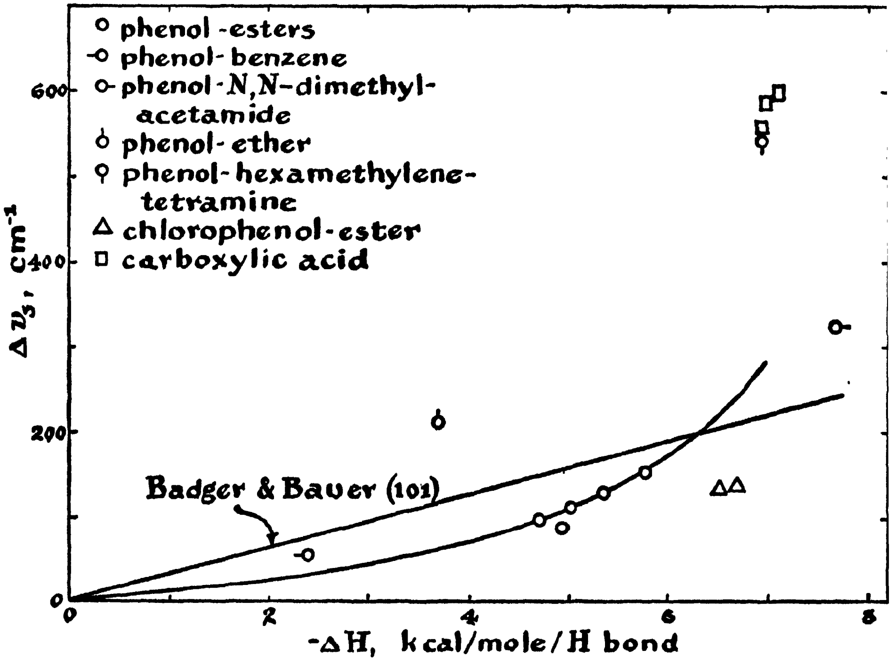

FIGURE 3-8 Comparison of $\Delta\nu_s$ and enthalpy of H bond formation.

In Table 3-I are shown values of $\Delta\nu_s$, $-\Delta H$, and the ratio $-\Delta\nu_s/\Delta H$. The phenol-ester data are listed in order of increasing $\Delta\nu_s$ (i.e., increasing base strength, see Table 3-II). The data not only show that $\Delta\nu_s/\Delta H$ is not a constant, they distinctly indicate that the ratio increases systematically as $\Delta\nu_s$ increases.

$\Delta\nu_s$ *and R*. Rundle and Parasol (1764) first noticed a relation between the wavelength of an O—H stretching frequency of a H bonded

TABLE 3-I Comparison of $\Delta\nu_s$ and Enthalpy of H Bond Formation (in hydrocarbon solvent)

ACID	BASE	$\Delta\nu_s$ (cm^{-1})	$-\Delta H$ (kcal/mole)	$-\Delta\nu_s/\Delta H$ (cm^{-1}/kcal/mole)	REFERENCES $\Delta\nu_s$	REFERENCES ΔH
Phenol	Benzene	56	2.4	23	a	h
	Methyl trichloroacetate	88	4.9	18	b	i
	Ethyl trichloroacetate	98	4.7	21	b	i
	Methyl chloroacetate	114	5.0	23	b	j
	Methyl acetate	132	5.3	25	b	j
	Ethyl acetate	154	5.7	27	b	j
	Ether (CCl_4)	270	3.7	73	a	k
	N,*N*-Dimethylacetamide	321	7.7	42	c	c
	Hexamethylenetetramine (CCl_4)	542	6.9	79	d	d
m-Chlorophenol	Methyl acetate	128	6.5	20	b	j
p-Chlorophenol	Methyl acetate	132	6.7	20	b	j
Acetic acid dimer	(gas)	556	6.9	81	e	l
Trifluoroacetic acid dimer	(gas)	585	7.0	83	f	l
Formic acid dimer	(gas)	600	7.1	84	g	l

[a] 979; [b] Unpublished data of H. W. Brown and G. C. Pimentel; [c] 1436; [d] 2054; [e] 2155; [f] 734; [g] 1643; [h] 1199; [i] 1480; [j] 1478; [k] 2047; [l] 1271.

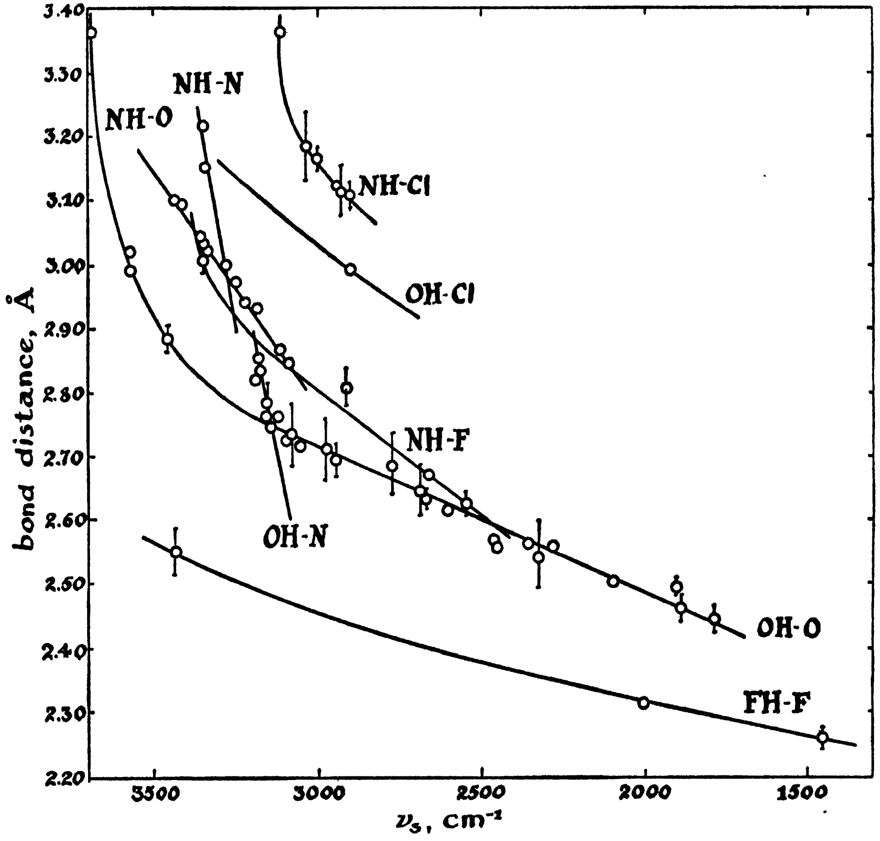

FIGURE 3-9 A—H stretching frequency, ν_s, *vs.* A····B bond distance in solids. [From Nakamoto, Margoshes, and Rundle, *J. Am. Chem. Soc.* 77, 6480 (1955).]

solid and the O····O bond distance, R. Shortly thereafter Lord and Merrifield (1258) found a linear correlation between $\Delta\nu_s$ and R. Furthermore, their data include one F—H···F system and one N—H···O system, implying that the linear relationship applies to any A—H···B bond. Pimentel and Sederholm (1637) examined the data for N—H···O systems and N—H···N systems, and concluded that a separate straight line is required for each type of H bond. They list the following equations as the best relations:

$$\begin{array}{lll}
\text{O—H} \cdots \text{O} & \Delta\nu_s = 4.43\cdot 10^3(2.84 - R) & \sigma(\Delta\nu_s) = 200\ \text{cm}^{-1} \\
\text{N—H} \cdots \text{O} & \Delta\nu_s = 0.548\cdot 10^3(3.21 - R) & \sigma(\Delta\nu_s) = 25\ \text{cm}^{-1} \\
\text{N—H} \cdots \text{N} & \Delta\nu_s = 1.05\cdot 10^3(3.38 - R) &
\end{array}$$

where $\Delta\nu_s$ is in cm^{-1}, R is in Å, σ = standard error of estimate.[a]

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[a] Standard error of estimate is defined in a footnote in Section 9.3.1.

Independently, Nakamoto, Margoshes, and Rundle (1488) also concluded that each type of H bond has a distinct $\Delta\nu$–R relationship. Their figure, which is reproduced in Fig. 3-9, includes data for a wide variety of bond types. These authors reach the important conclusion that *intra*molecular H bonds do not have the same $\Delta\nu_s$–R dependence as do intermolecular bonds. Magat also compiles $\Delta\nu_s$–R data (1316). More novel is Pirenne's attempt to investigate the dependence of the bending and twisting modes on R (1641). (See also 282.)

Lippincott and Schroeder (1242) have discussed the relation between $\Delta\nu_s$ and R in terms of a covalent description of the H bond (see Section 8.2.5). Their model leads to an asymptotic approach of $\Delta\nu_s$ toward zero for large R. This prediction is reasonable, and whether the covalent description is correct or not it points the obvious fault of the proposed linear relation between $\Delta\nu_s$ and R. Certainly, as the distance becomes large the H bond perturbation must become unimportant and $\Delta\nu_s$ must approach zero in a continuous fashion. The study by Glemser and Hartert (782) shows that the linear relation between $\Delta\nu_s$

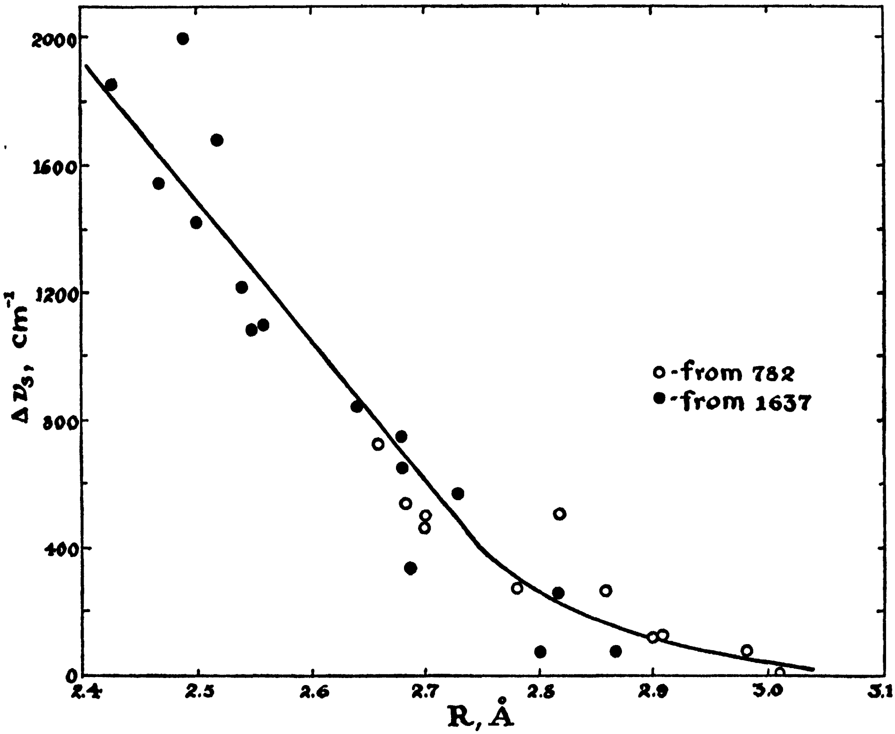

FIGURE 3-10 R *vs.* $\Delta\nu_s$ for O—H···O bonds in solids.

and R does not hold at large R. Their data on hydroxides, combined with those collected by Pimentel and Sederholm, suggest that $\Delta\nu_s$ approaches zero asymptotically at large R for O—H···O bonds, as shown in Fig. 3-10.

Equally interesting is the prediction of behavior at small R. A crude assumption is that the force constant approaches zero as the proton approaches a symmetrical position between the two oxygen atoms. Substituting $\Delta\nu_s = 3750$ cm^{-1} (the shift necessary to bring the perturbed frequency to zero), the relation applicable to O—H···O bonds predicts R = 1.99 Å. This is a suprisingly reasonable number for a symmetrical H bond, since it is just about double the normal O—H bond length (0.96 Å). Despite the superficial appeal of this limiting value, the linear relation must fail before $\Delta\nu_s$ is as large as the unperturbed value of ν_s. It is known that the O—H bond length increases upon H bond formation, and hence the limiting bond type where the proton is midway between the two oxygen atoms must be reached at an R in excess of 1.99 Å. Rundle *et al.* (1764, 1488) feel that the 2.44 Å O····O distance in nickel dimethylglyoxime corresponds to a symmetrical bond. However, measurements of r(O—H) indicate that this estimate may be too high and that the symmetrical O—H···O bond may have an O····O distance below 2.4 Å. (See Section 9.3.1.) Other IR studies of substances with particularly strong H bonds can be found in references 505, 229a, 851a, and 14a.

Unfortunately the relation between $\Delta\nu_s$ and R cannot be checked for solution and gas phase species because distance measurements are not readily determined. On the other hand, this difficulty enhances the value of the $\Delta\nu_s$–R correlation as a means of estimating the H bond distances in these systems. (See 282.)

$\Delta\nu_s$ *and r.* It has been generally assumed that the A—H bond length is lengthened in strong H bonds (e.g., see 1, 682), but only with the advent of neutron diffraction and proton resonance techniques have data become available. The expectation that the A····B heavy atom distance R would correlate inversely with the A—H distance has been suggested by two compilations of data. Nakamoto, Margoshes, and Rundle list some of the available data for O—H···O systems (1488), and Moulton and Kromhout contrast the distances for four N—H···O systems (1459) with the predictions of the covalent model of Lippincott and Schroeder (1241). Figure 3-11 shows the data now available for O—H···O systems. The equation of the least mean squares line is shown on the figure.

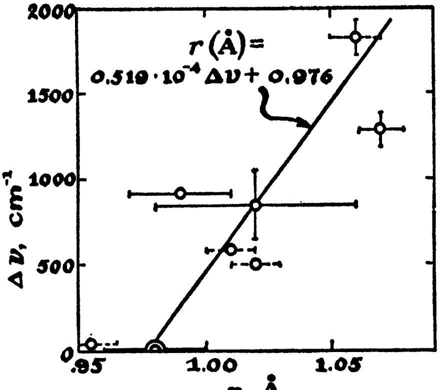

FIGURE 3-11 The relation between $\Delta\nu_s$ and r(O—H) for O—H···O bonds in solids.

$\Delta\nu_s$–Base Strength. Gordy and Stanford examined the self-consistency of $\Delta\nu_s$ as a criterion of base strength by comparing $\Delta\nu_s$ for various acids in a great variety of bases (801, 814, 812, 797). One of their figures is reproduced in Fig. 3-12. Although this extensive study established beyond a doubt the usefulness of $\Delta\nu_s$, the frequency measurements of Gordy and Stanford probably involve large uncertainties. For example, Tamres and co-workers remeasured $\Delta\nu_s$ for CH_3OD in nine solvents studied by Gordy and Stanford (1823, 1995, and 1824). The more recent values suggest that the data of Gordy and Stanford should be assigned uncertainties of about ±40 cm^{-1}. Consequently, the numerical data presented in Table 3-II are selected from more recent work where possible. (See also 1962.)

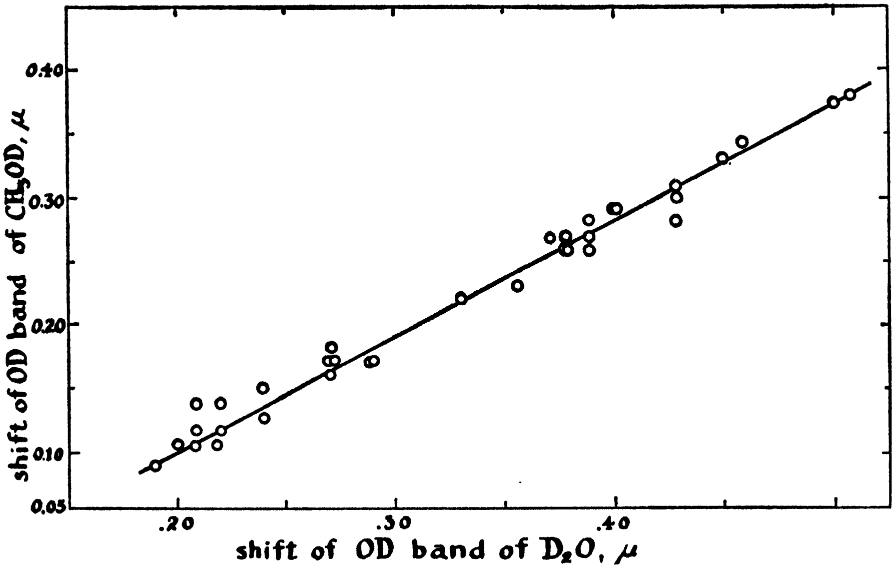

FIGURE 3-12 IR shifts: $\Delta\lambda_s$ of CH_3OD *vs.* $\Delta\lambda_s$ of D_2O in a variety of bases. [From Gordy, *J. Chem. Phys.* **9**, 222 (1941).]

TABLE 3-II $\Delta\nu_s$ as a Measure of Base Strength

SOLVENT	$\Delta\nu_s$ in cm^{-1}			REFERENCES		
	CH_3OD	Pyrrole	HCl	CH_3OD	Pyrrole	HCl
Aromatics						
Chlorobenzene	21	—	52	a	—	n
Benzene	24	39	81	a, b	h, i, j	n
Toluene	26	49	87	a	i	n
m-Xylene	29	52	108	a	i	n
Nitrobenzene	52	48	113	b	i	o
Mesitylene	34	58	119	a	i	n
Esters						
Ethyl acetate	51	—	254	c	—	p
Nitriles						
Acetonitrile	87	—	—	b	—	—
Ethers						
Anisole	94	—	250	d	—	q
Diethyl ether	96	141	438	e	h	n, q
n-Butyl ether	101	100	447	e	k	n
p-Dioxane	111	—	362	e	—	p
Ketones						
Acetophenone	101	92	—	f	i	—
Acetone	121	107	—	f	i	—
Amides						
N,N-Dimethylacetamide	147	—	—	d	—	—
Amines						
Pyridine	213	265	—	g, f	i, l, m	—
Triethylamine	289	295	—	g	h	—

[a] 1995; [b] 801; [c] 1824; [d] 812; [e] 1823; [f] 814; [g] 1996; [h] 979; [i] 1060; [j] 735; [k] 813; [l] 1239; [m] 329; [n] 1068; [o] 797; [p] 809; [q] 333.

It is suprising that $\Delta\nu_s$ has not been proposed as a measure of acid strength. With only a few examples, Barrow noted that $\Delta\nu_s$ (as well as **B**) shows a monotonic dependence on acid strength (139), whereas Huggins and Pimentel (also with few examples) found exceptions to this simple relationship (979). Table 3-III presents data for $\Delta\nu_s$ of ten acids of widely varying acid strength in four quite different bases. While $\Delta\nu_s$ correlates roughly with acid strength, there are ambiguities if different bases are compared.

A recent and novel study of *intra*molecular H bonding by Farmer, Hardie, and Thomson offers a comparative measure of base strengths

TABLE 3-III $\Delta\nu_s$ as a Measure of Acid Strength

ACID	$\Delta\nu_s$ in cm^{-1}				REFERENCES			
	Benzene	Diethyl ether	Acetone	Pyridine	Benzene	Ether	Acetone	Pyridine
$CDCl_3$	5	10	0	36	a	g	g, a	g
n-Butyl mercaptan	—	—	—	52	—	—	—	h
Thiophenol	—	19	—	114	—	h	—	h
Diphenylamine	25	71[q]	—	160	b	h	—	n
H_2O	25	—	82	247	c	—	c	c
Pyrrole	39	141	107	247	d, e, b	d	e	e
CH_3OH	57	133	118	234	d	d	l	l
Phenol	56	270	266	—	d	d, i, j	m	o
Acetic acid	—	—	—	461	—	—	—	p
HCl	81	438	—	—	f	f, k	—	—

[a] 980; [b] 735; [c] 823; [d] 979; [e] 1060; [f] 1068; [g] 1259; [h] 813; [i] 2053; [j] 138; [k] 333; [l] 1329; [m] 2174; [n] 329; [o] 2048; [p] 1401; [q] *n*-butyl ether.

(632). They examined the IR spectra of a variety of 2,2′disubstituted diazoaminobenzenes. The relative importance of the two possible tautomers is determined by the relative strengths of the two possible *intra*molecular H bonds. For further discussion, see Section 5.3.1.

$\Delta\nu_s$–Reactivity. The qualitative relation between base strength and $\Delta\nu_s$ suggests that ν_s might provide a quantitative index of reactivity. Support for this proposal was offered by Gordy and Stanford (814), who found that the values of $\Delta\nu_s$ for methanol-*d* in ketones and aldehydes are simply related to the log of the rate constants of semicarbazone formation. Furthermore, these authors showed a similar relation between $\Delta\nu_s$ and the basicity constants, pK_b, of a series of bases. (See also 863.) Ingraham, Corse, Bailey, and Stitt examined the effect of various *meta* and *para* substituents on the stretching frequencies of the free and the H bonded O—H groups of phenols and catechols (1016). Each of these frequencies shows an approximately linear dependence on the Hammett sigma function. Since the slopes of these two curves differ, the value of $\Delta\nu_s$ depends linearly on the Hammett sigma function.

Despite the promise of these early studies, relatively little activity has followed in predicting reactivities from IR data.

$\Delta\nu_s$–Henry's Law Constant. Josien and Fuson have made extensive studies of solvent effects on IR frequencies (1055, 1059), contributing much interesting and accurate data on H bonding systems. They note a systematic correlation between $\Delta\nu_s$ for either methanol or pyrrole and the Henry's Law constant of HCl in a series of aromatic solvents (1060). As the basicity of the aromatic increases, the constant decreases and $\Delta\nu_s$ rises. The data they compile are shown in Table 3-IV. For

TABLE 3-IV Henry's Law Constant, Relative Frequency Shift, and Heat of Mixing for Acids in Aromatic Solvents[a]

SOLVENT	HENRY'S LAW CONSTANT (HCl)	$(\Delta\nu_s/\nu_s)\cdot 100$ (CH_3OH)	$(\Delta\nu_s/\nu_s)\cdot 100$ (pyrrole)	HEAT OF MIXING ($CHCl_3$, 50 mole %)
Benzene	308	2.02	2.04	−90 cal/mole
Toluene	299	2.14	2.32	−157
m-Xylene	278	2.77	2.41	−202
Pseudocumene	272	2.85	—	—
Mesitylene	250	3.20	2.58	−216

[a] 1060.

comparison, the heats of mixing of chloroform in some of these solvents are given in the last column.

$\Delta\nu_s$–$\nu_{\frac{1}{2}}$. The enhancing of the band width of ν_s which accompanies H bond formation has been widely known for many years. Thus Mecke summarized in tabular form the band widths of the second overtone of ν_s for phenol in several solvents (1375). Yet, only recently have systematic examinations of band widths of the fundamental ν_s been made. Tsubomura (2054) has reported band widths for phenol in several bases. In a more complete study Huggins and Pimentel examined the frequency, band width, and intensity behaviors of the fundamental stretching mode of each of the acids pyrrole, methanol, and phenol in the bases benzene, ether, and triethylamine (979). The correlation between $\Delta\nu_s$ and $\nu_{\frac{1}{2}}$, shown in Fig. 3-13, is surprisingly close to a linear relation. A similar correlation has been found by Mirone and Fabbri for the bending mode of pyrrole in a variety of bases (1414).

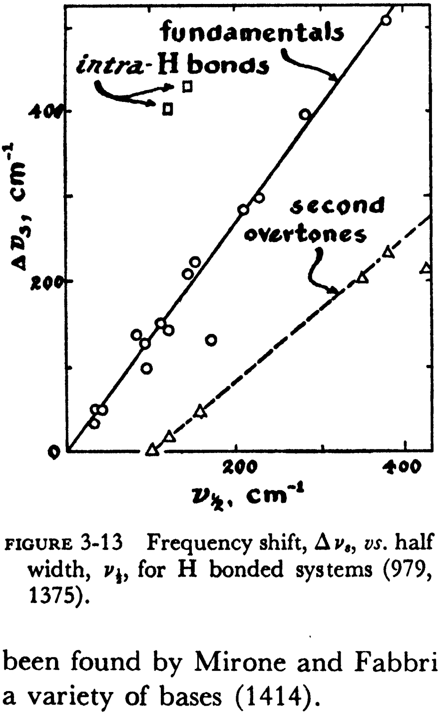

FIGURE 3-13 Frequency shift, $\Delta\nu_s$, *vs.* half width, $\nu_{\frac{1}{2}}$, for H bonded systems (979, 1375).

The data from the work of Lüttke and Mecke (1292, 1375) for the second overtone of the O—H stretch of phenol also provide a reasonably straight line, as shown by the broken line in Fig. 3-13. The slope of this line is distinctly lower than the corresponding line for the fundamental. Least squares treatments give the results:

fundamental $\nu_{\frac{1}{2}} = 0.72\Delta\nu + 2.5\ \text{cm}^{-1}$
2nd overtone $\nu_{\frac{1}{2}} = 1.16\Delta\nu + 100\ \text{cm}^{-1}$

One of the interesting aspects of the correlation of $\nu_{\frac{1}{2}}$ and $\Delta\nu_s$ for the fundamental mode is its applicability to a wide variety of H bonded systems and its inapplicability to the *intra*molecularly H bonded compounds, salicylaldehyde and methylsalicylate (2054) (indicated in Fig. 3-13 by squares). The linear relation offers a critical test of theories of the band width, and possibly more experience will show that it is a criterion for distinguishing inter- and *intra*molecular H bonds.

$\Delta\nu_s$–Δ**B**. Accompanying the band width increase caused by H bond formation is an increase in the integrated absorption **B** of the fundamental mode, ν_s, and a decrease in the intensity of the overtones. Table 3-V lists a portion of the data collected by Lüttke and Mecke (1292, 1375) to illustrate the magnitude of the changes.

TABLE 3-V Intensity, Band Width, and Frequency Shift of the Second Overtone of ν_s of Phenol in Various Bases[a]

SOLVENT	INTEGRATED INTENSITY, **B** (cm/mole)	$\nu_{1/2}$ (cm^{-1})	$\Delta\nu_s$ (cm^{-1})
Cyclohexane	8.0	100	(0)
CCl_4	8.2	110	10
CS_2	8.2	160	55
Toluene	9.0	340	200
Anisole	6.2	430	210
Nitrobenzene	5.5	370	220
Acetophenone	2.6	650	470
Diethyl ether	2.7	700	640
Acetone	3.1	750	740

[a] 1292, 1375.

Since then, several quantitative studies of intensities of this fundamental mode of H bonded species have appeared.[a] In assessing these data, comparisons of results obtained in different laboratories may be misleading, partly because of the notorious sensitivity of ν_s intensities to temperature changes, partly because the integrations may extend over different ranges or may be based on different band shape assumptions, and possibly because of inherent difficulties in absolute intensity measurements. Presumably this explains why the systematic dependence of intensity on $\Delta\nu_s$ is revealed in the internally consistent data of Huggins and Pimentel (979), and the same for $\Delta\nu_b$ in the data of Mirone (1414). Figure 3-14 shows the relatively simple relationship between the enhancement of intensity (relative to the solvent CCl_4) and the frequency shift (979). Once again it is seen that the behavior of compounds with *intra*molecular H bonds is drastically different from that of the intermolecular H bonded systems.

The correlations of $\Delta\nu_s$ with both $\nu_{1/2}$ and Δ**B** imply that these large and unusual spectral perturbations have a common source. In any

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[a] 693, 139, 980, 1259, 2054, 2052, 138, 2053.

event the three measurements together present a norm of behavior which might well serve as a criterion of the formation of a H bond. With more information, the correlations may aid in distinguishing *intra*molecular (and possibly nonlinear) H bonds from intermolecular H bonds.

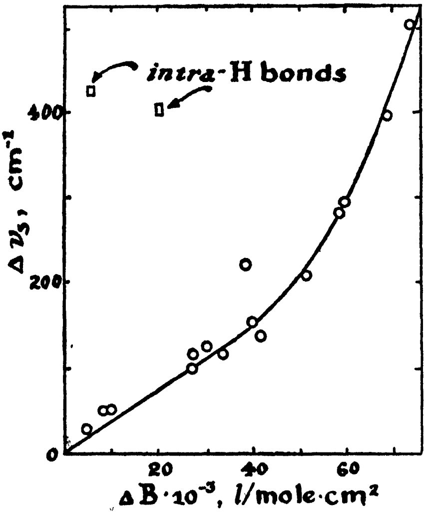

FIGURE 3-14 IR frequency shifts *vs.* intensity changes for H bonded systems. [From Huggins and Pimentel, *J. Phys. Chem.* **60,** 1617 (1956).]

In conclusion, it is desirable to note that the simple relationships between $\Delta\nu_s$, $\nu_{\frac{1}{2}}$, and $\Delta\mathbf{B}$ guarantee that $\nu_{\frac{1}{2}}$ and $\Delta\mathbf{B}$ will show correlations with all of the physical properties which have been related to $\Delta\nu_s$ [ΔH of solution, R(A· · · ·B), r(A—H), base strength, reactivity, and Henry's Law constant]. This has practical importance, because the intensity change on H bond formation is a more sensitive test for the presence of the H bond interaction than is $\Delta\nu_s$. Hence for systems forming weak H bonds, $\Delta\mathbf{B}$ may be the more informative IR datum [as was found for chloroform–aromatic systems (980)].

3.3.6 Infrared Measurements of Association Constant, K. One of the most important quantitative applications of intensity measurements of ν_s has been the determination of equilibrium constants and thermodynamic functions for H bond formation. The results are discussed in Chapter 7, but here we shall be concerned with the validity of these constants.

The essential problem is this: The determinations are almost always based upon intensity measurements for the band attributed to the monomeric species, and upon the assumption that the concentration of monomer is proportional to the absorption at this frequency. Of course this assumption is not correct if the dimeric or any higher polymeric species also absorbs at this frequency. For example, in a chain structure of methanol polymer the terminal O—H group would not be involved in H bonding, and this group might well absorb near the monomeric ν_s. Indeed, there is rather conclusive evidence that this would be the case. Kuhn (1161, 1162) studied many diols at high dilution where only *intra*molecular H bonding occurs. Similar studies were made for various substituted catechols (1,2-dihydroxybenzenes) by Ingraham, Corse, Bailey, and Stitt (1016). In each case the known molecular geometry guarantees that one of the O—H groups is H bonded and the other is not. Two bands are observed for each compound, one, ν_s (free), is near the monomeric frequency of the corresponding monohydroxy compound, and the other, ν_s (H bonded), is shifted to a lower frequency. Changing the *intra*molecular separation has the expected effect of altering the lower frequency, presumably because of a change in the strength of the H bond. The high frequency absorption, however, is almost independent of the H bond formation. Typical data are shown in Table 3-VI. It is a reasonable extrapolation that a terminal O—H group in an intermolecular H bonded polymer will be similarly unaffected by its action as a base.[a]

TABLE 3-VI Stretching Frequencies of Diols at High Dilution (Alkyl diols in CCl_4.[a] Catechols in C_2Cl_4.[b])

COMPOUND	ν_s (free) (cm^{-1})	ν_s (H bonded) (cm^{-1})	$\Delta\nu_s$ (H bonded) (cm^{-1})
1-Butanol	3634	—	—
1,3-Propanediol	3636	3558	+76
1,4-Butanediol	3634	3478	+156
trans-1,3-Cyclohexanediol	3620	—	—
cis-1,2-Cyclohexanediol	3626	3587	+33
trans-1,2-Cyclohexanediol	3634	3602	+18
cis-1,3-Cyclohexanediol	3619	3544	+76
Phenol	3610	—	—
Catechol	3612	3568	+42
4-Chlorophenol	3607	—	—
4-Chlorocatechol	3606	3564	+43

[a] 1162; [b] 1016.

In the light of this result we must conclude that the intensity of *th* *absorption at the monomeric* ν_s *will be proportional to monomer concentration only for cyclic structures* without terminal groups. Therefore it becomes

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[a] The only datum we have found contradicting this conclusion is also given by Kuhn (1162) for HCl-glycol solutions. Kuhn has indicated in a private communication that these experiments are probably unreliable.

most important to examine the evidence at hand indicating that the values of K measured by IR studies are meaningful.

The problem was recognized by early workers, notably Mecke and co-workers. Mecke, for example, presents a plot of the fraction α of monomeric CH_3OH in CCl_4 solutions as a function of mole fraction, x (1375). The data, reproduced in Fig. 3-15, give quite convincing proof that α determined from IR intensities is the same as α determined from the partial vapor pressure of CH_3OH. (See also 402.)

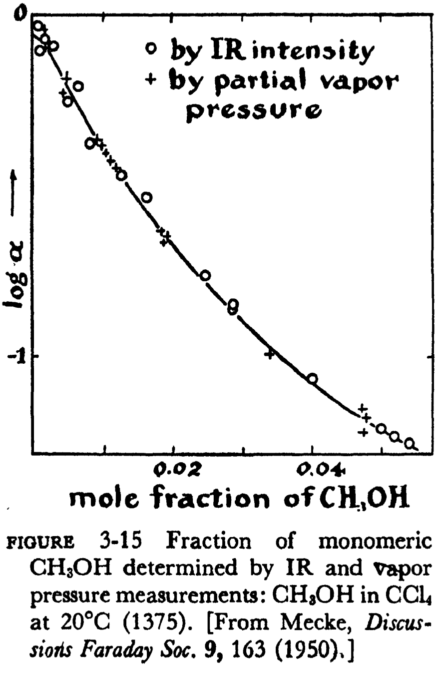

FIGURE 3-15 Fraction of monomeric CH_3OH determined by IR and vapor pressure measurements: CH_3OH in CCl_4 at 20°C (1375). [From Mecke, *Discussions Faraday Soc.* **9**, 163 (1950).]

A second type of study that corroborates the basic assumption is any measurement which specifically shows that the H bonded species are cyclic. Infrared data can offer such evidence, provided the only important species over a wide concentration range are monomers and dimers. For such a system the peak intensities of absorption by the monomer (I_M) and dimer (I_D) are simply related: the ratio I_D/I_M^2 is a constant. Such behavior has been observed and cited in favor of cyclic dimers of δ-valerolactam and of ε-caprolactam by Tsuboi (2050), and of γ-butyrolactam by Klemperer *et al.* (1117). However, no such deduction can be made for other amides (e.g., see 1117), phenols (e.g., see 411), or alcohols (e.g., see 1375 and 1150). There is much evidence in favor of cyclic dimers of carboxylic acids in the gas phase (1081), and some referring to solutions (1652 and 445). On the other hand, the IR data for liquid formic acid are more complicated. Chapman (373) concludes that the liquid contains a mixture of cyclic dimers and chain polymers. Dielectric data have been interpreted to show that formic acid is not entirely dimeric (1046). By use of "thermo-electric osmometry" Davies and Thomas have measured ΔH of dimerization of several amides and have concluded that trichloroacetamide and *N*-methyltrichloroacetamide form cyclic dimers, whereas *N*-methylacetamide, *N*-methylformamide, and *N*-methylbenzamide form open or chain dimers (1, 503). (See also 1898.)

In the important methanol system there are three more studies which give indirect evidence of cyclic dimers. Van Thiel, Becker, and Pimentel (2098) obtained IR spectra of methanol suspended in solid nitrogen at 20°K, and have assigned frequencies to dimers, trimers, and tetramers. The assignments lead to the conclusion that methanol dimers (and probably trimers) are undoubtedly cyclic both in the solid nitrogen at 20°K and in solutions at room temperature. [Similar results have been obtained for water (2097).] Becker and Liddel (1, 1228) made careful IR studies of the ΔH of dimerization of methanol in CCl_4. The value obtained, -9.2 ± 2.5 kcal/mole, is sufficiently high to warrant their interpretation that the dimer is probably cyclic. (See also 1227.) Finally, Becker (181) has reported proton magnetic resonance studies of ethanol solutions in CCl_4. These were interpreted with the aid of equilibrium data (from IR studies) to give characteristic H bond shifts of dimers and of higher polymers. The shift of the dimer is about half that of the polymer, suggesting a unique, possibly cyclic, structure of the dimer. (See also 1392 for presumed cyclic structures of hydroperoxides.)

The matrix isolation method was also applied to the study of the H bonding of water by Van Thiel *et al.* (2097). In solid nitrogen at 20°K the IR absorptions of dimeric water permit inferences concerning the structure of this species. Van Thiel *et al.* consider the possible structures shown in Fig. 3-16. The "bifurcated" structure was suggested by Errera, Gaspart, and Sack on the basis of IR spectra of H_2O and HDO in dioxane solutions (614). Van Thiel *et al.* reject both the open and bifurcated structures for H_2O dimer and conclude that a cyclic structure is formed (2097).

There is less substantiation of the structure of the dimer of phenol, but the evidence favors cyclic dimers and trimers. Mecke's early work was based on this assumption (1375). More recently the careful study by Rea (1698) has led him to propose that at any concentration of phenol in CCl_4 only a small fraction of the phenol is present as dimer, and that the more stable trimer is cyclic.

There has been a long controversy over the structures of the HF polymers since Simons and Hildebrand found that the vapor density data are consistent with the presence of but one polymeric species, a hexamer (1882). This apparently unique stability of $(HF)_6$ suggested

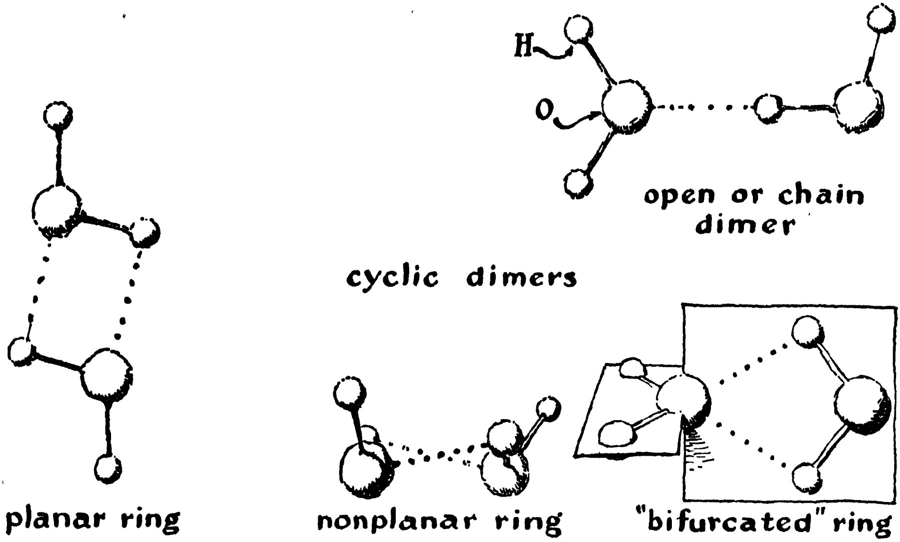

FIGURE 3-16 Possible structures of dimeric water.

a cyclic structure. Since that time a variety of techniques has been used to determine if other polymeric species are formed, and to learn if the structures are cyclic: PVT measurements (1253, 277); electron diffraction (173); x-ray diffraction (82); dielectric polarization (191, 1549); IR spectra; and theoretical considerations (1327, 1585, 2042). Despite all of this study, neither the existence nor the absence of cyclic structures has yet been proven conclusively.

In conclusion, then, the available evidence concerning the structure of dimeric units suggests that many H bonding compounds form cyclic dimers (carboxylic acids, lactams, alcohols, phenols, and some sterically hindered amides) but that some form open dimers (most amides). This conclusion is reassuring to the many quantitative studies which have been based upon the tacit assumption that the ν_s absorption of monomeric species is not coincident with terminal O—H absorption of polymers.

On the other hand, this conclusion opposes the usual assumption that the three atoms in the H bond, A—H· · ·B, lie on or very close to a common line. We might direct our attention to the experimental basis for that premise. As is discussed in Section 9.3.3, the actual positions of the hydrogen atoms have been measured for only a few crystals, and the deviations from linearity are of the order of ten or fifteen degrees. For many other crystals for which only the heavy atom positions are known, the hydrogen atom *could* be on the line of centers of A and B with only small disturbance of normal bond angles. In total, the structural data available for crystals *do* support the premise that the linear arrangement of A—H· · ·B is *energetically favored.* Presumably, in crystals the structure is usually so strongly influenced by the H bond formation that the molecules lodge in orientations close to this optimum arrangement. In *intra*molecular H bonds and in the smaller polymeric units the linear arrangement may be obtainable only with strains in other degrees of freedom, and a compromise (minimum energy) nonlinear configuration will result.

3.3.7 Intensity of ν_s. The spectacular increase in the integrated absorption of the fundamental ν_s upon H bond formation has been mentioned in Section 3.3.5. The absorption of the fundamental may increase by as much as an order of magnitude. This change in absorption, $\Delta\mathbf{B}$, seems to be every bit as characteristic of H bond formation as is the frequency shift, $\Delta\nu_s$. Even though a number of early workers recognized this intensity enhancement (e.g., see 488, 2181), the situation was misinterpreted in some cases because of the breadth of the band and because of the intensity behavior of the overtones. The overtones have somewhat lower integrated absorption coefficients after H bond formation. In fact, the combination of frequency shift, lower intensity, and extreme band width stimulated the early suggestion that the "disappearance" of the stretching mode be used as a criterion of H bonding (920, 919, 103).

This intensity behavior, together with that of the bending modes, is determined by the charge distribution in the H bond and its movement during vibration. Accordingly, its significance is discussed in detail in Section 8.3.3. We shall restrict our attention here to the magnitude of the increase in absorption for various systems. Although the change, $\Delta\mathbf{B}$, correlates with $\Delta\nu_s$, it is also of interest to examine the ratio of absorption after H bond formation divided by the absorption of the monomer in an inert solvent. Table 3-VII shows some of the intensification factors that have been published. The data for chloroform in various bases are included in anticipation of the discussion in Section 6.2.1, which establishes the H bonding powers of chloroform. For the phenol solutions the bases are listed in order of increasing base strength in accordance with Table 3-II. The data show that the effect is indeed a large one; except in the weakest interactions ν_s is at least five times more intense after H bond formation. (These data are representative; data for other systems can be found in the references given in Table 3-VII, and also in 1414 and 387.)

TABLE 3-VII Factors of Intensification of ν_s on H Bond Formation

ACID	BASE	B(H bond)·10^{-3} (liters cm^{-2} $mole^{-1}$)	$\frac{B(\text{H bond})}{B(\text{monomer})}$	REFS.
Phenol	Benzene	16	2.1	a
Phenol	Ethyl acetate	84	7.2	b
Phenol	Acetonitrile	50	4.3	b
Phenol	Diethyl ether	80.3	6.9	b
Phenol	Hexamethylene tetramine	124	10.7	b
n-Butyl alcohol	Diethyl ether	38	5.3	c
sec-Butyl alcohol	Diethyl ether	32	5.5	c
t-Butyl alcohol	Diethyl ether	26	6.2	c
γ-Butyrolactam dimer		41	14	a
Acetic acid dimer		74	37	a
Methanol polymer		24	5.0	a
H_2O polymer		—	12	a
N-Ethylacetamide polymer		44	19	a
$CDCl_3$	Benzene	0.31	6.2	d
$CDCl_3$	Ethyl acetate	—	9.5	e
$CDCl_3$	Acetone	0.54	10.8	d
$CDCl_3$	*N*-Ethylacetamide	1.70	34	d
$CDCl_3$	Pyridine	—	20.5	e
$CDCl_3$	Triethylamine	1.80	36	d

[a] 979; [b] 2053; [c] 139; [d] 980; [e] 1259.

3.3.8 Structure and Shape of ν_s. Surely one of the most characteristic and interesting spectral changes brought about by H bond formation is the extreme broadening of the A—H stretching mode absorption. This breadth, which was discussed as early as 1937 (see, for example, 103, 500, and 335), is observed for H bonded gases, pure liquids, solutions, and solids, and in both Raman and IR spectra [for examples of Raman studies, see the work of Batuev (161, 160, 165) and others (1188, 1330, 1464)]. A wide variety of H bonding systems displays the behavior, as noted earlier in the correlation of $\Delta\nu_s$ with $\nu_{\frac{1}{2}}$ (979). For liquid and solid phases the band width of ν_s in H bonded species may be an order of magnitude greater than that of ν_s in the monomeric solution species. Of apparent significance is the empirical observation that this behavior is unique to H bonded systems. The phenomenon has obvious diagnostic value as a criterion of H bonding, but it has deeper significance as a clue to the intimate details of the H bonding interaction.

Spectra which illustrate this band width broadening are shown in Figs. 3-17, 3-18, 3-19, 3-20, and 3-21. Figure 3-17 shows spectra of the monomeric CH_3OH species, of polymers, of the glass at 20°K, and of the annealed solid (annealed at 150°K). The band widths are, respectively, ~30 cm^{-1}, 290 cm^{-1}, 180 cm^{-1}, and 190 cm^{-1}. (For band width data on water, see 316.)

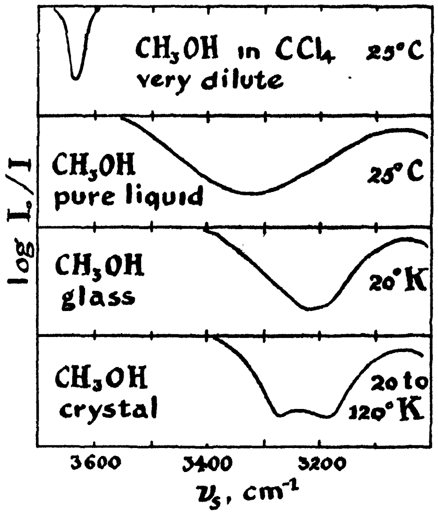

FIGURE 3-17 IR spectra of ν_s of methanol in condensed phases. [All unpublished data of M. Van Thiel and G. C. Pimentel.]

Figure 3-18 shows the spectra obtained recently by Millikan and Pitzer, of gaseous and solid formic acid (1410, 1411). They find band widths for monomer (gas phase), dimer (gas phase), high polymer (glass, 20–77°K), and solid (20–77°K) of, respectively ~50 cm^{-1}, ~500 cm^{-1}, ~600 cm^{-1}, and ~400 cm^{-1}. Figure 3-19 contrasts the ν_s band structures for the various deuterated formic acids (gas phase) (1411). The comparisons made by Bratož, Hadži, and Sheppard (270) include those spectra shown in Fig. 3-20. The spectral similarity in the ν_s region for a variety of H bonded carboxylic acids in CCl_4 solution is apparent. Here the band widths are about 400 cm^{-1} (979).

The spectra of Fig. 3-21 present the remarkable structure of ν_s of solid diethylamine hydrochloride and hydrobromide. All of the features in the spectral region 1600–2500 cm^{-1} are apparently associated with ν_s. Not a single feature in this richly structured band is lost on cooling the sample to 4°K.

An analysis of the shape and structure of ν_s in H bonded species must explain why the behavior is common to gas, liquid, and solid states of a variety of systems. Three proposals have been offered:

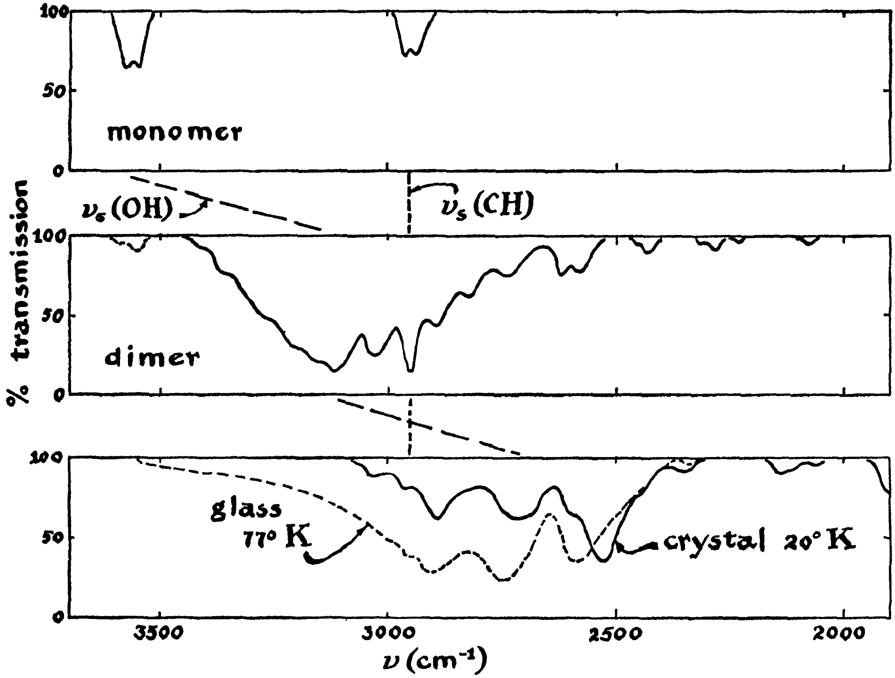

FIGURE 3-18 IR spectra of formic acid gaseous monomer, gaseous dimer, crystal, and glass. [From Millikan, Ph.D. Thesis, University of California (1956).]

1. The wide band of ν_s is caused by the superposition of many sharper bands of a variety of species.

2. The ν_s band is broadened by interaction between ν_s and the very low frequency deformations of the H bond, such as ν_σ and ν_β (see Fig. 3-1).

3. The structure of the ν_s band is caused by combinations of other fundamentals than ν_s intensified by Fermi resonance with ν_s.

Fénéant (638) proposed that a mixture of cyclic and open dimers and higher polymers accounts for the breadth and diffuse character of ν_s. Although there is no question that the band is caused by overlapping absorptions of a variety of species in *some* cases (e.g., in pure alcohol, phenol, amides), it is also clear that the breadth exists in many systems for which only a single H bonded species is important (e.g., in carboxylic acids, lactams; see, for example, 979). Hence proposal (1) does not account generally for the uniqueness of the H bonding interaction.

Fuson and Josien have offered a variant of (1) based on their observations of the spacings of deuterated acids (733). They propose that

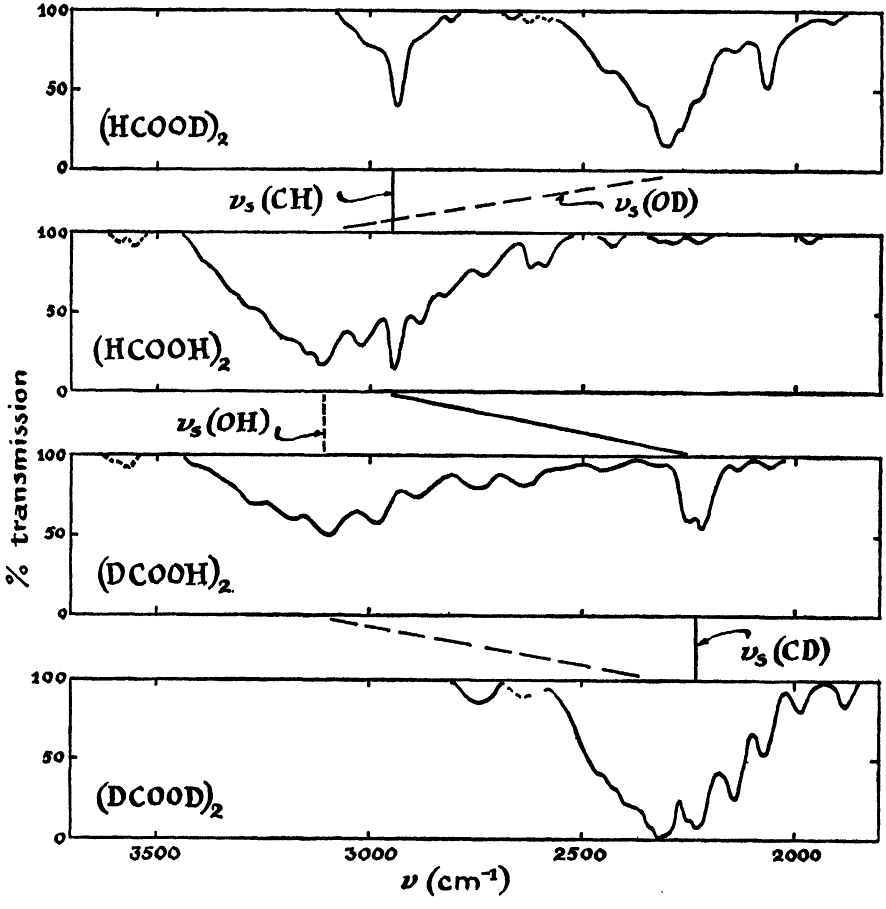

FIGURE 3-19 IR spectra of gaseous formic acid dimers. $p = 15$ mm, $T = 26$°C. [From Millikan, Ph.D. Thesis, University of California (1956).]

several H bonded species exist which differ because the proton can occupy any of several discrete positions between the heavy atoms. They devised this "quantized position" model because they concluded that deuteration radically alters the spacings superimposed on ν_s. This explanation has received little support.

Suggestion (2), that extremely low frequency modes are influential

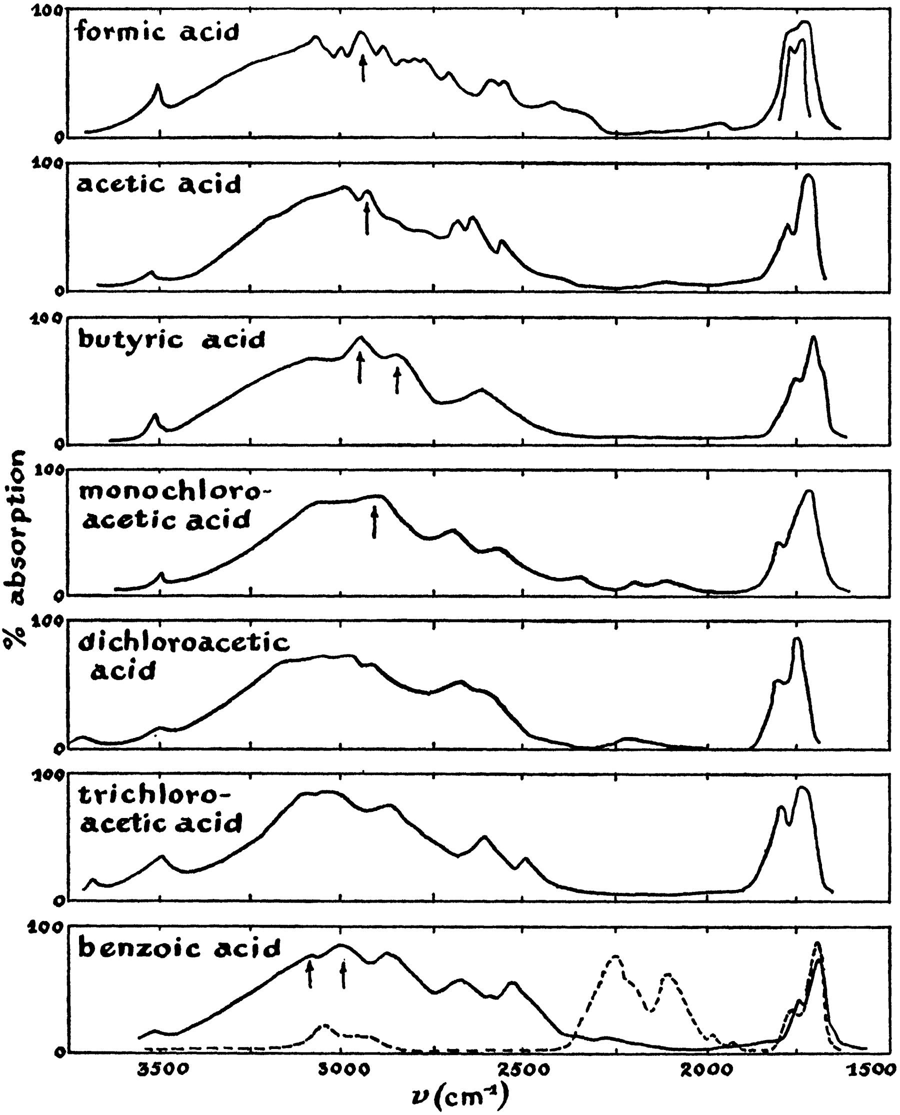

FIGURE 3-20 IR spectra of ν_s of carboxylic acids in CCl_4 solutions: 0.004 M, 2 mm cell. Broken line, deuterated acid; arrows indicate ν_s(C—H). [From Bratož, Hadži, and Sheppard, *Spectrochim. Acta* **8**, 252 (1956).]

in determining the band width and the structure, is the most popular theory. It was proposed by Badger and Bauer (103), Davies and Sutherland (500), and more recently by many other authors.[a] This

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[a] 1949, 388, 157, 155, 491, 1061, 733, 1946, 880, 373, 1409.

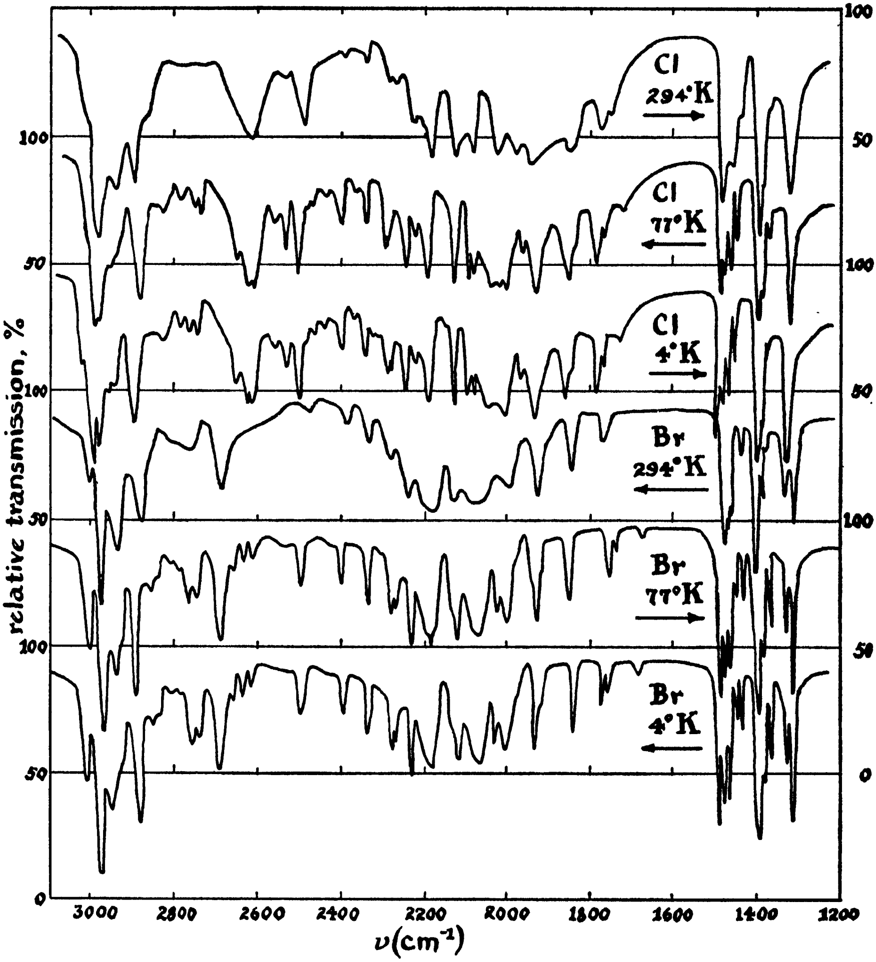

FIGURE 3-21 Spectra of triethylammonium chloride and bromide at various temperatures. (horizontal arrows indicate ordinate scale). [We acknowledge, with thanks, permission from R. C. Lord to reproduce these unpublished spectra.]

proposal has received considerable impetus with the discovery of repetitious spacings in the fine structure in the ν_s band (see, for example, Fig. 3-19). Unfortunately, different workers who have studied the carboxylic acid spectra do not agree on the spacings. This disagreement suggests that the band structure is so detailed that the selection of equal spacings may be arbitrary. Table 3-VIII shows spacings which various authors have chosen.

For several entries in Table 3-VIII the reference frequency is the

TABLE 3-VIII Intervals Reported Between Features in ν_s for Dimeric Acids

DIMERS OF	STATE	REF. FREQ. (cm^{-1})	INTERVALS (cm^{-1})	REFS.
HCOOH	.013 M CCl$_4$		200, 194, 186, 178[a]	c
HCOOH	liquid	3151	383, 193, 210	d
HCOOH	gas	3110	82, 71, 71, 71, 80	e
DCOOH	gas	3098	96, 113, 148, 115	e
DCOOD	gas	2323	97, 95, 80, 92, 97	e
CH$_3$COOH	.004 M CCl$_4$		~170, 156, 145[a]	c
CH$_3$COOH	CCl$_4$	3050	101, 239, 59, 89	f
CH$_3$COOH	CCl$_4$	3540	(2·215),[b] 203, 214, 196, 198, 197	g
CH$_3$COOD	CCl$_4$	2635	(2·117),[b] 118, 122, 113	g
CCl$_3$COOH	.003 M CCl$_4$		124, 114, 106, —, —, 78	c
CCl$_3$COOH	CCl$_4$	3046	143, 247, 153	f
CCl$_3$COOH	CCl$_4$	3497	(2·210),[b] 208, 221, 202, 206	h, i
CCl$_3$COOD	CCl$_4$	2591	(2·105),[b] 109, 104, 100	g, h
CF$_3$COOH	gas	3587	(2·221),[b] 227, 222	g
CF$_3$COOD	gas	2648	(2·118),[b] 119, 121, 114	g, h

[a] Chulanovski and Simova also propose spacings of about 35 cm^{-1} superimposed on the intervals given (see c).

[b] Fuson and Josien base their intervals upon the monomeric reference frequency; their model proposes that the first interval will be forbidden, hence the first observed frequency will be at a double spacing (see g).

[c] 388; [d] 373; [e] 1411; [f] 880; [g] 733; [h] 1061; [i] 491.

monomeric value of ν_s. This leads to the interpretation of Davies and Evans (491) that the ν_s band consists of a series of difference bands: $[\nu_s\ (\text{monomer}) - n\nu_\sigma]$. They suggest that ν_σ for the carboxylic acid dimers is about 210 cm^{-1}; similar spacings in the spectra of amides give ν_σ of 70–90 cm^{-1} for these weaker H bonds. The principal weakness of this proposal (as remarked by Bratož, *et al.*, 270) is that it implies a marked temperature dependence of the spectrum. Such sensitivity has not been reported.

The spectra of gaseous formic acid found by Millikan and Pitzer (1411) are distinctive because the spectral features indicate spacings independent of the deuteration, in contradiction to the results presented by Josien and Fuson for trifluoroacetic acid, for which the spacing seems to be halved on deuteration (1061). These formic acid spectra are further unusual because of the presence of distinctive structure on the low frequency side of the band center and diffuse contour on the high frequency side. Although favoring the interpretation of low frequency interaction, Millikan and Pitzer conclude that "no single hypothesis seems adequate to explain all the observed features of the . . . [ν_s] band of carboxylic acids." (1409).

Proposal (3), the third interpretation of the structure of ν_s, is principally due to Bratož, Hadži, and Sheppard (270 and 271), although it had been suggested earlier for other H bonding species (1503 and 760). While this interpretation is appealing in its simplicity, it requires an additional assumption, which explains why the Fermi resonance extends over such a spectral range, and it leaves untouched the curious differences between the structures of the high and low frequency sides of the ν_s band of formic acid. At this time it seems likely that the unique width is associated with the very low frequency modes (which are themselves unique), and that both proposals (1) and (3) participate in contributing fine structure to the band. Further discussion of this behavior can be found in Section 8.3.3.

We have reviewed three proposed explanations of the width of ν_s and the supporting arguments for each. In view of the uncertainty remaining, it is surprising that little use has been made of the low temperature behavior of the width and structure of ν_s. In fact, consideration of this behavior discloses a topic of substantial interest in itself. Newman and Badger (1503) found that the spectrum of solid acetylglycine was altered as the temperature was lowered to 88°K (−185°C). Although no major change in the contour of ν_s occurs, the structure of the band is generally sharpened, and a few new sharp bands appear. These same authors found similar sharpening at −185°C in the spectrum of KHF_2 (1502). This is the behavior observed by Landsberg and Baryshanskaya (1187) in Raman studies of the O—H band in hydrate salts (4–293°K). In contrast, Ferriso and Hornig found no change in the broad bands in the IR spectrum of H_3O^+ on cooling from 78°K to 8°K (644). They conclude that the band breadth must be caused by "frozen-in disorder." The same observation was made by Van Thiel, Becker, and Pimentel for annealed methanol solid (Fig. 3-17) over the temperature range 20–120°K. These authors note the absence of the unsymmetrical narrowing which would result at these extremely low temperatures if difference combinations involving ν_σ and ν_β (see Fig. 3-1) were involved. Their interpretation, similar to that of Ferriso and Hornig, is that the lattice defects remaining after annealing cause the widening. Apparently these defects are not lost at the low temperature because the rate of diffusion is too slow. Finally, we may examine the startling temperature behavior in the ν_s band of the diethyl ammonium halides. As seen in Fig. 3-21, a very large number of spectral features are found in the broad ν_s band, and not *one* of these is lost on cooling to 4°K. Again it is necessary to explain these features without invoking *any* difference combinations. (See also 268, 1509.)

An entirely new type of information on the band width has emerged from the matrix isolation studies of Van Thiel, Becker, and Pimentel (2098, 2097). In this technique the polymeric species are studied while suspended in solid nitrogen at 20°K. In contrast to the observations on solid methanol at 20°K, the matrix spectra consist of bands of moderate widths. Table 3-IX lists the observed band widths for methanol in a nitrogen matrix, and the pattern of frequency shifts of the various-sized polymeric units. Van Thiel *et al.* conclude that the band widths of the polymeric species in solution are due to a continuous range of configurations corresponding to nonlinear H bonds, and that these configurations are lost in the matrix studies. The bands are presumed to narrow as the matrix restricts the polymers to the most stable angular configuration. Of equal importance is the pattern of frequency shifts, revealed for the first time in these studies. Van Thiel *et al.* reject the possible explanations of a mechanical coupling interaction or an induction effect. Instead they infer a change in structure of the polymers. The low values of $\Delta\nu_s$ found for dimers and trimers are attributed to cyclic structures with bent, possibly weak, H bonds. The constant frequency shift for tetramers and all high polymers indicates that the H

TABLE 3-IX Frequency Shifts and Band Widths of Methanol Polymers in Solid Nitrogen at 20°K[a]

POLYMER	$\Delta\nu_s$ (cm^{-1})	$\nu_{\frac{1}{2}}$ (cm^{-1})
Monomer	(0)	20
Dimer	170	28
Trimer	215	~40
Tetramer	370, 410	—
High polymer	410	~100
Annealed solid	440	190

[a] 2098

bonds have become linear in the tetramer, and that an increase in polymeric size produces no further change in bond energy or $\Delta\nu$. Similar results have been obtained for water studied in the same fashion (2097). These experiments also reveal the twelve-fold change in absorption coefficient of ν_s resulting from H bond formation. Finally, matrix studies of formic acid have been reported by Millikan and Pitzer (1411). They suggest that the low frequency extreme of the broad ν_s band corresponds to the linear, hence strongest, H bond configuration and that the matrix constricts the H bonded dimer to this orientation.

There is no question that the matrix work has added to our knowledge of the band width behavior of ν_s and the frequency shift as a function of polymer size. Further use of this technique will be helpful, not only in the study of other systems but in corroborating the interpretations that have been made.

In summary, low temperature studies have great promise as a critical test of our understanding of the width and structure of ν_s. While it cannot be said that there exists a substantiated and generally applicable theory, current activity suggests that progress can be expected. Some of the most popular theoretical attacks are described and criticized in Section 8.3.3.

3.3.9 Deuteration Shift and Anharmonicity of ν_s. Considerable attention has been drawn recently to the possibility that unusual anharmonicity of the vibrations of the H bond accounts for the unique spectral band width of ν_s (268, 724). The suggestion that ν_s is unusually anharmonic was made by Lord and Merrifield (1258) on the basis of the deuteration shifts of four crystals. The ratios of the A—H stretching mode to the A—D mode are given as follows: triethylamine-hydrochloride, 1.29; pyridine-hydrochloride, 1.29; potassium dihydrogen phosphate, 1.35; and *N*-acetylglycine, 1.27. An unusual anharmonicity is suggested by the fact that three of these values are well below a normal value near 1.35. Even though a low deuteration shift is not positive evidence of anharmonicity, it is interesting to examine a larger range of systems to see if a low deuteration shift is generally observed. Some suitable data are presented in Table 3-X.

These data show no systematic difference from a normal value of ν_H/ν_D of H bonded species either in solution or in the gaseous state. Table 3-X, together with the data of Lord and Merrifield (1258), leaves the situation a little in doubt with reference to the solid state. Neither are the data sufficient to permit the conclusion that normal

TABLE 3-X Deuteration Shift of ν_s for H Bonded Species

ACID	BASE	ν_s (cm^{-1})	ν_H/ν_D	REFS.
Gases				
HCOOH(D)	Monomer	3570	1.36	a
HCOOH(D)	Dimer	3110	1.34	a
Liquids				
$CH_3OH(D)$	Monomer, CCl_4	3642	1.36	b, c, d
$CH_3OH(D)$	Benzene	3583	1.34	b, e
$CH_3OH(D)$	Acetone	3522	1.35	f, g, h
$CH_3OH(D)$	*p*-Dioxane	3516	1.36	d, f, i
$CH_3OH(D)$	Diethyl ether	3508	1.35	b, c, d
$CH_3OH(D)$	Pyridine	3408	1.38	f, g, j
$CH_3OH(D)$	Triethylamine	3246	1.35	b, c, j
$H_2O(D_2O)$	Pyridine	3412	1.35	k, l, m
$H_2O(D_2O)$	Pure	3395	1.36	k, n, o
Formamide	Pure	3330 (asym.) 3190 (sym.)	1.32	p
Methylformamide	Pure	3280	1.33	q
Methylacetamide	Polymer, CCl_4	3280	1.37	q
Solids				
$CH_3OH(D)$	—	3228	1.35	r
$H_2O(D_2O)$	—	3250	1.33	k, n, s
HCOOH(D)	—	2720	1.29	a
HCl(D)	—	2725	1.38	t, u
$HN_3(D)$	—	3120	1.34	v

[a] 1410, 1411; [b] 979; [c] 138; [d] 1823; [e] 1995; [f] 1329; [g] 814; [h] 1824; [i] 812; [j] 1996; [k] 823; [l] 614; [m] 797; [n] 683; [o] 1651; [p] 1419; [q] 1423; [r] Unpublished data of M. Van Thiel and G. C. Pimentel; [s] 757; [t] 957; [u] 956a; [v] 549.

ratios of ν_H/ν_D are usually observed or that the H bond is usually sufficiently anharmonic to give a low value of ν_H/ν_D.

More direct evidence concerning anharmonicity can be found in the frequencies of ν_s harmonics. Usual mechanical anharmonicity causes the $0-n$ transition[a] to be below n times ν_s by 1–3 percent. Figures 3-22, 3-23, and 3-24 show plots of ν_{0-n}/n *vs.* n for water, alcohols, and phenol. The data for water in various H bonding bases, Fig. 3-22, show most distinctly that the effect of the H bond is to *reduce* the anharmonicity compared to that of the gaseous monomer. The anharmonicity decreases as the H bond becomes stronger, actually becoming negative

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[a] The notation $0 - n$ refers to the transition in which the vibrational quantum number changes from zero (the ground state) to the value n. This is the $(n - 1)$st harmonic.

for the first harmonic in liquid water and in pyridine. For the higher harmonics, the anharmonicity seems to approach that of the gas phase. The data for the alcohols and phenol are from several sources and are much less reliable from the point of view of self-consistency. Insofar as the second harmonic is concerned (0–3), the effect of the H bond is to reduce anharmonicity. The behavior of the first harmonic (0–2) is not clear, particularly in the case of phenol where abnormally large anharmonicity seems to be a property of the monomer in CCl_4. The data for associated alcohols are by Freymann, who conducted one of the first investigations of anharmonicity (714).

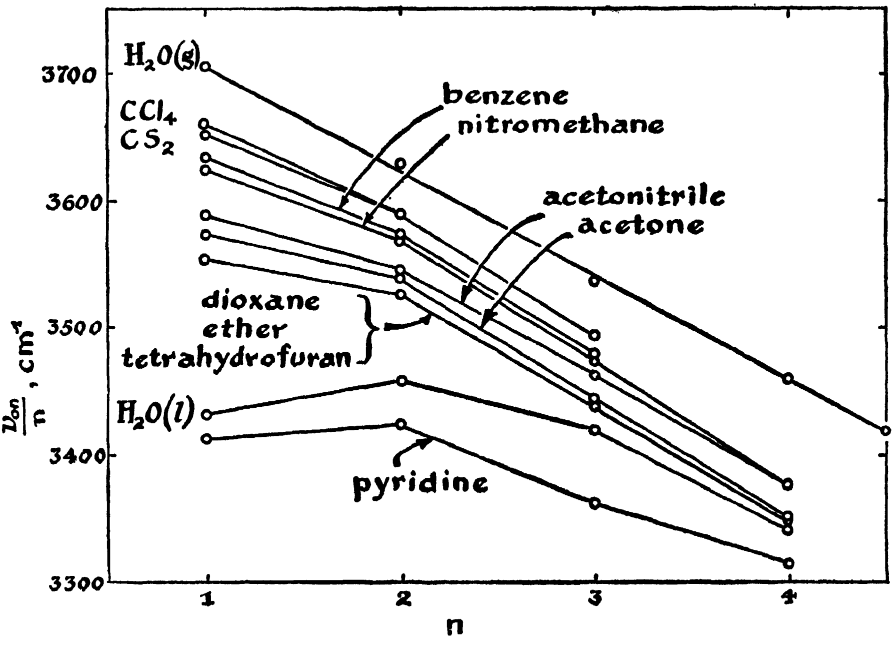

FIGURE 3-22 Reduced frequency (ν_{o-n}/n) as a function of vibrational quantum number, n: H_2O in various solvents. [From Greinacher, Lüttke, and Mecke, *Z. Elektrochem. Ber. dtsch. Bunsenges. physik. Chem.* **59**, 27 (1955), Verlag Chemie, Gmb H, Weinheim/Bergstr.]

There is one additional property of the overtones that might reveal the anharmonic character of ν_s: the absorption coefficient. The appearance of overtones in the IR spectrum, in violation of the harmonic oscillator selection rules, is attributed to electrical and mechanical anharmonicity. If the H bond caused additional anharmonicity, the intensity of the harmonics should increase with H bond formation.

Exactly the opposite has been observed, as shown, for example, by phenol in various bases (1292, 1375). As can be seen in Table 3-V, the intensity of the second overtone ν_s *decreases* as the base strength of the solvent increases.

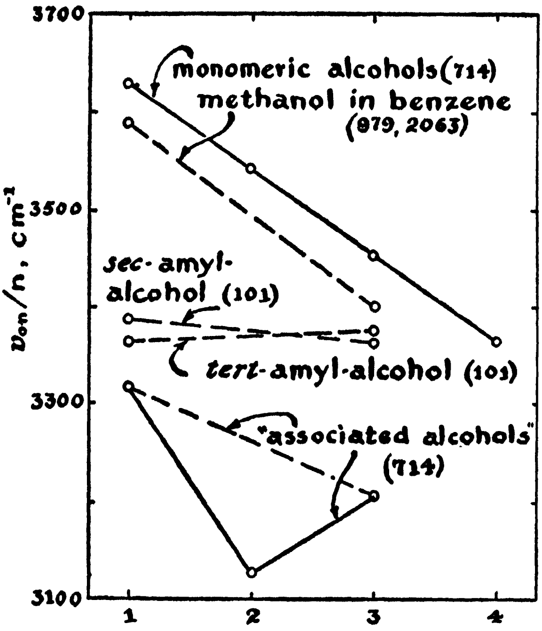

FIGURE 3-23 Anharmonicity of ν_s of alcohols.

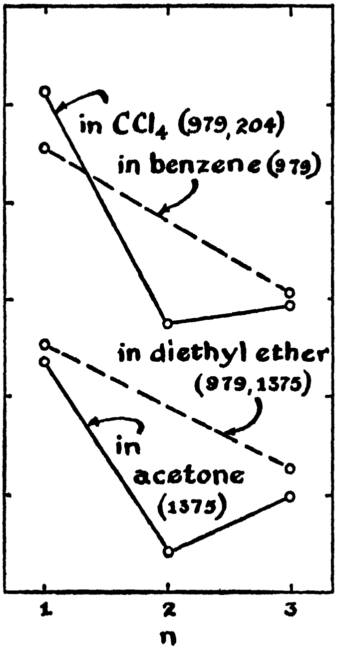

FIGURE 3-24 Anharmonicity of ν_s of phenol.

In summary, none of the three types of data available—deuteration shift, overtone frequencies, or overtone intensities—provides a basis for generalization that the effect of the H bond is to make ν_s more anharmonic. To the contrary, each type of data can be used to support the proposal that ν_s *is of normal anharmonicity or is possibly slightly more harmonic after H bond formation.*

Because of the structural arrangement, the carboxylic acid dimer is unusual. The O—H bonds of the two acid units of the dimer must vibrate in unison, in-phase or out-of-phase. If the cyclic dimers are planar or close to planar, only the out-of-phase mode of ν_s will be IR-active. This has particular significance in reference to the anharmonicity. By symmetry the potential function for the out-of-phase vibration *cannot involve odd powers* of the displacements. The absence of odd power terms suggests that this mode, at least, may well have unusually small anharmonicity.

3.3.10 Spectra of Crystals: Infrared Dichroism. The spectrum of a single crystal observed in polarized light depends upon the orientation of the crystal axes relative to the plane of polarization.[a] A similar situation exists for macroscopically oriented high polymers, obtained by extruding or stretching polymeric materials such as nylon, polyvinyl alcohol, and polyethylene. Ellis and co-workers were the first to make systematic studies of IR dichroism in H bonded systems (604, 779, 780). Further attention was drawn to the method by Mann and Thompson (1334), Crooks (463), and Ambrose, Elliott, and Temple (595, 38, 589, 4).

Experimentally, the spectrographic technique is rather simple once a suitable sample is obtained. Almost any conventional IR spectrometer can be adapted for polarized light studies by inserting in the optical path a polarizing unit consisting of a stack of six to twelve silver chloride sheets inclined at an angle of about 65° to the optical path (e.g., see 463, 1334, 1168).[b]

A crystal plane normal to one of the optic axes should be selected, otherwise elliptic polarization may result, and, the apparent dichroism may depend on sample thickness. With a suitable sample, the significance of the dichroism still must be examined with caution. Even for a characteristic vibration (such as an N—H or C═O stretching mode), the measurement indicates only the direction of the transition moment, whereas what is usually desired is the direction of the vibrating bond. The transition moment and the bond may not be parallel because of crystalline perturbations or because of *intra*molecular interactions with other parts of the molecule. A portion of the crystalline perturbations can be eliminated by the dilute mixed crystal technique [discussed in Section 3.2.2 (see 975)], but this type of experiment has been performed only for a few cases.

Usually the assumption is made that the spectrum of a molecular crystal is that of an array of molecules oriented in their crystal lattice positions but without *any* interaction. This model was tacitly used until it was formally proposed as a model by Ambrose, Elliott, and Temple (37), and independently by Pimentel and McClellan (1635). The

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[a] This phenomenon is conventionally called dichroism or pleochroism. The latter term, the more correct, is rarely used.

[b] Usually there is a small amount of polarization by the optics of the spectrometer.

latter authors called the model the "oriented gas model" and attempted to test its validity in a later study (1636) of a non–H bonding crystal.

There are three distinct types of information that can be extracted:

1. Information that will aid in assigning vibrational modes.
2. Information concerning the gross features of molecular and functional group orientation in a crystal sample.
3. Information that will provide a basis for the accurate calculation of bond angles.

Assignment of Vibrational Modes. There is little question that important information concerning vibrational assignments comes from polarized IR studies. For H bonded substances the dichroism of the ν_s stretching mode usually serves as a reference from which the dichroism of other modes can be predicted. Such arguments have been particularly useful in identifying ν_b and ν_t modes (see Fig. 3-1). Some of the H bonded crystals for which polarized IR studies have been an aid in vibrational assignment are listed in Table 3-XI.

TABLE 3-XI H Bonding Crystals for which IR Dichroism Studies Have Aided Vibrational Assignments

H BONDING GROUP	SUBSTANCE	REFS.	SUBSTANCE	REFS.
Amides	Acetanilide	a, b	Urea	j
	Chloroacetamide	c	Thiourea	j
	Trichloroacetamide	c	*N*-Acetylglycine	k
	Benzamide	c	Acetylglycine-*N*-methylamide	k
	ε-Caprolactam	d	Nylon	l, m, n
	Cyanuric acid	e	Chitin	o
	Diketopiperazine	f, g, h, i	*N*,*N*′-Diacetylhexamethylene-diamine	p
Acids	Benzoic acid	q	Boric acid	s
	Cinnamic acid	q	Oxalic acid·$2H_2O$	r
	α-Succinic acid	q	KH bisphenyl acetate	t
	β-Succinic acid	r	KHF_2	u, v
	Adipic acid	f, q, r		
Phenols	*o*-Nitrophenol	x	2-Nitroresorcinol	x
Amines	*o*-Nitroaniline	x	Ammonium fluoride	w
Alcohols	Pentaerythritol	i	Mica	y
	Polyvinyl alcohol	z	Ice	aa

[a] 4; [b] 463; [c] 1167; [d] 1168; [e] 1501; [f] 37; [g] 1855; [h] 1503; [i] 604; [j] 105; [k] 1430; [l] 38; [m] 595; [n] 590; [o] 473; [p] 1779; [q] 1169; [r] 779; [s] 958; [t] 505; [u] 1101; [v] 1502; [w] 255; [x] 692; [y] 2114; [z] 780; [aa] 2093. See also 1616, 206, 898.

Gross Features of Orientation. There seems to be no reason to doubt that the IR dichroism is informative of gross orientation of molecules and functional groups in crystals. Thus Kuratani was able to conclude that the C═O bond is not parallel to the N—H bond to which it is H bonded in ε-caprolactam (1168). This provides the basis for his proposal of cyclic dimers in the crystal. Francel made dichroic studies of *ortho*-substituted nitrobenzenes and found, for example, that the O—H and NO_2 groups of *o*-nitrophenol are both coplanar with the benzene ring (692). Another study by Kuratani of solid carboxylic acids (α-succinic, benzoic, cinnamic, and adipic acids) revealed qualitatively that the orientations of the H bonds are parallel to the long axes of the needle shaped crystals (1169).

Accurate Angular Orientations. The most interesting but most suspect conclusions drawn from dichroic studies are the estimates of bond angles. Fraser, for example, has studied the dichroism of fibrous protein, and presents quantitative statements about the angles and uncertainties of the transition moment directions of the amide group vibrations (695, 697). He reviews earlier measurements and concludes that the "transition moment directions are not invariant from compound to compound,"—a conclusion reached earlier by Elliott (589). Another of Elliott's studies (with Abbott, 4) reveals that the transition moment of the carbonyl stretching mode is accurately in the plane of the amide group, but it makes an angle of 20–24° to the C═O bond (see also 590). These studies raise questions about earlier work in which dichroic studies were interpreted in terms of bond orientations (using the "oriented gas" assumption). Thus Ambrose, Elliott, and Temple (38) had previously interpreted dichroic studies of nylon in terms of the angle between the N—H bond and the plane of the polymer skeleton. These uncertainties probably apply to the interesting interpretations of dichroic spectra which relate to the position of the hydrogen atom relative to the line connecting the heavy atoms. Several workers have concluded from studies of polarized IR spectra that the A—H···B configuration is not linear (1503, 780, 778, 604). Newman and Badger, for example, conclude that the angle between the N—H and the C—N bonds in the amide group of *N*-acetylglycine is about 100°. They add that the uncertainty does not "admit the possibility that the hydrogen atom lies on a line connecting the [H bonded] nitrogen and oxygen atoms" (which would require an angle of 132°) (1503). (See also 2114.)

We shall conclude this discussion with equivocation. On the one hand, polarized IR spectra of oriented samples surely aid in assignment of vibrational modes and in determination of gross features of orientation. On the other hand, there is ample reason for caution in the detailed quantitative interpretations. Even for the relatively weak crystal forces of naphthalene, deviations from the oriented gas model appear (1636). The stronger forces in H bonded crystals and the anisotropic influence of the H bond on IR absorption coefficients make these crystals much more prone to such deviation. As noted by Huggins and Pimentel (979), the interpretation of the dichroism of stretching modes in terms of bond orientations may be acceptable only for linear H bonds for which the stretching modes are enhanced by the dipole change induced along the bond. In the more usual case, where the linearity of the H bond is not established, it must be recognized that the dipole change may be parallel to the H···B bond. If so, it is not directly indicative of the A—H orientation.

3.4 Other Vibrational Modes

There has been much less study of other modes, such as the A—H bending and torsional vibrations, than of ν_s. Yet, the effects of the H bond on the spectral properties of these vibrations are quite as important as its effects on ν_s. We shall examine what is known about these vibrations in the hope of stimulating further work. Invariably the discussion must deal with two problems: first, the identification of the mode of interest, and second, the effect of the H bond upon it. Since these absorptions fall in the heavily populated "fingerprint" spectral region, seldom is either of these questions easily answered. The literature contains much conflict of opinion.

3.4.1 The In-Plane A—H Bending Mode, ν_b. Study of the in-plane A—H bending mode ν_b (see Fig. 3-1) is complicated by its "mixing" with other vibrational movements. This implies that there may be more than one vibrational mode which involves participation of ν_b, and the result is that spectral changes are neither readily apparent nor readily interpreted. Despite these difficulties, we can make some definite and informative generalizations concerning the effect of H bond formation on ν_b:

1. In-plane hydrogen bending modes fall in the spectral region 1000–1700 cm^{-1}.

2. In-plane bending modes shift *upward* in frequency with H bond formation. These upward shifts are smaller than the downward shifts

of the stretching modes, even when both are expressed on a relative basis, $\Delta\nu/\nu$.

3. While absorption bands of the bending modes may become broader, no striking change in absorption coefficients accompanies H bond formation.

In support of these generalizations, specific examples are presented below, in order of simplicity of interpretation.

Water. The bending mode of water provides a particularly favorable opportunity for study of H bond formation. Among the many reported studies of water as a pure liquid and in various solvents, the systematic work of Greinacher, Lüttke, and Mecke (823) is particularly informative. The data from their spectral measurements for water at high dilution in a variety of bases are collected in Table 3-XII. For comparison, the relative shifts in the stretching mode are also listed (the frequencies refer to the average of the symmetric and antisymmetric modes). It is clear that ν_b shifts progressively upward as the solvent base strength increases, and it is less sensitive than ν_s.

TABLE 3-XII Relative Frequency Shifts of the Stretching and Bending Modes of Water Dissolved in a Variety of Bases

$\Delta\nu = \nu_{\text{gas}} - \nu_{\text{solution}}$[a]

SOLVENT	$\Delta\nu_b/\nu_b$ (gas)	$\Delta\nu_s/\nu_s$ (gas)
(gas)	(0)	(0)
CH_3NO_2	−0.018	+0.021
CH_3CN	− .019	.031
$(CH_3)_2CO$	− .023	.034
Dioxane	− .027	.041
H_2O (liquid)	− .026	.075
Pyridine	− .034	.079
H_2O (crystal)	− .031	.121

[a] 823.

Another study of water which permits examination of the bending mode is the matrix isolation work of Van Thiel, Becker, and Pimentel (2097). Water was suspended in solid nitrogen at 20°K, and absorptions were assigned to dimers, trimers, and higher polymers. In Table 3-XIII, the shifts (referred to monomeric water suspended in solid nitrogen) and approximate band widths are presented.

TABLE 3-XIII Relative Frequency Shifts and Band Widths of Polymers of Water in Solid Nitrogen[a]

$\Delta\nu = \nu_1 - \nu_n$

ν_1 = av. of symmetric ν_s and asymmetric ν_s in monomer.

ν_n = ν_s of polymer of n units.

	$\Delta\nu_b/\nu_b$	$\nu_{b\frac{1}{2}}$ (cm^{-1})	$\Delta\nu_s/\nu_s$	$\nu_{s\frac{1}{2}}$ (cm^{-1})
Monomer	(0)	5	(0)	25
Dimer	−0.013	5	+0.036	25
High polymer	−0.02	35	+0.1	305

[a] 2097.

Perhaps a more interesting aspect of this study is the unique opportunity to examine the absorption coefficients as a function of polymer size. Figure 3-25 is a plot of the total integrated absorption of the stretching and bending modes relative to their values at mole fraction 0.001, presumed to refer to the monomeric state. As the mole fraction of water becomes large, the polymer size is considered to approach infinity. Thus the absorption coefficients of ν_s and ν_b change by factors of about 12 and 0.7, respectively, when the H bond of an infinite polymer is formed.

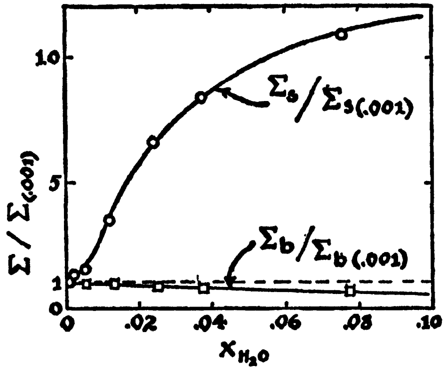

FIGURE 3-25 Total integrated absorption relative to monomeric water in solid nitrogen (2097). Σ_s = total absorption of stretching modes; Σ_b = total absorption of bending mode.

Summarizing, the bending mode of water shifts upward by 10–50 cm^{-1} upon H bond formation, much less than the downward shift observed for ν_s. The intensity of ν_b is lowered slightly, whereas the intensity of ν_s increases by a factor of 12.

Chloroform. The interaction of chloroform with basic solvents is shown in Section 6.2.1 to be of the H bonding type. In anticipation of this discussion, we mention here the intensity behavior of the C—H bending mode. Chloroform is particularly interesting because ν_b is well defined and readily studied. Huggins and Pimentel (980) studied deuterochloroform dissolved in CCl_4, in benzene, and in triethylamine. The chloroform C—D stretching mode in benzene solution is about six times as intense as it is in CCl_4, and in triethylamine about thirty-six times as intense as in CCl_4. In contrast, the absorption coefficient of the bending mode is the same in the basic solvents as in CCl_4. Thus the intensity behavior is the same as that of ν_b of water. The frequency of ν_b shifts, however, only in the stronger bases; e.g., in triethylamine solutions the deuterium stretching mode shifts by a factor of $\Delta\nu_b/\nu_b = -0.030$. Again the behavior is the same in direction as and similar in magnitude to the behavior of water.

Alcohols. The alcohols are an example of a class of substance for which the assignment of ν_b has been difficult and is not yet resolved. Table 3-XIV refers to only a part of the literature on the subject. (For other references, see 2003, 1965, 1151a.)

TABLE 3-XIV Assignments of the Bending Modes, ν_b, of Alcohols

AUTHOR	DATE	ν_b (monomer) (cm^{-1})	ν_b (H bonded) (cm^{-1})	$\Delta\nu_b/\nu_b$	REFS.
Noether	1942	1340	—	—	1519a
Davies	1948	1025	1110	−0.08	485
Thompson	1948	1050–1080	—	—	2022
Barnes *et al.*	1948	1050–1080	—	—	134
Quinan and Wiberley	1954	1010–1035	1020–1045	−0.01	1681 1680
Stuart and Sutherland	1956	1200–1330	1330, 1410	−0.1	1965
Tarte and Deponthière	1957	1240 *and* 1030	—	—	2003

In view of the remaining uncertainty, only the most recent work will be discussed. Stuart and Sutherland (1965), after a thorough study of many aliphatic alcohols, propose that ν_b occurs in the range 1200–1330 cm^{-1} in dilute solution. On the other hand, they find that the pure alcohols exhibit a broad association band which has been overlooked by all earlier workers because of its diffuse character. This broad band, which has two maxima near 1410 and 1330 cm^{-1}, implies a 10 percent shift in ν_b and a band width increase to about 200 cm^{-1} upon H bond formation. Stuart and Sutherland conclude that "the effects of H bonding on the deformation motions of the O—H group are quite complex and that steric effects, rotational isomerism, and interaction with C—H deformation frequencies may all be involved to some extent." The proposal that rotational isomerization plays a role is also suggested by Tarte and Deponthière (2003, 2004). From spectra of deuterated alcohols these workers find evidence that *two bands must be associated with ν_b*. Further work is in progress, but at this writing the assignment and H bond shift in alcohols remain in doubt. (See also 1312, 784.)

Phenols. Kuratani (1166) identified the absorptions involving O—H deformation of pentachlorophenol. Two bands shift on deuteration, and he concluded that 1195 cm^{-1} and 1280 cm^{-1} are coupled vibrations of ν_b(O—H) and ν_s(C—O). The assignments for phenol are in accord, as shown in Table 3-XV. For the H bond shift there is approximate agreement that $\Delta\nu_b/\nu_b$ is in the range of -0.01 to -0.05.

TABLE 3-XV Assignments of the Bending Mode, ν_b, of Phenol

AUTHOR	DATE	ν_b (monomer) (cm^{-1})	ν_b (H bonded) (cm^{-1})	$\Delta\nu_b/\nu_b$	REFS.
Barchewitz *et al.*	1953	1175	1230	−.047	127
		1340	1370	−.022	
Mecke and Rossmy	1955	1175	1211	−.031	1382
		1340	1353	−.010	

Carboxylic Acids. Kuratani (1166) and, independently, Hadži and Sheppard (853) propose that there is a coupling of the in-plane bending mode ν_b and the C—O stretching mode ν_s(C—O). There has been general acceptance of this interpretation (e.g., see 1550, 1073) and the usual ranges quoted are those proposed by Hadži and Sheppard, 1420 ± 20 cm^{-1} and 1300 ± 15 cm^{-1}.

Table 3-XVI presents some of the assignments for these modes in the monomeric and dimeric states. The relative shifts are uniformly high, near 0.1, with the notable exception of that of deuteroformic acid. This deviation cannot be discounted, because the assignments of formic acid are among the least ambiguous. Nevertheless, we can generalize that most workers propose that two vibrations of carboxylic acids involve ν_b and that both of these vibrations move upward in frequency upon H bond formation. The magnitudes of $\Delta\nu_b/\nu_b$ suggest that ν_b may be almost as sensitive to the H bond perturbation as ν_s ($\Delta\nu_s/\nu_s$ for acetic acid is about 0.14, 979). It must be remembered, of course, that

TABLE 3-XVI Assignments of the Bending Mode, ν_b, of Carboxylic Acids

ACID	AUTHOR	DATE	ν_b (monomer) (cm^{-1})	ν_b (H bonded) (cm^{-1})	$\Delta\nu_b/\nu_b$	REFS.
CD_3COOH	Davies	1948	1162	1285	−.106	485
CD_3COOD	Davies	1948	984	1046	−.063	485
60 acids	Flett	1951	—	1210–1320 1400–1440	—	670
CCl_3COOH	Kuratani	1952	—	1210–1320 1400–1440	—	1166
CF_3COOH (gas)	Fuson *et al.*	1952	1130	1203	−.065	734, 1062
CF_3COOD (gas)	Fuson *et al.*	1952	993	1093	−.10	734, 1062
CF_3COOH (gas)	Kagarise	1957	1122	1297	−.16	1073
CX_3COOH	Hadži and Sheppard	1953	—	1300 ± 15 1420 ± 20	—	853
DCOOD (gas)	Millikan and Pitzer	1957	1040	1055	−.014	1411, 1410

the IR data refer only to the asymmetric modes of a cyclic dimer, and the shifts may include some mechanical interaction effects.

Amides. The spectra of amides and *N*-substituted amides characteristically contain three prominent bands near 1700, 1500, and 1250 cm^{-1}. These bands, called, respectively, the amide I, II, and III bands, are considered to involve C=O stretching, C—N stretching, and N—H deformation. The controversy over the assignment of these bands is summarized well by Bellamy (188), and only notable recent contributions will be mentioned.

The amount of N—H deformation in each band is suggested by the factor ν_H/ν_D, where ν_D refers to the corresponding band in the *N*-deuterated compound. For the gas state these shifts are 1.002, 1.074, and 1.356 (1422). The obvious interpretation is that the large deuteration shift of the amide III band identifies it as the deformation mode, ν_b. This conclusion is warranted, however, only after normal coordinate analysis confirms the significance of ν_H/ν_D. Miyazawa, Shimanouchi, and Mizushima have made such calculations, and a portion of their results are presented in Table 3-XVII.[a] The boldface numbers in this table show that ν_b contributes substantially to both the amide II and III bands and that these vibrational modes are best described as characteristic of the C—N—H group. (The large deuteration shift of the amide III band must be attributed to mechanical interactions.)

With this assurance concerning the nature of these absorptions, we can investigate the effect of H bond formation. After extended studies of *N*-substituted amides, Miyazawa *et al.* (1424), summarized their assignments of the three bands. For *N*-methylacetamide in dilute CCl_4 solution they assigned the bands 1700 (I), 1500 (II), and 1260 cm^{-1} (III). For the pure liquid these bands are found to be shifted by values of $\Delta\nu/\nu$ of +0.028 (I), −0.045 (II), and −0.031 (III).

Miyazawa's study of formamide (1419) provides a comparison of gas and liquid phases. His reasonable assignment of the NH_2 deformation mode gives 1572 (gas), 1605 (liquid), and 1610 cm^{-1} (crystal). These

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[a] The description is in terms of the percentage of the potential energy associated with each internal coordinate, the most significant index of the character of a vibration. The numbers given in Table 3-XVII have been normalized by the sum of the contributions from all degrees of freedom. The other degrees of freedom are the N—CH_3 stretch, the O=C—N bend, the C—CH_3 in-plane bend, and the CH_3—N—C bend. The methyl groups were treated as point masses. We are extremely grateful to these authors for their permission to include these important calculations, which, at the time of this writing, are in press in the *Journal of Chemical Physics*.

TABLE 3-XVII The Character of the Amide Bands I, II, and III of *N*-Methylacetamide [Potential Energy Distribution (%) after Miyazawa, Shimanouchi, and Mizushima]

FREQ. AND VIBRATIONAL CHAR.	I	II	III
ν obs. (cm^{-1})	1653	1567	1299
ν calc. (cm^{-1})	1644	1509	1296
C=O stretch, ν_s(C=O)	**69%**	2%	8%
C—N stretch, ν_s(C—N)	9%	**36%**	**32%**
N—H bend, ν_b	8%	**51%**	**27%**
C—CH$_3$ stretch	4%	2%	**20%**
Other degrees of freedom	10%	9%	13%

frequencies give $\Delta\nu_b/\nu_b$ as -0.021 (gas-liquid) and -0.024 (gas-crystal).

According to these assignments, then, the effect of the H bond on the absorptions which include ν_b is a shift upward in frequency by a few percent without pronounced intensity or band width change. (See also 1384.)

3.4.2 The Out-of-Plane A—H Torsional Mode, ν_t**.** In addition to the deformation mode ν_b there are deformation modes for H bonded complexes which arise from torsional motions within the monomeric acid or from lost rotational degrees of freedom of the entire monomeric molecule. This mode, designated ν_t, is shown in Fig. 3-1.[a] Certain generalizations can be made concerning this mode and the effect of H bond formation:

1. This absorption occurs in the region below 800 cm^{-1} in H bonded liquids and solids. The spectral changes in ν_t caused by H bond formation are in some cases as spectacular as those occurring for ν_s. The frequency shifts upward, the intensity is high, and the band width increases.

2. The corresponding absorptions of monomeric species have been observed in only a few cases. This is because the mode absorbs in a low frequency region where experimental difficulties inhibit study.

3. The importance of definite identification of these modes stems from the interest in the energy change implied by deviation from a linear H bond configuration.

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[a] This mode is sometimes designated γ. It is called a "librational" mode when the torsional mode of the solid arises from a rotational degree of freedom of the gaseous molecule.

Water. Giguère and Harvey published an excellent summary of the many IR and Raman studies of liquid and solid H_2O and D_2O (757). (See also 1095, 1535a.) Values obtained by both methods, ranging from 450 to 780 cm^{-1}, have been reported for the "librational" motion of liquid H_2O and ice. Giguère and Harvey remeasured this absorption and found the values quoted in Table 3-XVIII. The band is broad [$\nu_{t\frac{1}{2}} = 150$ cm^{-1} (unpublished spectrum of ice by Zimmermann and Pimentel)] and more intense than the 1600 cm^{-1} bending mode in both liquid and solid phases. For liquid water the band width seems to be affected by the method of study. Plyler and Acquista (1650) reported that a film estimated to be 0.005 mm thick absorbed over the entire spectral region from 800 to 250 cm^{-1}. The spectra of Giguère, *et al.* (757), for which the sample is thought to be present in minute droplets, suggest a band width of 200–300 cm^{-1} at 9°C. We may note further that that Vanderberg and Ellis proposed three forms of ice, using IR techniques (2093).

TABLE 3-XVIII IR Absorption of Liquid and Solid H_2O and D_2O in the Region 500–900 cm^{-1}

	LIQUID	CRYSTAL		
	10°C	−15°C	−55°C	−170°C
H_2O	710	800	820	850
D_2O	530	590	610	630

The results in Table 3-XVIII merit special interest. It is clear that the vibration is a property solely of the H bonded species, because of the unequivocal rotational or translational "parentage" of the degree of freedom. The similar frequencies in liquid and solid suggest a similarity of movement and potential that might not have been expected in view of the regular packing of the lattice and the local disorder and range of bond angles that could exist in the liquid. This might well be evidence of ice-like local order in liquid water, as was assumed long ago by Bernal and Fowler (199), and later by Magat in his attempt to calculate the low frequency vibrations in liquid water (1319).

On the other hand, the change in the ν_t frequency which accompanies solidification of liquid water was considered by Giguère and Harvey (757) as indicating "a tightening of the H bonds (shortening of the $OH\cdots O$ distance)." This proposal draws attention to the possibility that the temperature dependence of ν_t of ice can be correlated with change in the lattice parameters of ice. The review by Lonsdale (1257a) reveals a systematic change in the O····O distance from 2.765 Å at 0°C to 2.741 Å at −180°C. This 1 percent reduction in the H bond length in ice is accompanied by a 5 percent increase in ν_t.[a]

Finally, it is interesting to contrast the absorption near 800 cm^{-1} with the bending mode of water near 1600 cm^{-1}. The lower frequency absorption is the more intense in both liquid and solid. More important is the frequency shift of the bending mode on H bonding, which is only about 35 cm^{-1}. This shift is presumably indicative of the additional force constant tending to maintain the H bond in a linear orientation, the same force constant presumed to give rise to the 800 cm^{-1} absorption. On the basis of the assignment of the 800 cm^{-1} absorption to a torsional or a librational movement [as suggested by Ellis (601), Cartwright (356), and Magat (1319)], we estimate that the ν_b mode should shift upward about 150 cm^{-1}. The implications of this discrepancy, the much higher intensity of ν_t over ν_b, and the extreme band width of ν_t are not yet clear, thus leaving interesting questions yet to be answered.

Ammonia. Ammonia is second in importance to water as a possible source of information about torsional modes. The molecule is sufficiently simple to encourage the hope that the spectra may be well understood. On the basis of Raman and IR studies of solid NH_3 and ND_3, Reding and Hornig assigned the NH_3 frequencies 362 and 284 cm^{-1} as fundamental torsional modes, and 53 cm^{-1} to a "parallel torsional oscillation in the lattice or translational lattice vibration" (1701, 1700, 1699). It seems necessary to select the torsion assignment in view of the deuterium isotope shift, 1.29. The higher frequencies are to be compared to the 820 cm^{-1} absorption of ice. They imply that the force constant for deformation of the ammonia H bond may be as much as a factor of ten less per H bond than the similar force constant of H_2O. This result, if correct, suggests that the potential function for torsional movement is extremely sensitive to the strength of the H bond.

Hydrogen Halides. Of several spectral studies of the solid hydrogen halides, only the work of Hornig *et al.* seems to give information concerning the torsional modes (957, 956a). The data for HCl have received the most attention. Hornig and Osberg assign absorptions at 2991 and 3171 cm^{-1} to combinations involving, respectively, "lattice frequencies

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[a] Zimmermann and Pimentel have calculated from ν_t the force constant which resists bending of the H bond, and have found a value of 0.09 · 10^{-11} dyne-cm (R. Zimmermann and G. C. Pimentel, in press). This force constant corresponds to that assigned to ν_β of formic acid, 0.03 · 10^{-11} dyne-cm (see Section 3.4.3).

(probably largely torsional) near 266 cm^{-1} and 446 cm^{-1}." This is only after discard of the observed low frequency absorptions of solid HCl (at 650, 496, and 315 cm^{-1}) because of their low intensities. Despite the doubt remaining in the assignment, this case is interesting because the results have been expressed in terms of force constants. Hornig and Osberg calculate torsional force constants in the range $0.03–0.04 \cdot 10^5$ dynes/cm.

Ammonium Salts. The IR spectra of solid NH_4Cl and NH_4Br (phases II and III) were carefully examined by Wagner and Hornig (2130, 2129). For each compound a combination involving the well characterized, triply degenerate bending mode (near 1400 cm^{-1}) indicates the existence of a low frequency mode. This vibration, assigned as the lattice torsion, is located at 390 cm^{-1} for NH_4Cl (phase III) and at 319 cm^{-1} for NH_4Br. Analogous combinations in the spectra of the deuterated compounds yield frequencies of 280 cm^{-1} for ND_4Cl and 230 cm^{-1} for ND_4Br. The same combination was found by Dows, Whittle, and Pimentel in the spectrum of solid ammonium azide, identifying the corresponding low frequency motion at 420 ± 20 cm^{-1} (550). Dows *et al.* note that "the relative magnitudes of the frequencies of these three alleged torsional modes . . . are qualitatively consistent with the H bond energies as inferred from the frequencies of the N—H stretching motions." Wagner and Hornig show that these values can be accounted for with a purely electrostatic potential function (2130).

Alcohols. The vibrational mode, ν_t, in which the hydrogen atom moves out of the C—O—H plane, derives from a hindered rotation of the O—H group in the gaseous molecule. This vibration has a mean frequency of about 225 cm^{-1} for gaseous CH_3OH (1965, 324).

Liquid alcohols display an extremely broad absorption near 650 cm^{-1} (half-width 200–300 cm^{-1}). Stuart and Sutherland recognized the importance of this band and have attributed it to the hindered rotation perturbed by the formation of the H bond (1967, 1966). They find this band centered at 670 cm^{-1} for pure liquid methanol, and at 475 cm^{-1} for methanol-*d*. The ratio of these frequencies, 1.41, is characteristic of a motion dominated by hydrogen atom movement. The band is present in CCl_4 and CS_2 solutions of methanol at concentrations above 1 M and is very much weaker at concentrations below 0.1 M. In spectra of dilute solutions, the absorption is presumed to shift below the limit of observation, to about 350 cm^{-1}. The over-all spectral behavior is as striking and unusual as that of the stretching mode, ν_s, as shown in Fig. 3-26. In sharp contrast are the relatively minor spectral

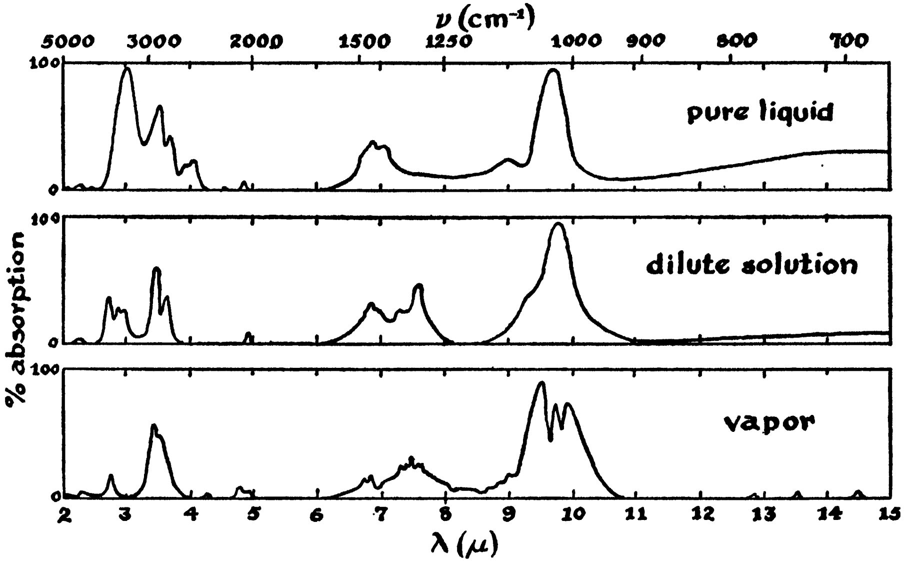

FIGURE 3-26 Spectra of methanol liquid, dilute solution, and vapor. Dilute solution, 0.1 M in CCl_4 or CS_2. [From Stuart and Sutherland, *J. Chem. Phys.* **24,** 561 (1956).]

changes in the region 1000–1500 cm^{-1}, the region containing the in-plane deformation mode.

Some interesting comparisons between the bands assigned to the ν_t and ν_s modes are presented in Table 3-XIX for both methanol and water. The similarity of behavior is evident except for the uncertainty remaining in the behavior of ν_b. The extreme band widths and high frequency shifts of ν_t and ν_s suggest that their behaviors have a common origin. Surely, continued study of the broad bands assigned to ν_t will be rewarding.

TABLE 3-XIX Comparison of H Bond Perturbations of ν_s, ν_b, and ν_t Modes of Methanol and Water

COMPOUND	SPECTRAL PROPERTY	ν_s	ν_b	ν_t
CH_3OH	$\Delta\nu$ (cm^{-1})	285[a]	?[b]	−445[c]
	$\nu_{1/2}$ (cm^{-1})	210[a]	?[b]	~200[c]
H_2O	$\Delta\nu$ (cm^{-1})	275[d]	−42[d]	−710[e]
	$\nu_{1/2}$ (cm^{-1})	365[f]	35[f]	~250[e]

[a] 979; [b] See discussion of ν_b of alcohols, Section 3.4.1; [c] 1967; [d] 823; [e] 757; [f] 2097.

Amides. Kessler and Sutherland (1099, 1098) noted broad absorption extending from 800 cm^{-1} to beyond 650 cm^{-1} as a characteristic feature of the IR spectra of proteins, nylon, synthetic polypeptides, and *N*-mono-substituted amides. They present three types of evidence which, together, show that this absorption is associated with the out-of-plane N—H bending mode, ν_t, in the H bonded species: (1) deuteration shows that the absorption is due to a hydrogen vibration; (2) dichroism for stretched nylon shows that the vibration is an out-of-plane mode, i.e., that the motion of the hydrogen atom is perpendicular to the plane of the peptide group; (3) dilution studies of CS_2 solutions show that the absorption is caused by associated species. Kessler and Sutherland conclude that "the width and diffuseness of the 700 cm^{-1} absorption is presumably due to H bonding." Although these workers were unable to locate a corresponding band attributable to the unbonded species, their evidence concerning the identification of ν_t is convincing.

The effect of the H bond on ν_t is shown in the IR studies by Miyazawa of *N*-substituted amides (1420, 1421). The paper by Miyazawa, Shimanouchi, and Mizushima (1424) summarizes their assignments for a number of these amides. Table 3-XX lists a portion of their data pertaining to ν_t, the out-of-plane N—H deformation [which they designate as amide V or π(N—H)].

TABLE 3-XX The Out-of-Plane N—H Deformation in *N*-Methylacetamide[a]

STATE	ν_t (N—H)	$\Delta\nu_t/\nu_t$
dilute solution	648 cm^{-1}	—
liquid	725	−0.12
crystal, +15°C[b]	745	−0.15
crystal, −60°C	790	−0.22

[a] 1424; [b] *N*-methylacetamide crystal has a transition at +10°C.

In the spectra of liquid *N*-methylacetamide and liquid *N*-ethylacetamide the absorptions near 710–725 cm^{-1} display band widths of about 50–75 cm^{-1}. These observations are consistent with the interpretations of Kessler and Sutherland except that the latter authors did not locate the absorption at 648 cm^{-1} in dilute solution spectra.

In conclusion, the assignment of the out-of-plane hydrogen motion of H bonded *N*-substituted amides seems to be reliable. The effects of the H bond on this mode include a large shift toward higher frequencies and some broadening of the band. Furthermore, the increase in frequency of ν_t of the solid as temperature is lowered is quite similar to the behavior of ice (see Table 3-XVIII).

Other workers who have studied low frequency N—H vibrations include DeGraaf and Sutherland (*N*-methylformamide, 513), Vrazovskiĭ and Gunder (acetamide, 2078), Mecke and Mecke (peptides and thiopeptides, 1384), Kuratani (chloro- and trichloroacetamide, 1167).

Carboxylic Acids. The out-of-plane O—H deformation modes, ν_t, of carboxylic acids have also been the subject of much controversy (e.g., for some assignments that disagree with the following discussion see 485, 734). Flett (670) examined the spectra of 60 carboxylic acids in the liquid or solid phase and noted that 43 of them absorbed in the region 900–940 cm^{-1}. Hadži and Sheppard (853) provided the key to present views on the ν_t assignment by identifying this broad absorption as the out-of-plane O—H deformation (935 ± 15 cm^{-1}).

Formic acid, the most thoroughly studied example, will be considered in detail. The assignments of this deformation in the monomeric form, where it is called a torsion, are well summarized and criticized by Millikan (1411). On the basis of this literature survey and their own spectra, Millikan and Pitzer make the assignments given in Table 3-XXI. The microwave studies of Lerner, Dailey, and Friend (1213) lead to an independent estimate of $\nu_t = 667$ cm^{-1} for monomeric HCOOH, confirming this assignment. Further, Millikan's studies of the pressure and temperature effects on the spectra of gaseous formic acid make his assignments the most reliable available for the IR-active torsional modes in the cyclic dimer. These also are shown in Table 3-XXI. Millikan poetically describes the band attributed to the dimeric

TABLE 3-XXI The Out-of-Plane O—H Deformations of Formic Acid[a]

SPECIES	HCOOH	DCOOD	HCOOD
Monomer	636 cm^{-1}	489 cm^{-1}	512 cm^{-1}
Dimer: IR active	917	675	695
R active	981	—	—
$\Delta\nu$	−281	−186	−183
$\Delta\nu/\nu$	−0.44	−0.38	−0.36

[a] 1410, 1411.

torsion: "it is relatively broad and exhibits a pleasantly rounded top devoid of fine structure."

The values of $\Delta\nu_t/\nu_t$ listed in Table 3-XXI (based on the IR-active component) average -0.39. Thus the effect of the H bond on this deformation mode is to broaden it and shift it upward in frequency by 40 percent.

3.4.3 The Hydrogen Bond Stretching and Bending Modes, ν_σ and ν_β. When two molecules form a H bonded complex, three translational and three rotational degrees of freedom become vibrational degrees of freedom of the complex. Of these, one involves stretching of the A····B bond, designated ν_σ; the other five are called deformations because each involves some sort of orientational change with respect to the H bond. If a cyclic dimer is formed, involving two H bonds, there are two degrees of freedom associated with stretching of the A····B bond, and only four deformation modes.

Of all the vibrational degrees of freedom of H bonded polymers, the ν_σ and ν_β are the most interesting. Their force constants are indicative of the potential function which determines the length and angular orientation of the H bond. These force constants, if known, could be used to estimate the degree to which a H bond can be distorted to accommodate other geometrical parameters in an *intra*molecular H bond (e.g., in a protein). Finally, because these vibrations are the lowest in frequency, they provide an important contribution to the entropy of polymer formation.

Unfortunately these vibrations are difficult to study because they are so low in frequency, and they may be diffuse or complex because of thermal excitation. There are few IR data available. There is quite a bit of pertinent Raman work, much of it performed by Russian workers, notably Batuev, Chulanovskiĭ, Gross, Raskin, Sechkarev, Simova, Skiripov, and Val'kov. The most thoroughly studied compounds are the carboxylic acids and water.

Formic Acid. In 1938 Davies and Sutherland predicted that the H bond stretching mode ν_σ would be very low and proposed that the band width of ν_s is due to "slow vibrations of one-half of the dimer with respect to the other." (500). J. O. Halford (856) gives reference to three Raman studies of liquid formic acid which reveal a shift near 200 cm^{-1}, and speculates that this might be caused by the symmetric ν_σ mode of a cyclic dimer. He shows by entropy arguments that this frequency is reasonable. Further examination by Simova (1884, 1883), and particularly by Gross and Val'kov (830), revealed Raman shifts of 255, 234, 212, 194, 180, 170, 140, 117, 82, and 57 cm^{-1}. At least the first six of these frequencies are assigned by Gross and Val'kov to the strongly anharmonic O····O symmetric stretching mode ν_σ. Bonner and Smith (243) record a Raman shift at 232 cm^{-1} in the spectrum of gaseous formic acid.

Slutsky and Bauer (1893) repeated the calculations of Halford, but used what seems to be an unreasonably high estimate of the bending force constant of the H bond. They calculate 172 and 124 cm^{-1} for the symmetric and asymmetric stretching modes, ν_σ, of the formic acid dimer.

The studies of Millikan and Pitzer (1411) and, later, of Miyazawa and Pitzer (1423a) are perhaps the most reliable. They examined the IR spectrum of gaseous formic acid vapor in the spectral region 400–150 cm^{-1} and discovered an intense absorption at 237 cm^{-1}. This absorption is assigned as the asymmetric stretching mode, ν_σ, and the Raman shift at 232 cm^{-1} (243) is assigned as the symmetric mode. These bands are probably correctly assigned, and they provide the best reference point available concerning the low frequency vibrations of the H bond. The frequencies confirm Halford's early estimate of the H bond stretching force constant, $0.4 \cdot 10^5$ dynes/cm. The remaining four vibrations are ring distortion modes, ν_β, and Miyazawa and Pitzer have calculated them on the basis of a "rigid monomer" model (1423a). The calculated frequencies are 243, 160, 103, and 60 cm^{-1}—frequencies which account for the entropy. The normal coordinate analysis yields a H bond stretching force constant of $0.33 \cdot 10^5$ dynes/cm and a bending force constant near $0.03 \cdot 10^{-11}$ dyne-cm. Miyazawa and Pitzer note that each of these force constants is about 5 percent of the corresponding force constant of the monomer: the O—H stretching force constant and the C—O—H bending force constant, respectively.

Other Carboxylic Acids. The low frequency modes of acetic acid and higher carboxylic acids are not as well understood as those of formic acid, and will not be discussed in detail. Raman shifts are reported for solid benzoic acid at 190 and 400 cm^{-1} (1693, 1694) and for solid tartaric acid at 52, 80, 101, 115, 144, and 164 cm^{-1} (1891, 1695). Gross and Val'kov conclude that the frequency of the O—H···O vibration is near 200 cm^{-1} and is unchanged either by deuterium substitution or by increase in the mass of the attached alkyl groups (830). Batuev's studies seem to be in disagreement with this conclusion (162, 163).

Further inferences about the ν_σ modes are drawn by several workers from spacings identified in the ν_8 band. These are listed in Table 3-VIII, and the inconsistency of conclusions reached by different authors is evident. The low frequency modes of acetic acid have been deduced from entropy calculations (856, 1893), but doubt is thrown on these estimates by Millikan and Pitzer's similar estimates for formic acid.

H_2O. The low frequency modes of water have been studied by many workers. Summaries of the Raman studies are given by Hibben (up to the year 1939) (916), and more recently by Giguère and Harvey (757) who tabulate the earlier data. (See also 1535a.) The results for absorptions below 1000 cm^{-1} are summarized in Table 3-XXII. The band near 800 cm^{-1} has been discussed in Section 3.4.2.

TABLE 3-XXII Summary of IR and Raman Spectra of H_2O and D_2O[a]

H_2O or D_2O	PHASE	IR or R	ν (cm^{-1})					
H_2O	Solid	IR			160 (1)			800 (1)
H_2O	Solid	R	53 (2)		212 (6)	260–292 (2)		601 (1)[b]
H_2O	Liquid	IR			160 (1)			500 (1)
								650 (2)
								710 (1)
H_2O	Liquid	R	60 (2)		145 (1)		440 (1)	
					175 (4)	300 (1)	500 (4)	760 (3)
					200 (1)			
D_2O	Solid	IR						590 (1)
D_2O	Solid	R		166,	203 (sh)[c]	218		
				236,	256, 275[d]			
D_2O	Liquid	IR			170 (2)		350 (2)	500 (3)
D_2O	Liquid	R	60 (1)	123 (1)	175 (3)		375 (2)	500 (1)
					190 (1)			

[a] For references, see 757. Above, numbers of observers are in parentheses; [b] 2087; [c] sh = sharp; [d] 828.

Distinct bands appear in the Raman spectra of H_2O (solid) and D_2O (solid) at 212 and 203 cm^{-1}, respectively. These are in the appropriate ratio for translational movements of the entire molecule and have been so assigned [see, for example, Cross, Burnham, and Leighton (465), and Gross and Val'kov (828)]. Furthermore, Blue made calculations of the heat capacity of ice which tend to corroborate that interpretation (234). In the Raman spectra of the liquid state there are corresponding absorptions at 175 cm^{-1} for both H_2O and D_2O. Cartwright found a broad IR absorption near 160 cm^{-1} for H_2O ice (356).[a] There is agreement that these absorptions are associated with translational modes (356, 1319, 465, 831).

The absorptions just described seem to be correctly identified as the stretching modes, ν_σ, of the H bond between water molecules. Assuming the simplest possible model, that ν_σ is equivalent to the vibration of a diatomic molecule with atoms of mass 18, the absorption at 212 cm^{-1} corresponds to a force constant of $0.2 \cdot 10^5$ dynes/cm. This is in acceptable accord with the value obtained for formic acid ($0.3 \cdot 10^5$ dynes/cm).

Uncertainty in the reality of the Raman shifts near 60 cm^{-1} makes it unfruitful to speculate about their assignment. Some of the higher absorptions have been considered to be overtones of ν_σ (e.g., 300 and 500 cm^{-1} of liquid water, 350 and 500 cm^{-1} of liquid D_2O) (831).

Other Substances. The ν_σ and ν_β modes of other H bonding substances are not as well understood. Raskin and Sechkarev (1694), for example, note that the Raman spectra of benzoic acid, benzyl chloride, and methyl benzoate, have similar absorptions in the frequency range 150–250 cm^{-1}, and conclude that the 197 cm^{-1} absorption of benzoic acid probably has an *intra*molecular origin. Nevertheless, low frequency Raman shifts of a number of molecules have been attributed to H bond stretching vibrations. For example, according to Hornig and Osberg, the force constant connecting H bonded molecules of HCl in the solid state is $0.035 \cdot 10^5$ dynes/cm (957). Similarly, Chapelle calculates from the elastic constants of $(NH_4)H_2PO_4$ the bonding constant for ν_σ of O—H···O to be $0.230 \cdot 10^5$ dynes/cm (366).

Other substances whose Raman spectra have been interpreted in terms of the ν_σ modes are listed in Table 3-XXIII.

3.4.4 Vibrations of the Base. The effects of H bond formation on vibrations not involving the H bonding proton tend to be smaller than those already discussed. Nevertheless there are well substantiated spectral changes in the base B when it participates in a H bond A—H···B. These changes are sometimes called "solvent effects," but it is clear that they accompany H bond formation and are distinguish-

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[a] Zimmermann and Pimentel have examined the IR spectrum of carefully annealed ice in the spectral region 200–1600 cm^{-1}. They have discovered a previously unreported absorption near 220 cm^{-1}. (R. Zimmermann and G. C. Pimentel, in press.)

TABLE 3-XXIII Low Frequency Absorptions Attributed to H Bond Stretching Modes

SUBSTANCE	STATE	FREQUENCIES	REFS.
NH_3	Solid	53 cm^{-1} "possibly translational lattice vibration"	1700
ND_3	Solid	41 cm^{-1}	1701
Resorcinol	—	Below 120 cm^{-1}	1656
Benzoic acid	Solid	—	1656
Phenol	Solid	155–195 cm^{-1}	1656
Trichloroacetic acid	—	—	1656
KH_2PO_4	Solid	95, 118 cm^{-1}: lattice frequencies	367
$NH_4H_2PO_4$	Solid	68, 97, 127, 175, 280 cm^{-1}: lattice frequencies	367
CH_3OH	Liquid	235, 264, and 295 cm^{-1}	1884
Formic acid	Solid	—	830

able from more general solvent perturbations. These H bond shifts will be discussed according to base types.

Carboxylic Acids. Most of the data relating to H bond effects in the base refer to carbonyl systems. The reason is evidently the easy detection and identification of the C=O stretching mode. In his 1938 review, Sutherland correctly deduced that the C=O stretching mode, ν_s(C=O), is shifted to lower frequencies on H bond formation without change in band width (1975). With the exception of the first example cited below, we will review only work of the last decade. (For reviews of earlier work, see 1975, 1095.)

One of the early efforts at a systematic study of carbonyl systems in acid solvents has historical importance. Murty and Seshadri published a series of papers describing their Raman investigations of solutions of carbonyl compounds in various solvents (1471–1476). Among the carbonyl bases were esters, aldehydes, and carboxylic acids. The solvents included phenol, various alcohols, water, chloroform, ethers, and carbon tetrachloride.

Some more recent data are collected in Table 3-XXIV.

The carboxylic acid carbonyl frequency is shifted to lower frequency by 1 to 6 percent in carboxylic acid dimers, which is much less than the relative shifts of ν_s. The mechanical splitting of the symmetric and antisymmetric carbonyl stretching modes is evident in the difference between the Raman and IR spectra of formic acid. Of course the average of these two is of interest, but often only one is measured.

TABLE 3-XXIV The Effect of the H Bond on the Carbonyl Stretching Mode of Carboxylic Acids

COMPOUND	STATE	IR OR R	$\Delta\nu_s(CO)/\nu(CO)$	$\Delta\nu_s/\nu_s$	REFS.
HCOOH	Gas	IR	+.008	+.127	1411
		R	+.055	+.101	
HCOOH	Crystal	IR	+.038	+.238	1411, 373
		R	+.091	—	
CH_3COOH	CCl_4 solution	IR	+.038	+.144	500, 979
CCl_3COOH	CCl_4 solution	IR	+.019	+.131	734, 880
CF_3COOH	CCl_4 solution	IR	+.013	+.127	734
CF_3COOH	Gas	IR	+.021	+.163	734

Thus, to decide what the trend in $\Delta\nu_s(C{=}O)/\nu_s(C{=}O)$ means in the series CH_3COOH, CCl_3COOH, and CF_3COOH, it is necessary to assume a parallel shift of the symmetric mode.

The intensity behavior of $\nu_s(C{=}O)$ was studied by Wenograd and Spurr (2157). Their measurements of the integrated carbonyl absorptions of monomeric and dimeric acids in the IR spectra are conveniently expressed in terms of the ratios of the absorption of dimer to that of monomer. These ratios are: for acetic acid, 1.15; propionic acid, 1.36; benzoic acid, 1.22; and toluic acid, 1.32. The corresponding ratios for the O—H stretching mode are an order of magnitude larger, in the range 10 (2157) to 35 (979).

The frequency and intensity behaviors of the carbonyl stretching mode are in interesting contrast to the corresponding changes in the O—H stretching mode. Although the H bond causes shifts in the same direction, to smaller frequencies, the carbonyl shifts are much less, even on a relative basis. Nevertheless, it is clear that the shifts correlate roughly in magnitude; the value of $\Delta\nu_s/\nu_s$ is about five to ten times as large as $\Delta\nu_s(C{=}O)/\nu_s(C{=}O)$. Finally, the very large enhancement of the intensity of the hydroxyl stretching mode is not shown in the carbonyl mode.[a]

Ketones. Ketones have been studied systematically by many workers[b], and not all of this work will be described. The shifts brought on by H bonding solvents are only a little larger than those attributed to less specific solvent effects. This has led some workers to ignore H bond formation (175). Josien and co-workers made extensive studies of the

[a] Other studies of the carboxylic acids are: 1022, 1095, 637, 1883, 164, 1475, 1472, 1471.
[b] 1288, 2052, 384, 1063, 175, 140, 1064, 1678, 1970, 1971.

vapor-solvent frequency shift and its dependence on refractive index (1064, 1063). Their plots of $(n^2 - 1)/(2n^2 + 1)$ *vs.* $\Delta\nu/\nu$ reveal deviations whenever H bonding can occur. Table 3-XXV summarizes their IR measurements for acetone, the solvents being listed in order of increasing values of $(n^2 - 1)/(2n^2 + 1)$. Their calculated values of $\Delta\nu_s(C{=}O)/\nu_s(C{=}O)$, referred to the gas phase, distinguish the solvents which might act as H bonding acids (shown in boldface type). In the fifth column the H bond interaction is even more distinctive in terms of the more conventional calculation of $\Delta\nu$ referred to an "inert solvent," hexane.

Of equal interest are the intensities measured by Bayliss *et al.* (175), some of which are listed in the last column of Table 3-XXV. They are expressed relative to the absorption in hexane solvent. Again the H bonding solvents cause an unusual enhancement of absorption coefficient. No band width increase is noted. (See also 2052.)

The Raman studies of Puranik (1678) are of particular value because he has investigated the effect of H bonding on the C—C (788 cm^{-1}) and C—H (2925 cm^{-1}) stretching modes of acetone as well as $\nu_s(C{=}O)$. He finds that decrease in the carbonyl mode is always accompanied by increase in the C—C stretching mode. The effect is largest for the solvent water, for which $\Delta\nu/\nu$ is found to be $+.008$ to $+.016$ for $\nu_s(C{=}O)$; $-.016$ for $\nu_s(C{-}C)$; and $-.003$ for $\nu_s(C{-}H)$. A range of the relative shift is quoted for $\nu_s(CO)$, the lower limit referring to pure acetone, the same reference used for the other two modes. The upper limit is the value appropriate to hexane as a reference solvent (384). (See also 207, 1151.)

Aldehydes, Esters, and Amides. Recent studies of $\nu_s(C{=}O)$ of aldehydes, esters, and amides, give results consistent with those described for ketones. H bonding causes a downward frequency shift of a few percent, and a slight enhancement of the intensity. Only a few examples will be discussed.

Puranik includes in his Raman studies the solution systems benzaldehyde-phenol and ester-phenol. In the former case, the 14 cm^{-1} decrease in $\nu_s(C{=}O)$ caused by diluting benzaldehyde with phenol is accompanied by a 7 cm^{-1} increase in $\nu_s(C{-}C)$ (at 1197 cm^{-1}) (1679). Puranik notes that the corresponding shifts of these two modes are observed for *ortho*-substituted aldehydes, such as salicylaldehyde. In the study of the spectral changes brought on by adding phenol to three esters, Puranik found the 23–29 cm^{-1} decrease in $\nu_s(C{=}O)$ to be accompanied by a 17–25 cm^{-1} increase in $\nu_s(C{=}O)$ (1677).

TABLE 3-XXV Effect of H Bonding on the C=O Stretching Mode of Acetone

SOLVENT	$(n^2 - 1)/(2n^2 + 1)$[a]	$\nu_s(C{=}O)$[a] (cm^{-1})	$\Delta\nu_s(C{=}O)/\nu_s(C{=}O)$[a]	$\nu_{hex} - \nu$	A/A_{hex}[b]
Vapor		1740	(0)	−17	—
Liquid	$18 \cdot 10^{-2}$	1716	$138 \cdot 10^{-4}$	7	—
C_2H_5OH	18	1709	**178**	**14**	—
Ethyl ether	18	1721	109	2	1.10
Hexane	19	1723	98	(0)	(1.00)
CH_2Cl_2	20	1713	**155**	**10**	
$CHCl_3$	21	1712	**161**	**11**	**1.57**
1,2-$C_2H_4Cl_2$	21	1714	**149**	**9**	
CCl_4	22	1719	120	4	1.25
C_6H_6	23	1716	138	7	1.25
Toluene	23	1719	121	4	
$CHBr_3$	25	1708	**184**	**15**	**1.69**
CS_2	26	1717	132	6	1.07

[a] 1063; [b] 175.

The effects of H bonding on the IR spectra of esters, lactones, ketones, aldehydes, and one amide (acetanilide) have been studied by Barrow *et al.* (1824, 140). Carbonyl frequencies are compared in the solvents CCl_4, $CHCl_3$, and CH_3OH, and the acidic solvents shift ν_s(C═O) downward by 5–15 cm^{-1}. The intensities are compared in the solvents CCl_4 and $CHCl_3$ and the ν_s(C═O) absorption coefficient is roughly 20 percent higher in chloroform for four ketones, two aldehydes, eight esters, acetyl chloride, and acetanilide (140).

Bellamy cites the examples *o*-, *m*-, and *p*-hydroxybenzaldehyde, demonstrating that the shift of ν_s(C═O) accompanies *intra*molecular H bonding as well (188). (See also 835, 1717, 802, 1117, 635, 2078.)

The studies by Miyazawa, Shimanouchi, and Mizushima (1422, 1424) have already been mentioned in the discussion of ν_b, the in-plane N—H bending mode. The amide I band, a carbonyl stretching mode, shifts downward with $\Delta\nu/\nu = +0.028$, whereas the amide II band, a mixture of ν_s(CN) and ν_b(NH), shifts upward with $\Delta\nu/\nu = -0.045$. Although this upward shift is in the direction expected for ν_b, Mizushima *et al.* feel that the shift should be attributed in part to double bond character induced in the C—N bond when the H bond is formed.[a]

Alcohols. As mentioned in the discussion of the hydrogen deformation mode of alcohols, ν_b, the assignment of some fundamental modes of alcohols is still uncertain. The C—O stretching mode is generally assigned to the rather intense absorption between 1000 and 1070 cm^{-1}, but this mode may involve significant O—H bending movement as well. Nevertheless, the conclusion reached by several workers is that the C—O stretching mode is significantly affected by H bond formation, shifting to lower frequencies and broadening somewhat. Rao, using Raman technique, noted that the ν_s(C—O) of methanol, ethanol, and phenol are shifted to lower frequencies in acetone (1687). This shows that the shift occurs as the alcohol acts as an acid. Chulanovskiĭ (383) assigns the broad infrared absorption at 1034 cm^{-1} to ν_s(C—O) of pure (H bonded) methanol, and the sharp absorption at 1118 cm^{-1} to unassociated molecules. He notes that $\Delta\nu_s(\text{C—O})/\nu_s(\text{C—O})$ is as large for ν_s(C—O) as for ν_s in methanol (+0.078 and +0.074, respectively). Chulanovskiĭ also speculates that two types of H bonded methanol molecules are distinguishable through structure in the 1034 cm^{-1} absorption: terminal methanol molecules for which the O—H

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[a] Private communication with Dr. T. Miyazawa.

group acts only as an acid, and polymeric molecules in which the O—H group acts as a base.

Stuart and Sutherland (1965) independently make essentially the same assignment as Chulanovskiĭ. They assign for a number of primary and secondary alcohols the monomeric ν_s(C—O) at 1110 cm^{-1} (sharp) and the associated alcohol ν_s(C—O) at 1080 cm^{-1} (broad). This gives a relative shift of +0.027. The corresponding assignments differ for tertiary alcohols. (See also 1489.)

Other Systems. The effect of H bonding on other vibrational modes of the acid or base have been studied for a few other systems: pyrrole-acetone (2061); dioxane-water (634); phenol (1540).

3.5 Summary

The very large volume of research study of the IR and Raman spectra of H bonded substances is justified by the magnitude and the significance of the spectral perturbations. The most obvious importance of these changes, which are summarized in outline form in Section 3.1.3, has been repeatedly emphasized: the spectral effects provide a criterion of H bonding which indicates specifically the role of the proton in the associative interaction.

Less widely recognized, however, is the importance of these changes as clues to the nature of the H bond interaction. The frequency behavior is indicative of the potential function maintaining the equilibrium configuration, and the intensity behavior shows the charge movement accompanying distortion of this configuration. One of the most interesting problems of the day is the deduction and prediction of structural configurations of H bonded substances of biological importance. Surely more complete information concerning the energetics of H bond formation will aid in these predictions, and the understanding of the vibrational behavior can furnish such information. The low frequency modes, designated ν_β and ν_σ, are probably the most useful, but, unfortunately, these are, as yet, the least studied.

The literature of the technique is rapidly increasing, an indication of growing importance of spectral studies of H bonding systems. Probably the most appropriate conclusion to a discussion of this extremely active and well developed field is to remark that much remains to be learned.

CHAPTER 4

Methods of Detection: Other Spectroscopic Techniques

> *The absorption spectrum of phenol was measured in various . . . mixed solvents. . . . With increasing concentration of dioxane . . . [a] new absorption . . . appears . . . which seems to be due to hydrogen bridged phenol molecules. . . . the anomalous phenomenon . . . is attributable to H bonding between solute and proton acceptor molecules.*[a]
>
> S. NAGAKURA and H. BABA *Tokyo, Japan, 1952*

In addition to IR and Raman studies there are other valuable spectroscopic techniques for examining H bonding systems. One of these, the study of the visible and ultraviolet spectra, was stimulated by Nagakura and Baba's recognition of the effect of H bonding on electronic spectra, as quoted above (1481). More recently, proton magnetic resonance studies of H bonding systems have attracted great interest. Other methods treated in this chapter are fluorescence, phototropism, and quadrupole coupling measurements. Proton magnetic resonance, x-ray diffraction, and neutron diffraction methods associated with the determination of crystal structures are discussed in Chapter 9.

[a] From *J. Am. Chem. Soc.* **74**, 5693-8 (1952).

4.1 Proton Magnetic Resonance

Since 1950 there has been a rapid development of the use of nuclear magnetic resonance (NMR) for the investigation of a variety of problems of chemical interest. The accumulating proton magnetic resonance studies of organic molecules give promise that the method will match IR spectroscopy as a diagnostic tool and a probe of molecular structure. The H bond is one of the specific bonding situations for which this promise has already been realized. The studies fall into the following classes:

1. H Bond chemical shifts
2. H Bond dissociation and exchange times
3. Relaxation processes
4. H Atom positions in H bonded crystals[a]

4.1.1 Experimental Aspects. A number of reviews which include discussion of the experimental aspects of NMR methods have been published (e.g., see 2159, 847, 1864, 1684, 1659a). The excellent book by Pople, Schneider, and Bernstein has a complete and authoritative chapter on H bonding, and furnishes valuable supplemental reading on all aspects of this topic (1659a).

The NMR measurement involves determination of the resonance attenuation of a radiofrequency signal by a sample placed in a strong magnetic field. The resonance depends upon the magnetic moments of one or more types of nuclei in the sample and upon the strength of the magnetic field in which the nuclei are placed. The measurement holds great interest for the chemist because the electron environment of the nucleus modifies the field felt by the nucleus, and the electron environment reflects the chemical binding of the molecule. This influence of the electrons is called the chemical shift.

Chemical shifts are measured with high resolution apparatus: field strengths of 10,000 and 14,000 gauss are usual. For these field strengths, respective radiofrequencies appropriate for the proton nuclear moment are 40 and 60 megacycles. Extreme requirements for homogeneity of the magnetic field limit the volume of the sample to a few tenths of a milliliter. Liquid samples are conveniently studied, and, with special provisions, they can be examined at temperatures ranging from −80 to 200°C. Solution studies can be made at solute concentrations as low as 0.1 M. However, this is not as low as needed for the convenient

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[a] The last topic is deferred to Section 9.3.

study of many H bonding systems. Only a few measurements of gases have been made, but these are of particular value. Solids display broad spectra unsuitable for high resolution spectroscopy.

Chemical shifts are often reported in terms of the dimensionless quantity δ:

$$\delta = \frac{H - H_r}{H_r} \cdot 10^6$$

where

H = resonance field of the compound of interest
H_r = resonance field of a reference compound

The reference substance varies: cyclohexane is a good choice. Water is often used but may prove to be a poor reference because of temperature sensitivity of its H bonding structure.

Unfortunately, a variety of alternative notations are in use. The quantity δ is often defined with opposite sign [e.g., Gutowsky, *et al.*, do so (1395)], and it is sometimes symbolized σ. Furthermore, δ is occasionally defined with a factor 10^5. We adopt the above definition of δ in agreement with Pople, Schneider, and Bernstein (1659a). Results are sometimes presented in terms of cycles per second, which can be converted to the dimensionless δ by dividing by the radiofrequency expressed in megacycles. One more notation we shall use is "shift to higher (or lower) field," a statement of the relative magnitude of H and H_r. A shift toward higher field, $H > H_r$, implies a positive δ.

To provide an idea of magnitudes, two values can be mentioned of δ referred to a "bare proton," a proton with no magnetic shielding by electrons: for cyclohexane, δ is +27.0, and for molecular hydrogen, δ is +27.5 (848).

Chemical dissociation and exchange times can be measured by high resolution methods. Coalescence of the NMR signals of protons in different H bonded species indicates that association and dissociation of these species occur in a time which is short compared to the characteristic time of measurement. Dissociation times of the order of a millisecond can be measured.

Relaxation behavior is deduced from measurements of various transient phenomena. Current interpretations of these phenomena dictate the definition of two processes by which the orientations of the nuclear magnetic moments reach the equilibrium distribution. These processes are described by characteristic times, designated T_1 and T_2. The first, T_1, is called the "thermal" or "longitudinal" relaxation time.

It characterizes the process by which energy is transferred between the nuclear spin system and its environment. The environment is called the "lattice." (The word lattice in this use has an esoteric meaning, since it refers to solution and gas environments.) Hence the process determining T_1 is sometimes called "spin-lattice" energy exchange. The second characteristic time, T_2, is called the "transverse" relaxation time. It characterizes the process by which certain coherency of orientation of spins is lost, a process which does not require spin-lattice energy transfer. The immediate point of interest is that H bonding influences both T_1 and T_2.

Solids display broad line spectra which can be studied with lower resolution apparatus. The band shapes are determined by the magnetic environments of the nuclei responsible for the resonance. One feature of band shape, the band width, has been treated theoretically; in this treatment the mean square width or "second moment" of the band contour is related to the inverse cube of the distances between neighboring spins (849, 1714). Thus, proton positions in a nucleus can be deduced *if* the heavy atom positions are known from x-ray or electron diffraction studies (1684).

4.1.2 Hydrogen Bond Chemical Shifts.

Early in the development of NMR measurement as a chemist's tool, a large H bond chemical shift was observed. This H bond effect was quickly recognized because of the coincidence that one of the first examples of clear-cut and readily interpreted chemical shifts in organic molecules was the proton resonance spectrum of ethanol. The spectra contained a peculiarity: the resonance attributed to the O—H proton was found to vary considerably with temperature (1562). The cause of this unusual behavior was recognized by Liddel and Ramsey (1230), and was correctly identified as the temperature dependency of H bond formation. With this interpretation Liddel and Ramsey predicted that dilution of ethanol in an inert solvent would produce the same shift as that brought about by a temperature rise. Corroboration was immediate: the first report, by Arnold and Packard, of the measurement of this concentration effect (63) actually appeared on the same journal page as did Liddel and Ramsey's prediction.

The Hydrogen Bond NMR Shift in Pure Substances. It has been a prophetic circumstance that the recognition of the H bond proton resonance chemical shift involved one of the pioneers of the IR study of the H bond (U. Liddel). The NMR H bond effect will undoubtedly be as informative as the IR frequency shifts. There are many similarities in IR and NMR studies, and the same experimental variables influence both measurements and confuse their interpretations. To avoid the pitfalls already mapped by IR studies, *NMR measurements should be made with attention to the suggestions listed in Section 3.2.5.*

Before this danger was realized, Meyer, Saika, and Gutowsky published their classical collection of NMR chemical shifts (1395). Their assignments of characteristic proton chemical shifts to H bonding substances are important in diagnostic application, but the significance of the shifts is not clear. The measurements refer to pure liquids with H bonding which introduces chemical shifts as large as those brought about by the *intra*molecular environment. These H bonding shifts are temperature- and solvent-sensitive, they are subject to steric influence, and they refer to a mixture of polymeric species. This is dramatically evident in Fig. 4-1, the NMR spectrum of various ethanol-CCl_4 mixtures. The same qualitative effects are obtained by raising the temperature (e.g., see 1659a). In either case, as H bonds are broken there is a shift of the O—H NMR signal toward higher fields. At extremely high dilution the O—H chemical shift is on the *high field* side of the CH_3 signal, completely negating the earliest interpretation that the high electronegativity of oxygen reduces the electron density near the O—H

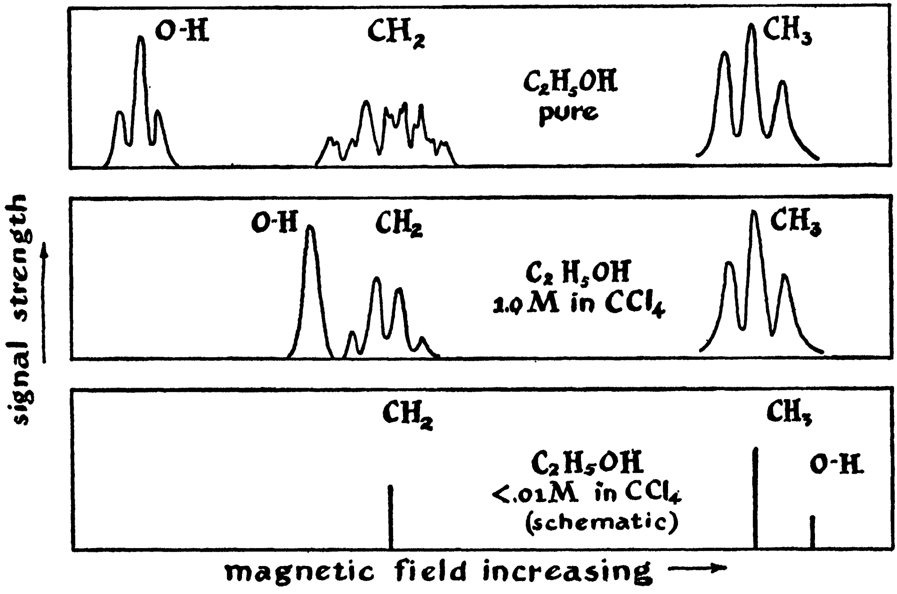

FIGURE 4-1 NMR spectra of ethanol and of ethanol in CCl_4.

proton and accounts for the position of the O—H shift of pure ethanol.

The same uncertainty is present in the search for a relation between electronegativity and chemical shift by Gutowsky and Hoffman (848). The difference they discover in the chemical shifts of the liquids H_2O and H_2S (respectively, -3.82 and -0.82, compared to cyclopentane) is consistent with a naive interpretation in terms of decreasing electronegativity. The high electronegativity of oxygen is expected to result in a low electron density on the hydrogen atoms and consequently a low diamagnetic shielding. This is an appealing explanation of the difference in the chemical shifts of H_2O and H_2S, but, surprisingly, it is not correct. The error of this analysis is revealed by the chemical shifts of the gases. Deprived of liquid state interactions, the chemical shifts are not even qualitatively in the order dictated by electronegativity. Figure 4-2 shows the chemical shifts of gaseous hydrides (relative to methane, as presented by Schneider, 1811) plotted against position in the periodic table. The absence of the expected trend is obvious: the NMR shifts of the first row hydrides are all about the same, whereas the line connecting the values for the second row hydrides slopes in the opposite direction. We emphasize this because it invalidates the naive interpretation of NMR chemical shifts, including those caused by H bonding.

The effect of the H bond is revealed by subtracting the proton resonance of the gas from that of the liquid just above the melting point. Schneider has done this (1811), presenting the "association" shift data shown in Fig. 4-3. There are several interesting features:

1. The H bond shifts are generally as large as the variations among the chemical shifts of the gases.

2. The H bond shifts are all negative, toward lower fields, implying a decrease in dimagnetic shielding.

3. The association shifts of the substances forming strong H bonds, HF and H_2O, are distinctly larger than the shifts of the other substances. (HF is even larger, negatively, than H_2O.)

4. Some of the individual shifts are surprising: the shift of HI exceeds those of HCl and HBr; acetylene and H_2S show larger shifts than ammonia.

Systematic Studies of Solutions. Since NMR shifts are strongly affected by the extent of H bonding, measurements on pure liquids, or solution measurements at a single concentration, are not very informative. This is evident in Fig. 4-4, which shows the concentration dependencies of the chemical shifts of various phenols in CCl_4, as given by Huggins,

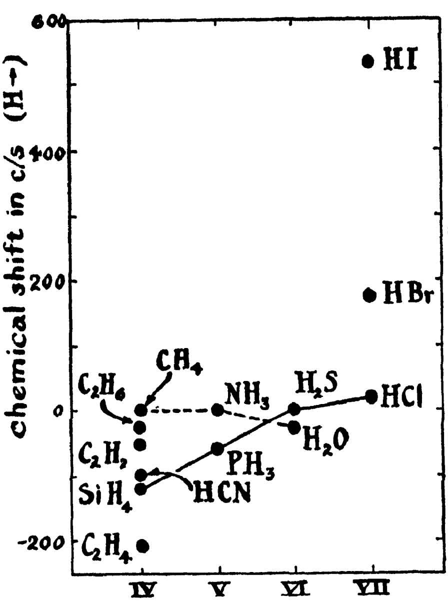

FIGURE 4-2 Chemical Shift of gaseous hydrides (relative to gaseous methane) *vs.* column in the periodic table. [Schneider, Bernstein, and Pople, *J. Chem. Phys.* **28**, 604 (1958).]

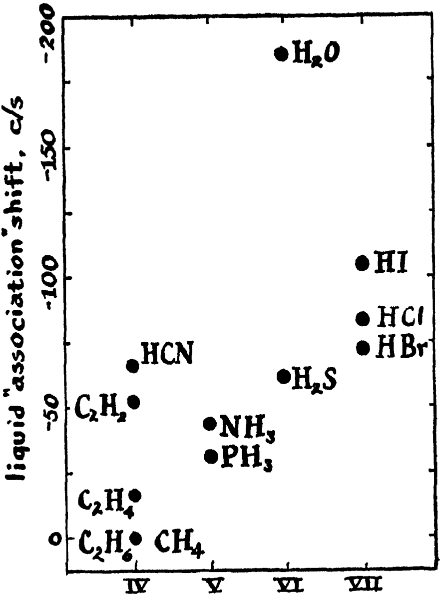

FIGURE 4-3 Liquid "association" shift of liquid hydrides relative to the gaseous state *vs.* column in the periodic table. [Schneider, Bernstein, and Pople, *J. Chem. Phys.* **28**, 605 (1958).]

Pimentel, and Shoolery (981). It is amply clear that a determination of the chemical shift of any of these compounds at a single concentration would convey little information. With the complete concentration behavior, however, these authors were able to correlate the curve shapes with the known H bonding properties of these substances. Each phenol displays only a single O—H proton resonance signal, implying that none of the H bonded species present has an average lifetime longer than about a millisecond. The limiting behavior at low concentration is dominated by the monomer-dimer equilibrium and approaches the weighted arithmetic mean

$$\delta = \alpha\delta_M + (1 - \alpha)\delta_D \qquad (1)$$

where the weighting factor, α, is the fraction of the O—H protons present as monomer, and δ_M and δ_D are the characteristic NMR shifts assigned to the monomer and dimer, respectively. The limiting value of δ and the slope, $d\delta/dx$ at zero concentration of the phenol are (981):

$$\delta_o = \delta_M \tag{2}$$

$$(d\delta/dx)_o = 2K(\delta_D - \delta_M) \tag{3}$$

where

x = *apparent* mole fraction of total phenol

K = *association* equilibrium constant in mole fraction units

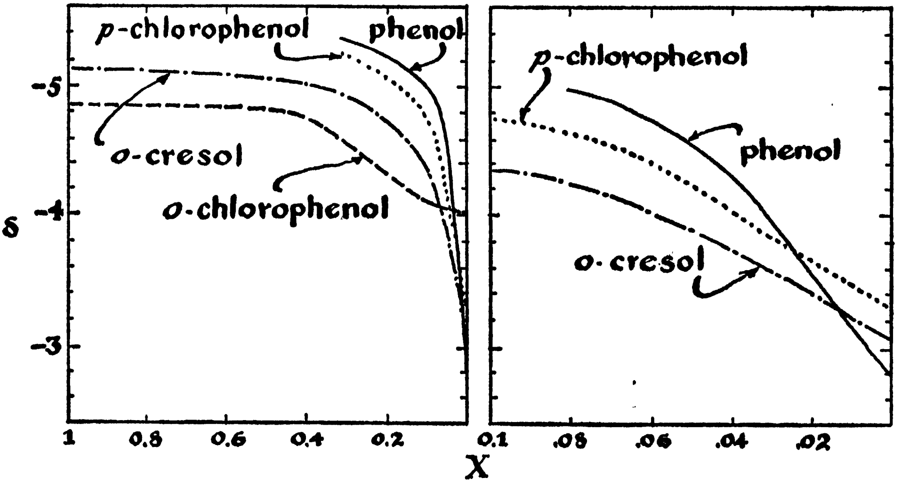

FIGURE 4-4 NMR shifts of phenols in CCl_4 *vs.* apparent mole fraction, x (expanded scale on right). [Huggins, Pimentel, and Shoolery, *J. Phys. Chem.* **60**, 1312 (1956).]

The interpretation of the concentration dependence of a H bonding compound which forms a H bond with the solvent is more complicated. Figure 4-5 shows the concentration dependence of acetic acid in acetone, in 1,1-dichloroethane, and in CCl_4 (981, 1811). There is a small but real difference between CCl_4 and 1,1-dichloroethane as solvents, the latter causing the break-up of H bonded aggregates at a higher concentration. However, the behaviors in these solvents are in sharp contrast to that in acetone. This solvent causes significant shift toward high field of the acetic acid NMR signal even at mole fraction 0.5.

There are two other noteworthy features of Fig. 4-5. First the change of δ is much larger for acetic acid than for the phenols, despite the fact that at zero concentration the acetic acid is in part H bonded to acetone. Huggins *et al.* estimate $(\delta_D - \delta_M)$ to be 9 ± 2, at least five times as big as this difference for phenol (981). The other interesting facet of the curve for CCl_4 is that the dilution shift at concentrations above 0.1 M is toward lower field. As observed by Schneider (1811), this is the direction opposite that expected. It is only at extremely low concentration that further dilution causes the expected shift toward higher field. Schneider proposed the reasonable explanation that disordered chain association in pure acetic acid is replaced by the stronger H bonding of cyclic dimers on initial dilution, thus accounting for the low field shift (1811).

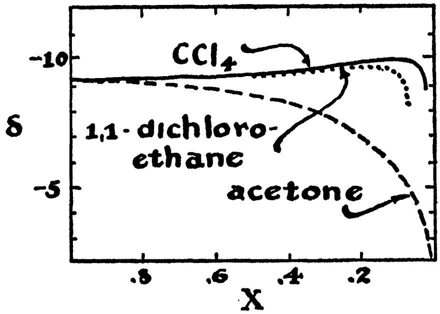

FIGURE 4-5 NMR shifts of acetic acid in various solvents *vs.* apparent mole fraction, *x*. [From Schneider (1).]

The presence of competing H bond equilibria makes difficult a detailed interpretation of the acetic acid-acetone system. A more tractable system is the mixture type identified as (2) in Tables 2-X and 2-XII, i.e., a mixture of a simple acid and a simple base. Since there are few acids which have no basic groups, we must turn to chloroform solutions, in anticipation of the discussion concerning its H bonding properties (Section 6.2.1). The NMR shifts of chloroform have been measured over the entire concentration range in several solvents.

Huggins, Pimentel, and Shoolery measured NMR shifts of chloroform in acetone and in triethylamine (982). This study furnishes corroborative evidence that the chloroform-base interaction can be classified as a H bond. More important, however, it serves as a prototype of the use of NMR chemical shifts in the study of complex formation. Huggins *et al.* based their analysis on an expression analogous to equation (*1*). They show that two data—the experimental values of δ in pure chloroform and at infinite dilution, combined with the equilibrium constant for association—permit calculation of the entire concentration dependence of δ. This implies that the measurement of δ over the range from pure liquid to infinite dilution gives an estimate of the equilibrium constant. Of course the temperature dependence of the constant gives the heat of association. The appropriate equations are given in reference 982 where they are used to obtain K and ΔH for the association of chloroform with the bases acetone and triethylamine.

A more complete study of chloroform in various solvents was con-

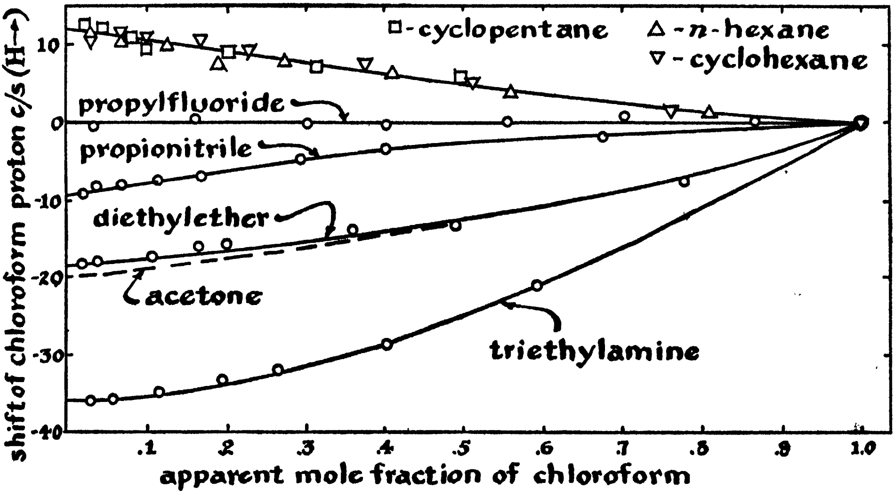

FIGURE 4-6 NMR shifts of chloroform in various solvents *vs.* apparent mole fraction chloroform. [Korinek and Schneider, *Can. J. of Chem.* **35**, 1159 (1957).]

ducted by Korinek and Schneider (1131). Their data are shown in Fig. 4-6. These authors consider that the shift obtained by dilution of pure chloroform with the alkanes implies self-association of the chloroform [as was first observed and suggested by Reeves and Schneider (1705)].[a]

Probably the most informative quantitative NMR study of H bonding is that of Becker, Liddel, and Shoolery (181). These workers extended their measurements of ethanol in CCl_4 to extremely low mole fraction, 0.003. The S-shaped concentration dependence of δ, shown in Fig. 4-7, differs from the curves of phenols (which extend only to mole fraction 0.01; see Fig. 4-4). Becker and co-workers make a clever analysis of the NMR data with the aid of IR measurements on the

[a] In comparing the work of Schneider and co-workers to that of Huggins, Pimentel, and Shoolery, we should note a different use of reference standards. Schneider and Reeves discuss their use of an external reference sample (1705). In this use, it is generally assumed that the volume susceptibilities of solution components are additive. This assumption is made doubtful by the existence of solvent-solute complex formation. Huggins *et al.*, on the other hand, use an *internal* reference, i.e., a reference solute dissolved in the solution of interest. Thus a correction for bulk diamagnetic susceptibility is obviated by putting the solute in the same magnetic environment as the species of interest.

Doubt has been cast on the bulk diamagnetic susceptibility correction by the work of Bothner-By and Glick (248a). These authors find for a number of solution mixtures (none involving strong H bonding) that the theoretical factor of $2\pi/3 = 2.09$ must be replaced by an empirical figure averaging about 2.6. This empirical correction and its variability seem to introduce an uncertainty of a few cycles in the concentration dependence of δ in H bonding solutions whether internal or external references are used.

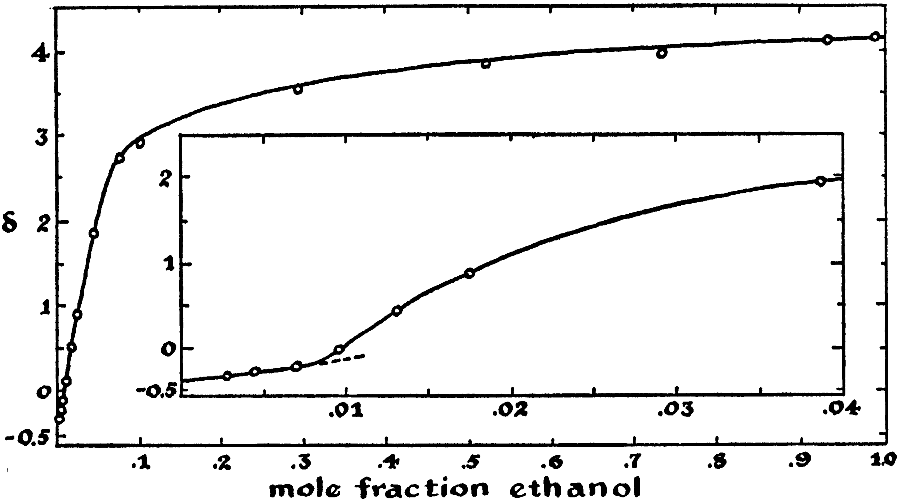

FIGURE 4-7 NMR chemical shift of ethanol in CCl_4. [Becker, Liddel, and Shoolery, *J. Molec. Spectroscopy* **2**, 1–8 (1958).]

same solutions. The IR data give the fraction of the O—H protons that are *not* involved in H bonds. This permits subtraction of that portion of δ attributable to these protons. The remainder is an average which is determined by all of the H bonded species present. This average, δ_P, must approach the dimeric shift δ_D at low concentration. Figure 4-8 shows the values tabulated by Becker *et al.* plotted against mole fraction of ethanol. The low concentration limit, δ_D, is shifted from the monomeric value only about half as much as are the values of δ_P at higher concentrations. Furthermore, δ_P of the larger polymers is almost independent of concentration after dimers become unimportant. The behavior is strikingly similar to the IR matrix isolation studies discussed in Section 3.3.8, and it leads Becker *et al.* to the same conclusion as was drawn from the matrix work—the alcohol dimers differ radically from the larger polymers. They propose that the dimers are probably cyclic and the higher polymers have open or chain structures. Aside from this interesting result, the studies are a model in emphasizing the importance of concentration studies below 0.1 M and in demonstrating the advantage derived from combining IR and NMR data (see also 1795a).

Other NMR studies of H bonding systems at various concentrations have been made but have been interpreted in less detail. Cohen and Reid found the limiting shift at zero concentration, δ_0, of H_2O, CH_3OH,

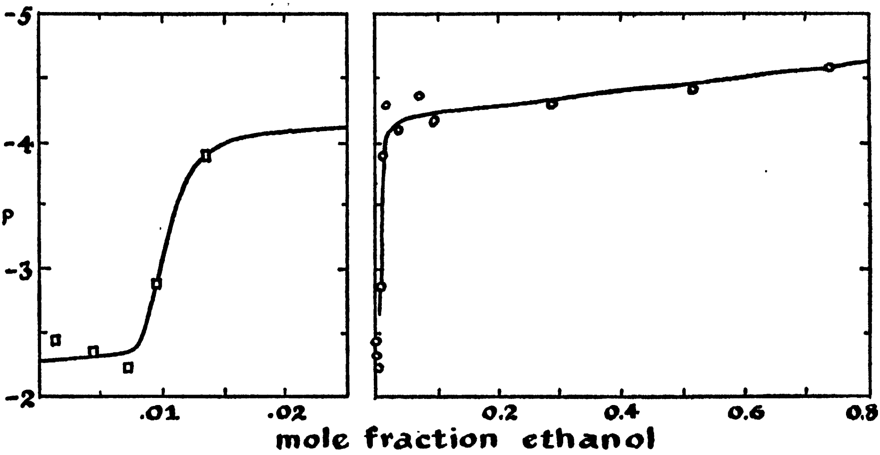

FIGURE 4-8 Average NMR chemical shift of ethanol in CCl_4 after subtraction of monomer contribution (expanded scale on left). [Becker, Liddel, and Shoolery, *J. Molec. Spectroscopy* 2, 1–8 (1958).]

C_2H_5OH, and phenol in CCl_4; H_2O and CH_3OH in $CHCl_3$; and H_2O in C_6H_6 (412). Their results are interesting in several respects. For example, the limiting shift, δ_o, of methanol in $CHCl_3$ differs by -0.06 from δ_o of methanol in CCl_4. In benzene the NMR shift of H_2O is even more unexpected in that the δ_o is moved by $+0.05$ relative to water in CCl_4. This positive shift, the opposite to that observed for the usual H bond formation, has been studied in detail by Reeves and Schneider (1705) for a variety of aromatics. The behavior has been explained by Bernstein, Schneider, and Pople in terms of a "diamagnetic circulating current" in the pi electron system (202; see also 1658, 1811).

Bhar and his associates studied carboxylic acids in water (213, 214). As water is added to either pure acetic acid or propionic acid, δ decreases steadily except for a curious hump in the curve at 50 percent water *by volume*. This feature is not evident in the acetic acid-water resonance data given by Gutowsky and Saika (851). Batdorf conducted NMR studies of phenols (148). His results are similar to but less detailed than those shown in Fig. 4-4. Crawford and Foster used the spin echo technique for NMR spectra of alcohols but not specifically with interest in H bonding (460).

Aqueous Electrolyte Solutions. Gutowsky and Saika measured the NMR of aqueous solutions of the strong acids HCl, $HClO_4$, HNO_3, and H_2SO_4, and of the strong bases NaOH and KOH (851). They derive estimates of the characteristic NMR shifts of aqueous H_3O^+ ($-1.05 \pm .05$) and OH^- (-1.0) (all δ's in this section are given relative to H_2O). The resonance data of $HClO_4$ and HNO_3 are interpreted in terms of incomplete dissociation.

Hood, Redlich, and Reilly repeated the measurements of aqueous HCl, $HClO_4$, and HNO_3, extending the concentration ranges of $HClO_4$ and HNO_3 to the pure acids (953). For HNO_3 mole fractions exceeding 0.5 the resonance behavior is interpreted as indicating the presence of two species, HNO_3 monohydrate and anhydrous HNO_3. In a subsequent paper these same authors report NMR studies of aqueous trifluoroacetic acid (952). Hood and co-workers also derive acid dissociation constants from their data. Shoolery and Alder determined the NMR of water in concentrated aqueous salt solutions (1863). Some salts bring about positive shifts, and some negative shifts, all of the order of 0.1. Shoolery and Alder interpret the shifts in terms of breakdown of the H bond structure of water working in opposition to the polarization caused by the cations.

In each of the references cited in this section the pertinent authors note that the data are influenced by changes in the H bond structure of water. The observed effects are of the same magnitude as are H bonding changes. Yet the interpretations, though appealing in their simplicities, do not involve H bonding. Gutowsky and Saika (851) explain the NMR data for HCl by assuming that the only change brought about by HCl is the reaction to form H_3O^+. If a change of the H bonding structure of water occurs, that effect would be assimilated in the characteristic δ assigned to H_3O^+. In conclusion, the work which has been completed to date suggests that NMR studies of electrolyte solutions may well contain interesting information about the H bonding in aqueous solutions, but, if so, most of this information is yet to be obtained.

4.1.3 Hydrogen Bond Dissociation and Exchange Times. At room temperature, H bonding solutions usually display just one proton resonance associated with the H bonding proton. This has been interpreted as reflecting movement of a given molecule among the several polymeric species present in a time short compared to the characteristic measurement time (about 10^{-3} seconds) (e.g., see 1230, 851, 982, 212). In principle the temperature could be reduced until the H bonded polymers have average lifetimes in the range 10^{-3} seconds, to permit measurement. Such data eventually will provide information concerning the potential function for H bond formation.

Two articles deserve special mention. Ogg has presented NMR spectra of anhydrous liquid ammonia and liquid ammonia containing an estimated 10^{-7} mole fraction of water (1539). The triplet spectrum obtained for dry NH_3 was attributed to spin-spin interaction between the protons and the N^{14} nucleus. The presence of the presumed trace of H_2O (attributed to moisture adsorbed on glass surfaces) causes coalescence of the features of the triplet into a singlet. Ogg attributes the disappearance of the spin-spin structure to the rapid transfer of protons between ammonia molecules via the reaction $H_2O + NH_3 = OH^- + NH_4^+$. Although this interpretation is not well established, the article points out a promising line of study. (See also 212.)

The second article presents NMR spectra of ethanol–water mixtures. Weinberg and Zimmerman found that the alcohol O—H resonance is distinct from the water O—H resonance when the water concentration is below 20 percent by weight (2146). At 27 percent by weight water (corresponding to a 0.5 mole ratio) the two resonances coalesce, and remain so at higher water concentrations. These workers attribute the coalescence to the onset of proton exchange between water and alcohol with an exchange time of 0.05 seconds.

4.1.4 Relaxation Processes. The NMR line widths in liquids and gases are found experimentally to be much smaller than for the same molecules in the solid state. This behavior is the result of the averaging effect caused by rapid variation of the perturbing environment in the mobile phases. In a solution, any factor which tends to slow the variation of the local environment of a molecule may also increase the line width. Both high viscosity and molecular association processes work toward slowing these variations, and hence contribute to line width. Since the line width is related to the relaxation times T_1 and T_2 (and is proportional to $1/T_2$), measurements of T_1 and T_2 may reveal viscosity changes and association.

A relatively popular measurement has been the NMR line width as a function of viscosity. Bloombergen, Purcell, and Pound (233) pioneered by measuring relaxation times in glycerol as a function of temperature. They considered that the sole effect of temperature was the change of viscosity. More recently, Conger (421) and Morgan and co-workers (1448, 1449) examined the effect of ions such as Cr^{+3} on the NMR relaxation in H_2O-glycerol solutions. Morgan *et al.* studied several complex ions of Cr^{+3} [e.g., $Cr(H_2O)_6^{+3}$, $Cr(NH_3)_6^{+3}$, $Cr(F_6)^{-3}$, etc.] and realized that the observed changes in H_2O-glycerol solutions are not caused entirely by viscosity changes. As additional factors they suggest that the number and strength of the H bonds in the solvent environment play a role. It remains to be seen whether the earlier viscosity studies require re-examination.

Giulotto, Lanzi, and Tosca (773) plotted $1/T_1$ for the NMR shift of phenol as a function of concentration in CCl_4 solutions. A maximum at 0.2 mole fraction is interpreted as indicating that the H bonded "molecular clusters" increase in size as concentration increases, but that the clusters lose their rigidity above 0.2 mole fraction. It is interesting that at this concentration approximately 15 percent of the molecules are still present as monomers (1375), and no doubt there are substantial concentrations of dimers and trimers. The loss of rigidity at higher concentrations might be associated with a transition from cyclic structures of dimers and trimers to open structures for tetramers and higher polymers, as Van Thiel, Becker, and Pimentel suggested for H bonded methanol polymers (2098).

Solomon and Bloombergen (1921) estimated that the activation energy for proton exchange between H_3O^+ ion and HF is 1,940 ±250 cal/mole in liquid HF (H_2O mole fraction near 10^{-4}). Bloom (232) interprets proton relaxation times in dilute aqueous solutions of $MnCl_2$ in terms of a 2.1 microsecond lifetime of a water molecule in the first hydration sphere of Mn^{++}.

Promising studies have been made of relaxation processes of H bonding molecules adsorbed on solid surfaces. Mays and Brady (1366) measured the NMR behavior of water on TiO_2 and found that the H_2O molecules become immobilized when the coverage reaches one monolayer. At higher coverages the line width suggests an ice-like structure. Hickmott and Selwood (917) measured the proton relaxation of alcohols and water adsorbed on catalytic solids. These two studies point to an exciting new frontier in the study of H bonding—the role of the H bond in the special chemical properties of adsorbed molecules.

4.1.5 Comparison of Infrared and Nuclear Magnetic Resonance Methods. The NMR measurements of H bonding systems are few in number but great in promise. Effective use of this technique depends rather critically upon the possibility of varying the sample temperature. At high temperatures, dissociation of the H bonded complexes can be obtained even at the rather high concentrations necessary for detection. At low temperatures the different H bonded species may be observable individually.

We can profitably contrast the capabilities of the IR and NMR techniques. There are a number of advantages in IR methods: different H bonded complexes can be individually distinguished; lower concentrations can be used; gas and solid phases are readily studied; wider temperature ranges are accessible. On the other hand, there are some inherent capabilities of NMR measurements which give them unique value. As a means of detecting H bonds, the method certainly rivals and possibly excels the IR measurements. Of course there are all too few criteria for H bonding which show the specific rôle of the hydrogen atom in the interaction. The H bond NMR shift is a welcome addition. With reference to the electronic redistribution accompanying H bond formation, NMR shifts give new, though not yet well understood, information. The opacity of water as an IR solvent gives NMR spectroscopy an advantage. Finally, the special power of the magnetic methods for determining rates of H bond formation and rupture awaits exploitation.

Having placed the IR and NMR methods in competition, we conclude by pointing out the importance of welding them as powerful supplementary tools. The potentialities of the newer method will be more fully exploited when aided by the more familiar IR technique.

4.2 Ultraviolet and Visible Spectroscopy

It is to be expected that the UV-visible spectrum of a molecule may be altered by the formation of a H bond if the chromophoric portion of the molecule is perturbed by the H bond. Such is indeed the case: H bond formation often is accompanied by readily measurable spectral changes which contain interesting and useful information. Yet it is only within the last decade that UV-visible spectra have received concerted attention as a means of studying H bonding.

The following principal generalizations about the effect of H bond formation on electronic transitions can be made.

1. Electronic transitions (both in emission and absorption) of either acidic or basic substances in solution may show shifts of the band maximum upon H bond formation. In absorption spectra both positive and negative shifts, $\Delta\nu_a$, have been observed. These shifts correspond to energies, $h\Delta\nu_a$, usually of the order of, but smaller than, H bond energies. In absorption spectra, no pronounced change of absorption coefficient accompanies the shift, but vibrational fine structure may become diffuse.

2. The frequency shifts often provide spectral features sufficiently

separated for quantitative determination of the concentrations of bonded and unbonded species. Such data measured at different temperatures give estimates of thermodynamic quantities: equilibrium constants, ΔH, and ΔS of H bond formation.

3. It is commonly accepted that $n \longrightarrow \pi^*$ transitions of a base always shift toward higher frequency[a] upon H bond formation (the "$n \longrightarrow \pi^*$ blue shift").

4. In contrast, $\pi \longrightarrow \pi^*$ transitions usually shift toward lower frequencies (red shift) upon H bond formation.

5. The shifts contain information concerning the difference in ΔH of H bond formation of the ground and the excited states, but this information must be interpreted in terms of the Franck-Condon principle.

6. The intensity of fluorescence is in some cases increased and in others decreased by H bond formation.

7. The phenomenon of phototropism may be influenced or perhaps determined by *intra*molecular H bond formation.

8. Far UV absorption by H bonded species (~2000 Å) may be connected with dissociation of the H bond.

4.2.1 Hydrogen Bond Frequency Shifts in Electronic Absorption Spectra. It is not surprising that the influence of H bonding on the frequency of absorption was first recognized in organic dyes. Dyes, which are specifically constituted to absorb in the visible region, offer an easily detected spectral change, the visual color. The desire to control the color of a dye gives an extra incentive to find the cause of this change. Thus, among the earliest discoverers of the effect of H bonding on electronic transitions was Dukunikhin, who proposed an influence of *intra*molecular H bonds on the color of indigo (530). Gill and Stonehill go further by recording the colors of indigo and indanthrone derivatives in various solvents, and they conclude that H bonding "has significant application in color chemistry" (766). Other studies of dye color changes induced by H bonding are numerous, though in some cases the role of the H bond was not recognized.[b]

[a] A shift toward higher frequency is called a blue shift or a hypsochromic shift. Similarly, a shift toward lower frequency is called a red or bathychromic shift. We will use the blue shift, red shift notation. The designation $n \longrightarrow \pi^*$ refers to the excitation of an electron from a nonbonding orbital (an "n" orbital) to an excited pi orbital of the chromophoric group (a π^* orbital). The $\pi \longrightarrow \pi^*$ transition is restricted to pi orbitals of the chromophore, usually from a bonding to an antibonding orbital. The $n \longrightarrow \pi^*$ transitions are forbidden, whereas the $\pi \longrightarrow \pi^*$ transitions may be allowed.

[b] 113, 1889, 1888, 1457, 24, 1843, 1287, 1689, 529 (review), 1553, 1285, 1973, 1611, 2040, 2023, 1660, 178, 1333, 1082, 319–322, 107, 1846, 1747, 285, 361, 1848, 1612, 1145, 769.

Lutskiĭ directed attention to the H bond in simpler molecules by proposing that the influence of ethanol solvent on the UV spectrum of an *ortho*hydroxy keto- or nitro aromatic provides a criterion for an *intra*molecular H bond (1287, 1285). Brieglieb and Strohmeier were able to detect the influence of H bonded dimer formation on the spectra of acetic acid vapor at different temperatures (near 2100 Å) (279). There have followed many valuable studies directed at the effect of H bonding on the electronic transitions of acids such as phenols,[a] aniline (1483, 1481, 2056), benzoic acid and derivatives (2076, 1998, 671, 190), acetanilides (2075, 2074), HF (1771, 1770), naphthols (1479, 1484), sulfinic acids (521), and amides (1436). The most extensive work, that of Nagakura, Baba, and co-workers,[b] is of particular importance because it led to theoretical consideration of the nature of the H bond (see Section 8.3.2). (See also 2056, 1418, 1850.)

Despite all of this early work, recognition and interpretation of the effect of H bond formation on electronic transitions have been inhibited by the difficulty of distinguishing it from non-H bonding solvent interactions. For example, Coggeshall and Lang (410) observed for 21 phenols that the UV spectra were altered when the solvent was changed from a paraffin to ethanol. The absence of a marked temperature dependence caused them to conclude that the effect was *not* caused by H bonding, but rather by "stabilization of excited polar states through interactions with the alcohol molecules." Bayliss and McRae (177) discuss solvent effects more generally, in terms of solvent polarization, dipole-dipole, dipole-polarization, and H bonding forces. They conclude that "one of the outstanding questions [is] whether dipole-dipole interaction or H bonding is the more important type of solute-solvent interaction." (176; see also 676.) Their data, converted into shifts from the reference solvent *n*-heptane, are presented in Tables 4-I and 4-II. A glance at the shifts suggests immediately that the dominant interaction *is* indeed H bonding, since there is no pronounced sensitivity to dielectric constant, to solvent dipole moment (acetone), or to polarizability (benzene, CCl_4). Pimentel has presented arguments (1633) to support the view that H bonding, when present, will generally dominate the other effects considered by Bayliss and McRae (see also 1482).

Brealey and Kasha were probably the first to place appropriate emphasis on the importance of H bonding in their interpretation of

[a] 410, 1478–1482, 92, 2056, 1807, 1102, 91, 1580, 1412, 1103, 1071, 190.

[b] 1478–1484, 1429, 92, 91, 1412, 1997.

TABLE 4-I Solvent Shifts and Absorption Coefficients for Electronic Transitions[a] ($n \longrightarrow \pi^*$ transitions)

$\Delta\nu = \nu - \nu(n\text{-heptane})$
ϵ_m = absorption coefficient

SOLVENT	SOLVENT REFRACTIVE INDEX (2800 Å)	ACETONE ν (n-heptane) = 35,840 cm^{-1}		NITROMETHANE ν (n-heptane) = 36,020 cm^{-1}		CROTONALDEHYDE ν (n-heptane) = 30,580 cm^{-1}	
		$\Delta\nu$ (cm^{-1})	ϵ_m	$\Delta\nu$ (cm^{-1})	ϵ_m	$\Delta\nu$ (cm^{-1})	ϵ_m
Gas	—	+360	11.2	+280	8	−90	18
Acetone	1.40	—	—	—	—	+20	24
n-Heptane	1.42	(0)	13.0	(0)	18.2	(0)	24
Cyclohexane	1.47	−100	14.7	−70	18.2	−30	21
CCl_4	1.52	−130	20.1	+100	20.5	—	—
Benzene	1.62	−70	17.5	—	—	+280	32
$CHCl_3$	1.50	+410	17.3	+270	19.6	—	—
C_2H_5OH	1.37	+930	16.0	+480	16.9	+2420	40
H_2O	1.36	+1920	17.9	+1180	15.4	—	—

[a] 176.

the $n \longrightarrow \pi^*$ blue shift phenomenon (274). This phenomenon refers to an empirical correlation among solution spectra (1083, 1297) that the absorption maximum of an electronic transition of $n \longrightarrow \pi^*$ type shifts progressively toward higher frequency (blue shift) as the solvent is changed from alkane to alcohol to water. Brealey and Kasha corroborate for pyridazine and benzophenone that the electronic shift is associated with formation of H bonded species (274). Tables 4-III, 4-IV, and 4-V summarize much of the data available on solvent shifts for carbonyl bases, miscellaneous bases, and proton donors. Unless otherwise noted, the original references are listed in the useful compilation of McConnell (1297). (Other studies not listed involve the compounds anisole (2075), antipyrine (1156, 1157), aromatics in water (235), azulene (2141), cysteine (511), phenyl ether (2075), formaldehyde (413), iodobenzene (2075), phenol-methylchloroacetates (1480), phenol-quinone (2239), pyridine (891, 227, 1074, 1159), pyridine-1-oxide, and other heterocyclic-*N*-oxides (1156, 1157).

TABLE 4-II Solvent Shifts and Absorption Coefficients for Electronic Transitions[a] ($\pi \longrightarrow \pi^*$ transitions)

$\Delta\nu = \nu - \nu(n\text{-heptane})$
ϵ_m = absorption coefficient

SOLVENT	NITROMETHANE ν (n-heptane) = 39,740 cm^{-1}		CROTONALDEHYDE ν (n-heptane) = 47,040 cm^{-1}	
	$\Delta\nu$ (cm^{-1})	ϵ_m	$\Delta\nu$ (cm^{-1})	ϵ_m
n-Heptane	(0)	8350	(0)	16,000
Cyclohexane	−200	8900	−290	13,000
CCl_4	−570	9790	—	—
H_2O	−2370	8190	−2280	15,000

[a] 176.

The last columns of Tables 4-III and 4-IV list the accepted assignments of the transitions under study. If we recognize these identifications, the available data seem to corroborate the generalization that the $n \longrightarrow \pi^*$ bands show blue shifts and the other transitions show red shifts. (For a possible exception, see 1156, 1157.) Unfortunately, it is difficult to establish the nature of these transitions, and in many cases the classification is based mainly on the blue shift behavior. A legitimate test should involve only those transitions which can be established

TABLE 4-III H Bond Solvent Shifts for Transitions in Carbonyl Bases

BASE	ν_o (cm^{-1})	METHANOL $\Delta\nu_a$ (cm^{-1})	WATER $\Delta\nu_a$ (cm^{-1})	TRANSITION
Biacetyl	23,700	+300[a]	+800[a]	—
Nitromethane	36,020	+480[a,b,c]	+1180[b]	$n \longrightarrow \pi^*$
p-Quinone	22,500	—	+1600	$n \longrightarrow \pi^*$
Acetaldehyde	35,000	—	+1500	$n \longrightarrow \pi^*$
Diazoacetic ester	25,500	+800	+1500	$n \longrightarrow \pi^*$
Acetone	35,960	+930[b,c]	+1920[b]	$n \longrightarrow \pi^*$
		+1200[c,d]		
Ethylacetate	44,000	—	+1900	$n \longrightarrow \pi^*$
Mesityloxide	30,760	+1000	+3200	$n \longrightarrow \pi^*$
		+1180[c,d]		
Benzophenone	28,850	+2000	—	$n \longrightarrow \pi^*$
		+1170[c,d]		
Crotonaldehyde	30,580	+2420[b,c]	—	$n \longrightarrow \pi^*$
Glyoxal	36,000	—	+11,000	$n \longrightarrow \pi^*$
	22,000	—	+20,000	$n \longrightarrow \pi^*$
Diazoacetic ester	41,000	−550	−600	$\pi \longrightarrow \pi^*$
Benzophenone	40,000	−900	—	$\pi \longrightarrow \pi^*$
p-Quinone	42,000	—	−1500	$\pi \longrightarrow \pi^*$
Mesityloxide	43,000	−1000	−1700	$\pi \longrightarrow \pi^*$
Crotonaldehyde	47,040	—	−2280	$\pi \longrightarrow \pi^*$
Nitromethane	39,740	—	−2370	$\pi \longrightarrow \pi^*$
p-Br acetophenone	39,530	−470[e]	−480[e]	*CT*[f]
Acetophenone	42,010	−690[e]	−1190[e]	*CT*
p-Cl acetophenone	40,160	−770[e]	−1100[e]	*CT*
p-CH_3 acetophenone	40,490	−810[e]	−1580[e]	*CT*

[a] 676; [b] 176; [c] ethanol solvent; [d] 274; [e] 1998; [f] *CT* = charge transfer.

as $n \longrightarrow \pi^*$ transitions without reference to the solvent effect. Other types of evidence either are seldom available (such as polarization measurements) or are ambiguous (such as extinction coefficient, vibrational structure, etc.). Apparently the widespread confidence in the $n \longrightarrow \pi^*$ blue shift proposal is based upon the over-all self-consistency of the assignments.

It can be added that the shifts are of the order of H bond enthalpies (1–7 kcal per H bond corresponds to 350–2500 cm^{-1} shift), and that the shift in water is often about twice as large as in methanol.

The significance of these shifts requires consideration of the role of

TABLE 4-IV H Bond Solvent Shifts in Miscellaneous Bases

BASE	ν_0 (cm^{-1})	METHANOL $\Delta\nu_a$ (cm^{-1})	WATER $\Delta\nu_a$ (cm^{-1})	TRANSITION
Nitrosobenzene	13,000	+50	+450	$n \rightarrow \pi^*$
Azobenzene	22,360	+160	—	$n \rightarrow \pi^*$
o-Methoxybenzene azobenzene	22,000	+300	—	$n \rightarrow \pi^*$
Pyrazine	31,500	+700	+1800	$n \rightarrow \pi^*$
p-Methoxybenzene azobenzene	23,000	+500	—	$n \rightarrow \pi^*$
p,p'-Diethoxythiobenzophenone	17,000	+500	—	$n \rightarrow \pi^*$
Pyridazine	29,450	+2440[a]	+4000[b]	$n \rightarrow \pi^*$
2-Amino-5,6-dimethyl-*as*-triazine	26,670[e]	+1530[c,d]	+2330[d]	$n \rightarrow \pi^*$
3-Amino-*as*-triazine	25,350[e]	+1680[c,d]	+3250[d]	$n \rightarrow \pi^*$
Pyrazine	37,500	—	−150	$\pi \rightarrow \pi^*$
p-Methoxybenzene azobenzene	29,500	−300	—	$\pi \rightarrow \pi^*$
p,p'-Diethoxythiobenzophenone	29,000	−700	—	$\pi \rightarrow \pi^*$
2-Amino-5,6-dimethyl-*as*-triazine	32,160[e]	−1100[d]	−610[d]	$\pi \rightarrow \pi^*$
	44,250[e]	−580[d]	0[d]	$\pi \rightarrow \pi^*$
3-Amino-*as*-triazine	32,260[e]	−1400[c,d]	−1200[d]	$\pi \rightarrow \pi^*$
	45,455[e]	−1595[c,d]	−1205[d]	$\pi \rightarrow \pi^*$

[a] 274; [b] 862; [c] ethanol solvent; [d] 934; [e] cyclohexane solvent.

the Franck-Condon principle. Pimentel (1633) has discussed the detailed interpretation, and observes that the shift caused by a H bonding interaction is, in absorption,

$$\Delta\nu = W_o - W_1 + w_1$$

In this expression the enthalpy of H bond formation is designated by $-W$ ($W = -\Delta H$), W_o and W_1 referring to the ground and excited states, respectively. The quantity w_1 is the excitation energy required by the Franck-Condon principle. Thus, the frequency shift gives the difference between the H bond enthalpy in the ground state and in the excited state plus the quantity w_1. Since w_1 is always positive, the shift will always be more positive (more to the blue) than implied by $W_o - W_1$, whether W_o exceeds or is less than W_1.

We may now interpret the blue shift of the $n \rightarrow \pi^*$ transition. Presumably the excitation of a nonbonding electron localized on a basic functional group to an antibonding pi orbital shifts electron density away from the basic group. This reduces its base strength, and results in a weaker H bond in the excited state. The red shift of a $\pi \rightarrow \pi^*$ transition in a base can be attributed to electron redistribution with

TABLE 4-V H Bond Solvent Shifts for Electronic Transitions of Proton Donors

ACID	BASE	REFERENCE SOLVENT	ν_0 (cm^{-1})	$\Delta\nu_a$ (cm^{-1})
Phenol	Benzene	Heptane	36,010^{a}	−140
Phenol	Methylacetate	Heptane	36,010^{a,b}	−240
Phenol	Ethylacetate	"naphtha"	36,930^{b}	−310
			36,040^{a}	−350
Phenol	Dioxane	Heptane	36,010^{a}	−350
Phenol	Ether	Heptane	36,010^{c,d}	−360
	Diethyl ether	"petroleum ether"	36,010^{e}	−423
Phenol	Acetone	"petroleum ether"	36,010^{e}	−397
Phenol	*N,N*-Dimethylacetamide	"petroleum ether"	36,400^{e}	−500
Phenol	Triethylamine	*n*-Heptane	36,010^{c}	−580
m-Chlorophenol	Methylacetate	*n*-Heptane	35,520^{b}	−230
			36,470^{a}	−270
α-Naphthol	Ether	*n*-Heptane	30,800^{c}	−140
α-Naphthol	Triethylamine	*n*-Heptane	30,800^{c}	−280
			34,540^{c}	−928
p-Naphthol	Ether	*n*-Heptane	30,800^{c}	−410
β-Naphthol	Triethylamine	*n*-Heptane	33,910^{c}	−184
			30,800^{c}	−590
Aniline	Benzene	Heptane	34,730^{a}	−160
Aniline	Dioxane	Heptane	34,730^{a}	−280
Aniline	Ether	Heptane	34,730^{a}	−410
			^{d}	−540
Acetanilide	Diethyl ether	"petroleum ether"	35,600^{e}	−189

[a] 1481; [b] 1478; [c] 1484; [d] 2056; [e] 1436.

enhanced electron density in the more peripheral portions of the molecule (a characteristic difference between bonding and antibonding orbitals) where the electrons are more accessible for H bond formation (1633). (See also 1850, 640a.)

It seems certain that the shifts caused by H bond formation contain interesting information for those cases for which the interpretation is not seriously complicated by other solvent interactions. In addition to empirical correlations which aid in establishing the type of transition, these shifts provide clues to the locale and nature of electron redistribution in the electronic transition. They furnish the only experimental evidence available concerning the H bonding properties of electronically excited states.

4.2.2 Hydrogen Bond Effects in Fluorescence. The importance of coupling emission studies with absorption spectra has been noted (1633). Together, these spectra permit determination of the zero-zero transition which measures directly the difference between H bond enthalpies of ground and excited states. (For the $n \longrightarrow \pi^*$ transitions, fluorescence data may be difficult to obtain, as noted by Kasha; see footnote 11 of 1633.) Of equal interest but more complicated interpretation is the effect of H bond formation on the intensity of fluorescence. Unfortunately, relatively little work has been reported.

Suhrmann and Perkampus (1973) observed the effect of acids on the fluorescence of 1,2,4-trimethyl-3-hydroxyphenazine. Acetic acid and alcohols seem to quench the fluorescence as well as alter the color of this pigment. Fujimori found the color and intensity of fluorescence of anthrone derivatives to be very sensitive to the H bonding perturbation (727). More revealing are the continued studies of Mataga, Koizumi, and co-workers (1356–1359). The fluorescence intensity of β-naphthol in *n*-hexane increases somewhat on addition of dioxane or acetate esters, with the exception of ethylchloroacetate which is extremely effective in quenching the fluorescence (1356, 1358). Their studies of *N*-heterocyclic bases show that the fluorescence quantum yield is changed upon H bond formation (1357, 1359). For acridine in benzene solution the relative yield of fluorescence is affected on addition of H bonding acid as follows: $CHCl_3$, 0.6; C_2H_5OH, 1.0; benzyl alcohol, 1.0; dichloroacetic acid, 9.5; and trichloroacetic acid, 11 (1359). See also studies of trypaflavin in solid solution (2214a), quinoline (1892), and aminonitrostilbene (1240). Special mention is warranted for the studies of Terinin, Yakovkin, and Volobuev on the fluorescence of benzaldehyde adsorbed on metal surfaces (2016, 2015). The color and intensity of the fluorescence reveal H bonding of the adsorbed material.

4.2.3 Phototropism. A compound is called phototropic if its color changes on irradiation with UV light. It seems amply clear that the electronic excitation by UV light induces an isomerization to a second configuration with an altered absorption spectrum. About 200 phototropic organic compounds are known (1234), and in at least some of these cases H bonding either influences the ease of isomerization or plays a role in the change of spectral absorption. Hausser, Jerchel, and Kuhn studied formazans, which form *intra*molecular N—H···N bonds (892). They propose that possibly the transformation between red and yellow forms requires a rupture and reforming of the H bond. W. Brode, Wyman, and co-workers examined a series of indigo and thioindigo dyes (286, 283, 284). One of the roles that the H bond may play is in preventing photochemical isomerization in some of the halogen substituted indigo dyes by preferentially stabilizing the *trans* configuration (284). Lindemann, on the other hand, suggests that the phototropy of anils (such as salicylidene-*m*-toluidine) involves the conversion from a configuration with *intra*molecular H bonds to a configuration with intermolecular H bonds. (See also 1929.)

In connection with this general phenomenon, note that Anslow and co-workers have proposed that dissociation of the H bond is important in certain UV transitions of H bonded species (57, 56, 1839). Anslow attempted to derive H bond energies from the observation of continua presumed to be associated with the breaking of the H bond. Her interpretation is not generally accepted (e.g., see criticisms of Davies, Holliday, and Ketelaar, *Discussions Faraday Soc.* **9**, 332–334, 1950).

4.3 Quadrupole Spectra

Allen reviews the experimental techniques and the information which can be obtained from pure quadrupole spectra of solids (28). The quadrupole coupling constant is determined by the curvature of the potential field near the nucleus (i.e., the second derivative of V with respect to distance). Therefore it is influenced by changes of the electron distribution near the nucleus. The method is, of course, restricted to compounds containing at least one nucleus with a nonzero quadrupole moment, and reveals only the electron distribution near that nucleus. Thus it is not applicable to the nuclei H^1, C^{12}, or O^{16}, but it does apply to D^2, N^{14}, Cl^{35}, and Cl^{37}.

Allen lists quadrupole coupling constants for a number of chlorine substituted acetic acids and acetamides (29, 28), and he discusses results for solid HCl. Although it is clear that he expects an effect of H bonding and anticipates the direction, Allen's data do not suffice to establish it.

More recently, O'Konski and Flautt have made quadrupole resonance studies of solid ammonia (1543). They observe a 12.6 percent decrease of the coupling constant upon condensation of NH_3 gas, and attribute the change to an increase of ionic character upon formation of H bonds. The even larger shift for ND_3 (21 percent) is hence interpreted as evidence that deuterium bonds are stronger than the hydrogen bonds.

CHAPTER 5

*Intra*molecular Hydrogen Bonds

> . . . meta- *and* para- *compounds . . . differ markedly from the* ortho- *compounds (a) in being less volatile, (b) in being more miscible (in the liquid state) with water, and (c) in being less miscible with benzene . . . this change depends on the simultaneous presence of two substituents of a reactive character, it must be due to some interaction between them; and as we find that it occurs only in the* ortho- *position, we may conclude that it is due to ring formation.*[a]
>
> N. V. SIDGWICK and K. CALLOW *Oxford, 1924*

Sidgwick and Callow were among the first to list criteria of formation of *intra*molecular H bonds (1875a). Their conclusion that ring formation is present in the *ortho* compounds is based upon the absence of the effects of the intermolecular H bonding shown by *meta* and *para* compounds. This chapter will provide many examples of the resulting nearly normal character of chelated compounds.

5.1 Introduction

Some of the important substances in which H bonds are formed are proteins, polypeptides, sugars, lignins, gelatin, starch, and other substances from living tissues. This area shares with polymer formation a prominent position among the most intriguing chemical problems. The

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[a] From *J. Chem. Soc.* **1924,** 530.

20-year old prediction (990) by M. L. Huggins that "the most fruitful applications of H bridge theory will be to a better understanding of complicated organic substances . . . ," still points in the correct direction.

To a large extent, the complex molecules in living matter have structures and properties that are determined by *intra*molecular H bonds. Although this type of H bond has some features in common with intermolecular H bonds, there are appreciable differences. We have already mentioned some of these differences, but it will be useful to codify the variations before discussing H bonding in proteins.

*Intra*molecular H bonds are conveniently treated separately from intermolecular H bonds for two reasons. First, they form only under specific, stringent spatial requirements; second, their formation does not create molecular association. Contrast intermolecular H bonds: there is no such spatial restriction, and most of the changes in physical properties result directly from association. Badger has reviewed *intra*molecular H bonds (99).

The spatial requirements produce an isomeric effect; e.g., the *ortho* isomer is distinguished from the *meta* or *para*, *cis* is distinguished from *trans*, and diequatorial or equatorial axial positions are favored over diaxial. Furthermore, it is likely that most *intra*molecular H bonds deviate from the optimum linear configuration described earlier (Section 3.3.6). Absence of association, the second factor, means that *intra*molecular H bond formation does *not* produce deviations from "normal" behavior.

*Intra*molecular H bonds do not form "chains" of molecules, but there may be many of these bonds in a single large molecule. Indeed, they are a major structural feature of proteins and are important in some synthetic polymers. Often they are present in an orderly, repetitive arrangement.

In the following sections we shall examine the effects of *intra*molecular H bond formation on the properties of the system and contrast them with intermolecular H bond behavior. We shall use, as far as possible, illustrative data on the simplest compounds, since the conclusions are most direct. Proteins form such an important class of *intra*molecular H bonded compounds that they are the subject of an entire chapter (Chapter 10). Internal H bonds in gases have been studied very little.

5.2 Some Examples

Although *ortho* substituted benzene compounds are probably the most commonly cited examples of *intra*molecular H bonds, other types of molecules show the same phenomena. A few of the well recognized and relatively simple cases are shown in Fig. 5-1. Toward the end of this chapter (Fig. 5-7), some more speculative examples are given.

The compounds shown in Fig. 5-1 illustrate several points. *Intra*molecular H bonds occur quite generally, and the same groups (O—H, N—H, C=O) that provided the principal examples of intermolecular H bonds are most prominent in chelation. The rings formed by internal H bonds usually have five, six, or seven atoms in them, although again proteins are a conspicuous exception. Another expression of the same fact is to say that the two H bonding functional groups must be located in certain relation to each other. They are most commonly in positions described as *ortho*, *peri*, α, or β.

5.3 Comparison of Properties

We begin our detailed discussion of *intra*molecular H bonds with a summary, Table 5-I, showing in a general way how the two methods of satisfying H bonding ability affect various physical (and a few chemical) properties. Most of these properties have been discussed in Chapters 2–4, where intermolecular bonds were emphasized. In Table 5-I the comparison for both inter- and *intra*molecular compounds is with a "normal" substance, i.e., one with no H bonding, such as a hydrocarbon.

Notice the large number of properties (at top of Table 5-I) for which normal behavior can be expected in chelates. This tendency is perhaps the most characteristic generality for *intra*molecular H bonded compounds. However, it is not unanimous for all properties.

5.3.1 Infrared Spectral Behavior. The spectral differences between chelated and nonchelated substances are large and readily apparent. In fact, the initial recognition of IR spectra as a useful criterion of H bonding was based on studies of chelating compounds (see Section 3.1.1). In general behavior, the vibrational bands are affected in the same manner by *intra*- and intermolecular H bonding. However, the changes differ in that a given shift in ν_s is accompanied by increases in band width

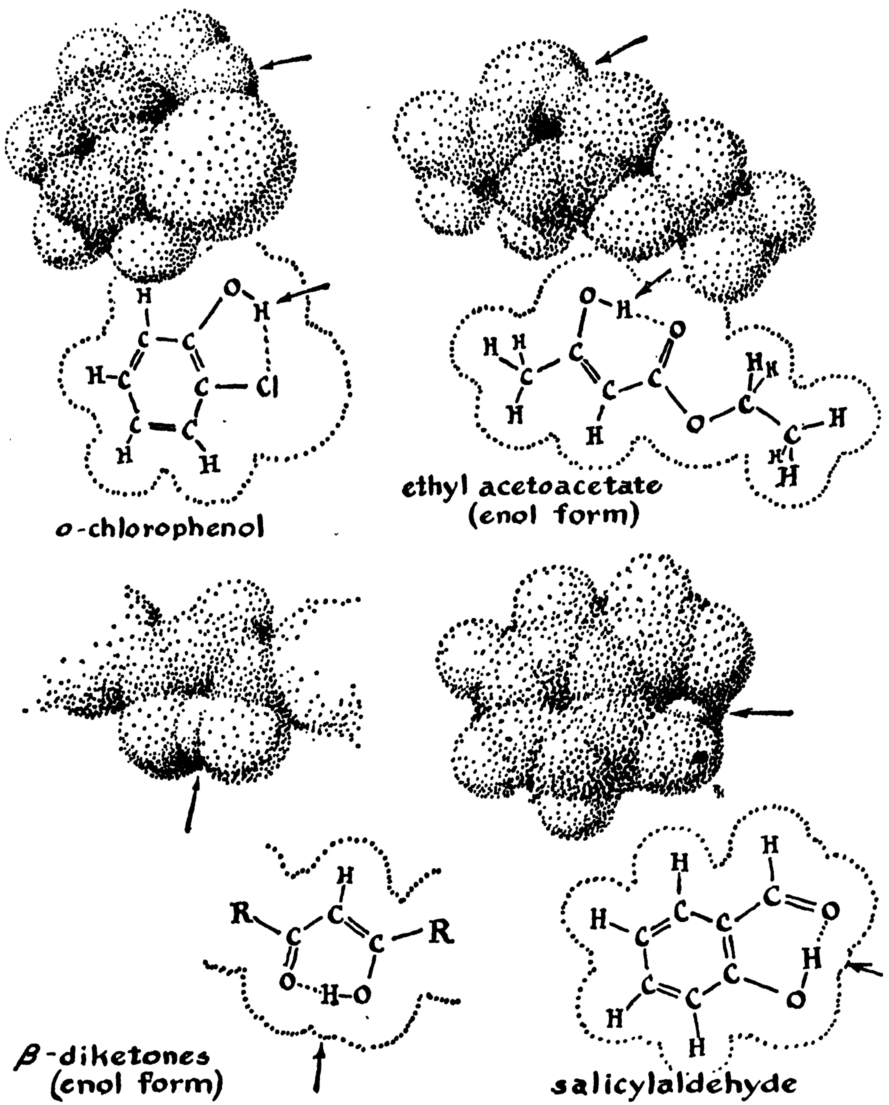
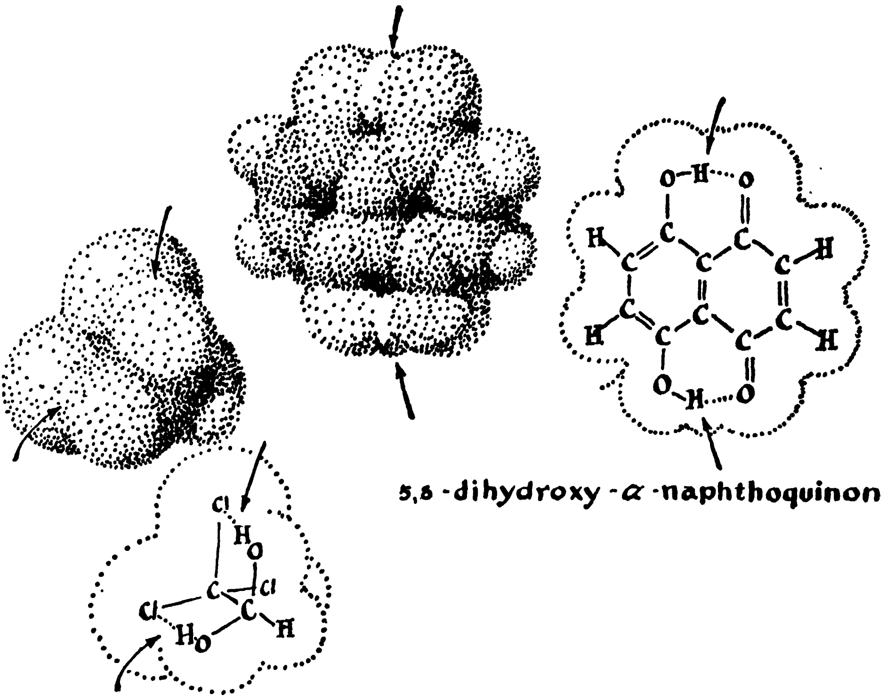


FIGURE 5-1 Some common *intra*molecular H bonds. *This page:* *o*-chlorophenol; ethyl acetoacetate (enol form); β-diketones (enol form); salicylaldehyde. *Facing page:* 5,8-dihydroxy-α-napthoquinone; chloral hydrate; α-acetylamino acetamide.

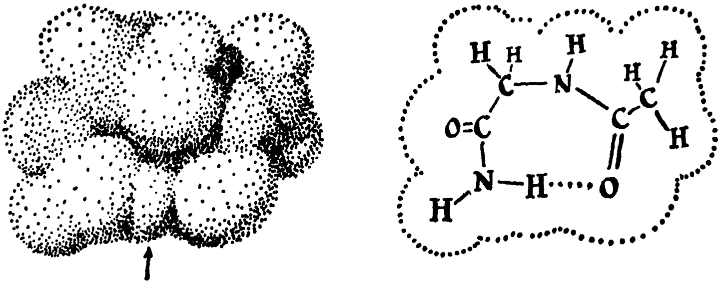
and intensity which are much smaller than those for intermolecular H bonds (see Figs. 3-13 and 3-14).

Some examples of IR spectral behavior for other modes of vibration are contained in a paper by Bratož, Hadži, and Rossmy (269). They



5,8-dihydroxy-α-naphthoquinone

chloral hydrate



α-acetylamino acetamide

assigned $\nu_s(OH) = 2700 \pm 100$ cm^{-1} (broad), $\nu_b(OH) = 1435 \pm 35$ cm^{-1}, and $\nu_t(OH) = 948 \pm 12$ cm^{-1} for five β-diketones and β-ketoesters. The choice of $\nu_b(OH)$ in these chelated compounds may be compared to that for ν_b in monomeric alcohols (Table 3-XIV). The higher frequency of ν_b for the chelated compound is in qualitative agreement with the known effects of H bonding on ν_b. For ν_t the high value selected by Bratož *et al.* is also consistent with the direction of shift observed for

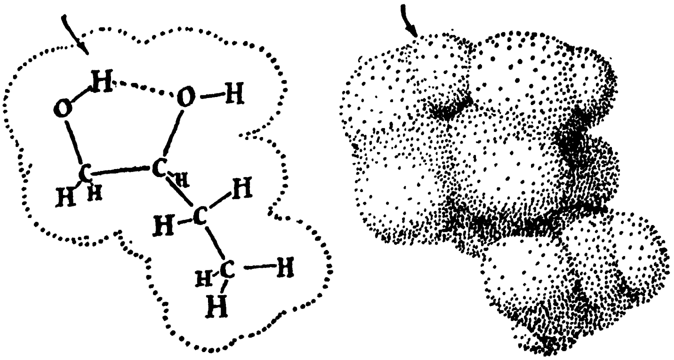
TABLE 5-I A General Comparison of the Behavior of Inter- and *Intra*molecular H Bonds

PROPERTY	COMPOUND WITH INTRAMOLECULAR H BOND	COMPOUND WITH INTERMOLECULAR H BOND	REFS.
1. Structural form	Most common in *ortho*, *cis*, *peri*, diequatorial, equatorial axial positions	Most common in *meta*, *para*, *trans*, diaxial positions	
2. Molecular weight	Normal	Increased	
3. Molar volume	Lower	Lower	
Molar refraction	Higher		68
Viscosity	Lower	Higher	1097
Parachor	Lower	Lower	
4. Vapor pressure	Normal	Decreased	
5. Conductivity			
Thermal	Normal	Higher	1144, 1571
Acoustic	Normal	Higher	1027
Electrical	Normal	Can be high if H bond network forms	2234, 307
6. Solvent power	Normal	Higher if H bonds to solute	
7. Melting point	Normal	Higher	
Boiling point	Normal	Higher	
8. Vibration spectra			
Location: stretch	Shifted down	Shifted down	
Location: bend	Shifted up	Shifted up	
Concentration dependence	None	Present	

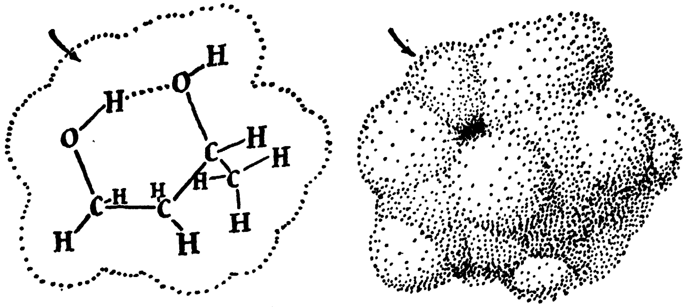
Frequency shift, $\Delta\nu_s$	Determined by functional groups and size of ring formed	Determined by functional groups	
Effect of phase change	Little	Much	
Correlations			
Intensity of ν_s	Increased somewhat	Increased very much	
Half width of ν_s	Increased somewhat	Increased very much	
9. Dielectric properties			
ϵ, solids	Normal	Higher	
ϵ, liquids	Variable according to shape of molecule	Variable according to shape of molecule	
Dipole moment	Lower than calc. from structure	Higher	1286
Conc. dependence of dipole moment	None	Increase with conc.	1380
10. Reaction mechanism	Often determined by *intra*molecular H bonds	Often determined by intermolecular H bonds	See Section 5.3.8
Reaction rate	Can make faster or slower	Can make faster or slower	See Section 5.3.8
11. Linearity of bond	Usually bent	Usually straight	
12. NMR chemical shift			
Direction	Shifts to lower field	Shifts to lower field	981
Concentration dependence	Small	Large	
13. Optical properties			
Rotation	Can be large if form spiro rings	Usually none	1734
Electronic absorption	Shifted	Shifted	
Phototropy	Often exhibited	Seldom exhibited	1234
14. Surface tension	Lower	Higher	

intermolecular H bonding (see Section 3.4.2). (See also 852 for assignments of ν_b and ν_t in hydroxyquinones.)

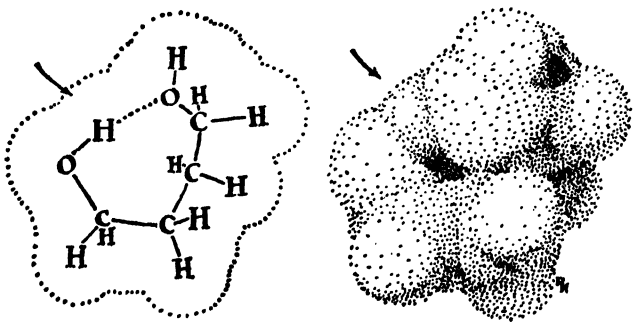
As a further example, Urbański reports that both the symmetric (1567 cm^{-1}) and asymmetric (1340–1361 cm^{-1}) NO_2 stretching modes in nitroalcohols are shifted to lower frequencies (1543–1555 cm^{-1} and



1,2-butanediol



1,3-butanediol



1,4-butanediol

FIGURE 5-2 Structures resulting from H bonded rings of various sizes.

1310–1319 cm^{-1}) when the NO_2 is adjacent to an O—H group (2080). Again this direction of shift is that expected for a stretching mode of the basic group (see Section 3.4.4).

In solutions there is a dissimilarity in spectral response which gives a conclusive distinction between inter- and *intra*molecular H bonds. *Intra*molecular bonding (and H bonded spectral behavior) is retained even at the lowest concentrations. In contrast, the spectral changes resulting from intermolecular H bonding are lost at low concentrations as the association is disrupted.

One of the most rewarding applications of IR spectral data is in the deduction of structural conformations. One such use has just been mentioned: the identification of enol formation for β-diketones, β-keto-esters, β-ketoaldehydes, etc. (269). Another use is the verification of an *ortho* or *cis* relationship between two functional groups which can form a H bond. A less obvious but potentially more powerful application is in the deduction of structural conformation in the more flexible, saturated cyclic compounds. The systematic work of Kuhn (1162), quoted in Table 3-VI, demonstrates the possibilities. For the cyclohexane diols the presence of just one ν_s(OH) band gives convincing evidence of a conformation in which the O—H groups are separated such that *intra*molecular H bonding cannot occur. If two ν_s bands appear, the lower frequency band is assigned to a H bond. For noncyclic compounds the pattern of shifts in the last column of Table 3-VI shows that the frequency contains additional information about the geometry of chelate ring formation. Thus the difference between $\Delta\nu_s$ of 1,3-propanediol (76 cm^{-1}) and 1,4-butanediol (156 cm^{-1}) reflects the stronger H bond in the latter, the less-strained, seven-membered chelate ring. Figure 5-2 illustrates the differences in 5-, 6-, and 7-atom, H bonded rings. This large difference is a sensitive criterion of the geometrical relationship, a criterion which should be valuable in the deduction of the structures of more complicated chelated molecules such as proteins and alkaloids.

A few recent studies in which IR spectra have been helpful in fixing conformations are listed in Table 5-II.

The determination of H bond base strength from spectral studies is possible for chelated substances as well as for intermolecular H bonded materials (see Table 3-II). Chelated substances provide a unique opportunity to know and control the spatial arrangement of the interacting groups. In a study of this type, Hoyer examined many *ortho*-substituted phenols (962) and found increasing base strengths as follows:

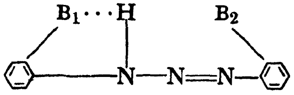
$\mathrm{I} < \mathrm{Br} < \mathrm{Cl} < (\mathrm{F})$, —$NO_2$, $>$C=O (ketone, ester), —N=N—

A different tack is taken by Farmer, Hardie, and Thomson (632), who examined the tautomerism of *ortho*-disubstituted diazoaminobenzenes. Whichever of the two possible tautomers, I or II, is present in the larger concentration is influenced by the N—H interactions with B_1

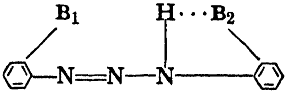
TABLE 5-II *Intra*molecular H Bonding and the Determination of Molecular Conformation by IR

COMPOUNDS	REFS.
Spiro [4, 4] nonanediols	323
Anthraquinone derivatives	963
Chloramphenicol	1979
3-Hydroxy-2-butanone	558
Diethyltartrate	2057
Ethyllactate	2057
3-Hydroxy-2-naphthanilide	966
Tropolone	1170
2-Hydroxy-2′,*x*′-dinitrostilbene	967
Nitrous acid	1547
Phenacylpyridines	266

I



II



and with B_2. If the N—H group forms a H bond with both B_1 and B_2, the relative concentrations of the two tautomers measure the relative values of ΔH of H bond formation. The IR spectra of the symmetrically disubstituted diazoaminobenzenes ($B_1 = B_2$) are presumed to define characteristic frequencies and intensities that permit identification of a particular tautomer. For example, these workers estimate that the ratio of I to II is 4.5 when B_1 is —$CO_2C_2H_5$ and B_2 is —NO_2, and between 2 and 3 when B_1 is —$COCH_3$ and B_2 is —NO_2. If all of this change[a] is

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[a] This is clearly only a first approximation, since no consideration has been given to entropy effects or to possible resonance differences between I and II which are determined in part by the skeleton.

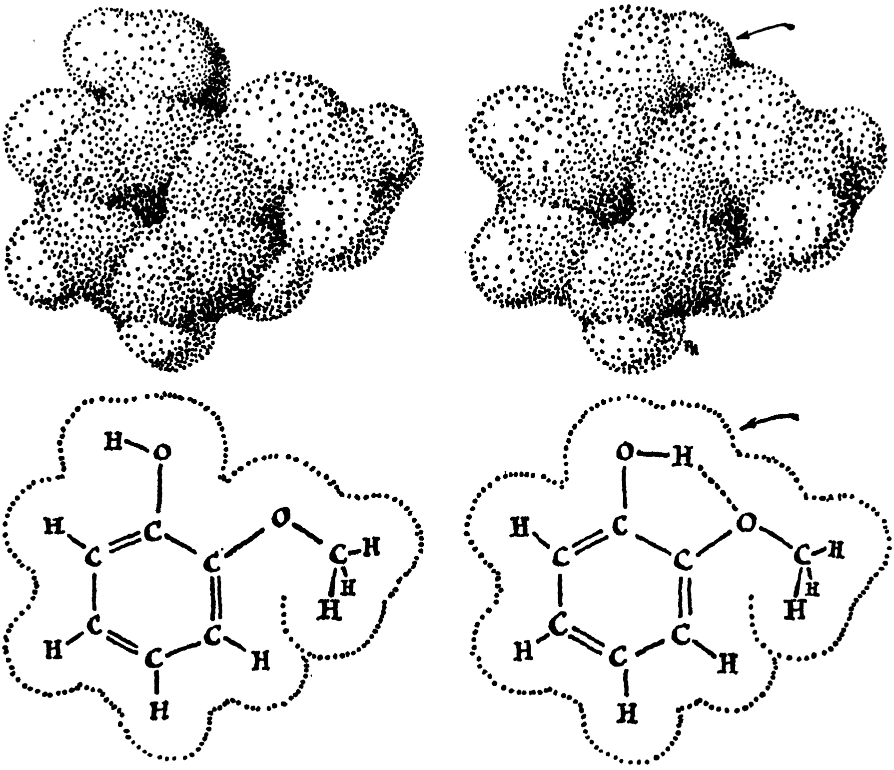
attributed to a difference in the ΔH of H bond formation, we calculate that (under the conditions defined by this molecular conformation) the N—H bond to the acetyl carbonyl is 0.4–0.7 kcal more stable than the N—H bond to —NO_2. Similarly, the H bond to the ethyl ester carbonyl is 0.9 kcal more stable than that to —NO_2, hence 0.5–0.2 kcal more stable than the N—H· · ·acetyl bond. These results probably give the most direct path for attempting correlations between ΔH and spectral properties of interacting groups. Farmer *et al.* have as yet studied few compounds, but the technique obviously has potential.

5.3.2 Thermodynamic Properties. There is not enough thermodynamic data available to enable formulation of a general rule regarding the values for *intra*molecular H bonds. Appendix B contains ΔH for a few cases, but there is no noticeable trend. See Chapter 7 for a discussion of the thermodynamic properties of H bonds.

5.3.3 Dielectric Properties. It is not possible to make a simple general statement of the effect of internal H bonds on electrical behavior. The orientation of the various dipoles within the functional group and the arrangement of groups in the molecule determine the measured quantities ϵ and μ. Hydrogen bonding always affects the dipole orientations, but the resulting change in ϵ and μ varies both in direction and magnitude. For example, there are crystals of both inter- and *intra*molecular H bonded substances with molecular positions such that the dipole vectors tend to have the same orientation, giving a high dielectric constant. In other crystals, the opposite is true: the H bonds restrict the dipoles to orientations which give a low dielectric constant. See Table 2-II for a few values of dielectric constant and dipole moment, and the beginning of Section 2.1.2 for generalizations.

Dielectric studies have been applied principally to the problem of deciding between several possible structures. A typical H bonded example may be taken from one of Curran's papers (467); *o*-methoxyphenol (guaiacol) has two possible planar configurations whose dipole moments, as calculated by the vector addition method, are widely different (Fig. 5-3). The measured value of 2.41 D indicates that the *intra*molecularly H bonded form exists in the benzene and dioxane solutions used. A large number of phenols, aniline derivatives, and other disubstituted aromatic compounds have been studied in a similar fashion, and the wide occurrence of the *ortho* effect has been demonstrated. If two adjacent positions of the ring have proper substituents, a H bond will form.

This argument holds also for saturated ring and alkyl compounds,



trans-trans $\mu = 0.8$ D *cis-trans* $\mu = 2.45$ D

FIGURE 5-3 Possible planar configurations of *o*-methoxyphenol (guaiacol).

but the additional flexibility of the carbon skeleton adds to the difficulty of interpretation.

5.3.4 Melting and Boiling Points. Generally, molecules forming *intra*molecular H bonds have melting and boiling points about equal to those of non-H bonded molecules of similar size and shape. This reflects the unimolecular state of *intra*molecularly bonded materials. Without multiple units, the molecular weight is normal, and hence boiling point and vapor pressure are similar in *intra*molecular H bonded substances and substances in which no H bonding can occur. Table 5-III illustrates the "normality" of the phase change temperatures in internally H bonded substances. Two papers dealing specifically with boiling points of internally H bonded substances are those by Lutskiĭ (1273), and the Martinets (1346).

One way of distinguishing chelation from intermolecular association is based on one aspect of melting point behavior. The melting point of

TABLE 5-III Comparison of Melting Points of *Intra-* and Intermolecular H Bonded Liquids[a]

COMPOUND	MOLECULAR WEIGHT	MELTING POINT (°K)	TYPE OF H BOND
o-Hydroxybenzaldehyde	122	266	*intra*
o-Aminobenzaldehyde	121	312	*intra*
o-Methoxybenzaldehyde	136	309	none
p-Hydroxybenzaldehyde	122	388	inter
p-Aminobenzaldehyde	121	344	inter
p-Methoxybenzaldehyde	136	273	none
1-Hydroxy-2-acetonaphthone	186	376	*intra*
3-Hydroxy-2-acetonaphthone	186	385	*intra*
4-Hydroxy-2-acetonaphthone	186	446	inter
6-Hydroxy-2-acetonaphthone	186	444	inter
2-Acetonaphthone	169	329	none

[a] See also Table 2-VIII.

the substance is lowered by the addition of some compound (usually water). The water, by virtue of its H bonding ability, displaces the *intra-* or intermolecular H bonds already present. But for the associated systems this produces a more pronounced change in structure and a greater depression of freezing point. Table 5-IV lists typical results.

TABLE 5-IV The Use of "Wet" and "Dry" Melting Points to Discriminate Between *Intra-* and Intermolecular H Bonding

COMPOUND	REFS.	MELTING POINT (°C) DRY	WET	Δ m.p.	H BOND TYPE
o-Acetamidoacetophenone	371	78	63	15	*intra*
p-Acetamidoacetophenone		167	117	50	inter
N-(*o*-nitrophenyl)benzamide[a]	371	93	85	8	*intra*
N-(*p*-nitrophenyl)benzamide[b]		196	167	29	inter
o-Hydroxydiphenylsulfone	42	96–98	83.5	12.5	*intra*
p-Hydroxydiphenylsulfone		135–136.2	84	51	inter
1-Nitro-2-acetnaphthalide	371	123	110	13	*intra*
4-Nitro-1-acetnaphthalide		190	144	46	inter
8-Nitro-2-acetnaphthalide		195	154	41	inter

[a] Called *o*-nitrobenzanilide by original authors.

[b] Called *p*-nitrobenzanilide by original authors.

Binary mixtures containing an *intra*molecular H bonded component often have normal melting point diagrams, compound formation being inhibited or absent. A striking example is shown in Fig. 5-4 (taken from 571). The *o*-nitrophenol-acetamide pair shows just a eutectic—the H bonding capacity of the nitrophenol is used internally, not in attaching to acetamide. In contrast, both *meta* and *para* isomers form compounds with acetamide.

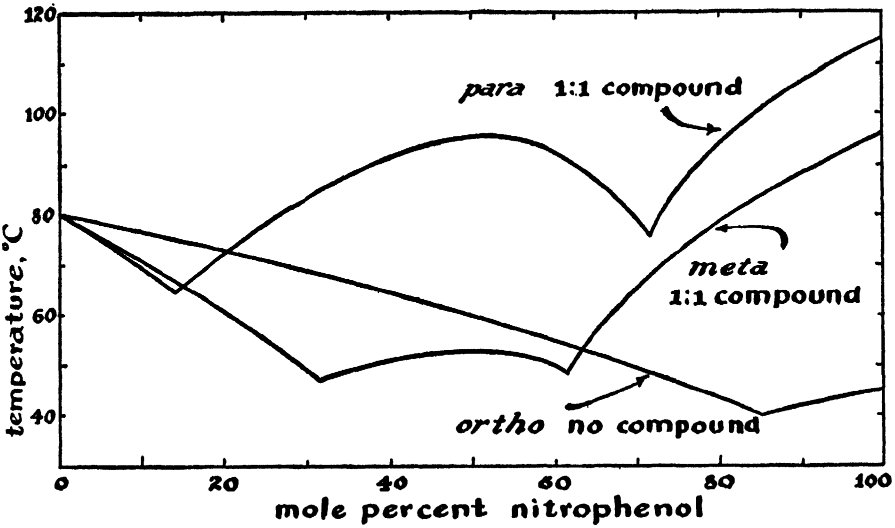


FIGURE 5-4 Melting point diagrams for nitrophenol-acetamide mixtures. [From Dzhelomanova, Rudenko, and Dionis'ev, *J. Gen. Chem. U.S.S.R.* **26,** 1866 (1956).]

5.3.5 Solubility. According to our classification system, all *intra*molecular bonded materials should be Class AB. Consequently, they should be soluble in solvents from Classes AB, B, and A, provided the solvent can successfully compete with the internal H bonding. Because of the internal satisfaction of the H bonding tendency, Class N solvents should be better solvents for internally H bonded materials than for nonchelated compounds. This is the behavior observed, as shown in Table 5-V for dihydroxybenzenes in CCl_4. In the stronger acid and base solvents, the loss of chelation is suggested. Further, for this case, the table shows a similarity in the solubilities of *ortho* and *meta* isomers.

The solubility behavior of chelated compounds is indirectly shown in another way for diketones that can enolize. Meyer (1394) determined the enol/keto ratios for several diketones and found that with various solvents the ratios increased in the order H_2O < methanol < $CHCl_3$ <

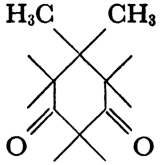
TABLE 5-V Solubility of Dihydroxybenzenes in Several Solvents[a]

SOLVENT	CLASS	SOLUBILITY OF THE DIHYDROXYBENZENES (moles/100 g sat. soln. at 40°C) ORTHO	META	PARA	REMARKS
CCl_4	N	0.64	0.2	0.1	
Benzene	N or B	1.84	0.6	0.2	Too weak a base to disrupt *intra*molecular H bonds
$CHCl_3$	A	3.3	0.8	—	Too weak an acid
H_2O	AB	22	30	2.1	Both solvent and solute are H bonded
Ethanol	AB	44	45	22	Strong acid for H bonding
Acetone	B	54	56	19	Strong base for H bonding

[a] 1827, pp. 364–366, 391, 394, 396.

ethanol < benzene ≪ hexane. Thus, the form which has *intra*molecular H bonds is least prevalent in the first solvents, where solubility depends on H bonding to solvent and increases as that factor becomes less important.

Angell and Werner (53) report that a cyclic β diketone, dimedon,



does not enolize because an internal H bond is sterically impossible.

5.3.6 Ionization. Ionization, particularly of dibasic acids, is also affected by H bonds within the molecule. Usually, the first ionization constant is abnormally large and the second abnormally small, the latter effect being more pronounced. McDaniel and Brown (1299), extending a proposal by Jones and Soper (1048), concluded this behavior was caused by H bonding. Some data selected from their papers and others (375, 2162, 532) are shown in Table 5-VI. In each pair of compounds, only the second can form *intra*molecular H bonds. The table indicates clearly the significant role of chelation in altering ionization constants. Of course there may be other factors besides chelation, as suggested by Westheimer and Benfey (2163).

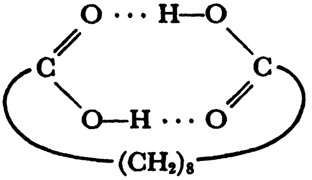
Dondon (532) points out that a high K_1/K_2 ratio is not expected if the

TABLE 5-VI Ionization Constants for Some Multicarboxylic Acids in Water at 25°C

ACID	$10^4 \cdot K_1$	$10^7 \cdot K_2$	K_1/K_2
Fumaric ("*trans* maleic")	9.57	413	23.2
Maleic	120	5.95	20,200
Succinic	0.64	33.3	19.2
Tetramethylsuccinic	3.19	0.52	6,130
trans-Cyclopropane-1,2-dicarboxylic	2.2	74	29.7
cis-Cyclopropane-1,2-dicarboxylic	4.7	3.4	1,380
trans-Caronic[a]	1.52	47.8	31.8
cis-Caronic[a]	45.9	0.0494	929,000
p-Phthalic	3.1	152	20
o-Phthalic	12.1	36	333
	K_2	K_3	K_2/K_3
Ethylenediaminetetraacetic	$2 \cdot 10^{-3}$	$6.3 \cdot 10^{-8}$	31,800
	K_3	K_4	K_3/K_4
Diethylenetriaminepentaacetic	$3.3 \cdot 10^{-5}$	$1.7 \cdot 10^{-9}$	19,400
	K_4	K_5	K_4/K_5
Triethylenetetraminehexaacetic	$5.5 \cdot 10^{-7}$	$2.1 \cdot 10^{-10}$	2,620

[a] *gem*-Dimethylcyclopropane-1,2-dicarboxylic acid.

molecule can form an "inner dimer" as it might for a long dibasic acid (e.g., in the C_{10} dibasic acid, $K_1/K_2 = 10$).



In polybasic acids, the effect of chelation appears between later *K*'s. For example, in ethylenediaminetetra-acetic acid the first two hydrogen ions can dissociate readily, but the third and later ionizations are greatly hindered by H bonding.

The ionization of hydroxy-substituted benzoic acids is also affected by chelation. If *intra*molecular H bonding is possible, the carboxylic acid ionization constant is raised due to the stabilization of the anion (265, 114, 273). This is illustrated in Table 5-VII.

TABLE 5-VII Increased Ionization by H Bonded Anions

ACID	$10^5 \cdot K$	K/K Benzoic
Benzoic	6.27	(1.00)
o-Hydroxybenzoic	101	16.1
p-Hydroxybenzoic	2.95	0.47
2,6-Dihydroxybenzoic	5200	830

This dramatic consequence of chelation has been interpreted theoretically by several workers. Hunter applied his views on mesohydric tautomerism (see our Chapter 6) (1001). Davison disagrees, arguing that the spectra do not show the H bonded ion (508). Nash (1492) proposed resonance forms different from Hunter's.

Some less reliable H bond interpretations of dissociation data have been made. For example, Dippy (526) proposed that a C—H···O bond from γ carbon to C=O formed a ring in C_4-C_9 acids, to account for the fact that their ionization constants do not fall as rapidly as do those of C_2 and C_3 acids. A case in aromatic compounds is given by Arnold and Sprung (64). Some later work (907) makes use of the same idea to explain the K_A of a partially fluorinated valeric acid, ($CF_3(CH_2)_3COOH$). This scheme of H bonding has not been substantiated, and there is still controversy—the discussion at the end of one of Katchalsky's papers is illustrative (1089).

Gero (745) explains the irregular acidity values of a series of methylenediamines as being caused, in part, by internal H bonding in the trimethylene compound. As a final example, the work of Jaffé and coworkers (1030) illustrates the effects of these bonds in aromatic phosphonic acids. The phosphono group (—PO_3H_2) can accept a hydrogen atom, which increases ionization, or donate one, which decreases ionization of the group.

The last case illustrates the complicated behavior possible if both *intra-* and intermolecular H bonding are present. Such combinations, called "mixed association" by Lutskiĭ (1274), are common among compounds with several proton donor and acceptor groups. Forecasting which type will dominate is difficult. Other examples besides the phosphonic acids are dihydroxy, hydroxy, or amino acids, and polybasic acids.

5.3.7 Optical Properties. The most obvious effect of *intra*molecular H bonding on optical properties is the part it plays in determining the color of compounds. Section 4.2.1 treats dyes as well as other compounds in which the spectral influence of H bonding is outside the visual range. The extended generalizations there can be summarized as follows: H bond formation can cause shifts of the electronic spectra in either direction, the direction being usually predictable from the type of transition occurring. Some color forming reactions have been suggested as means for determining the presence of H bonds and distinguishing between internal and intermolecular types (1689, 1610). Such reactions should be applied with caution, since their specificity is unproved.

The frequency shifts caused by *intra*molecular H bonds furnish an aid to structure determination. Examples of compounds which are not included in the earlier discussion of dyes (Section 4.2.1) are given in Table 5-VIII.

TABLE 5-VIII Compounds for which *Intra*molecular H Bonds Cause Frequency Shifts in the UV-Visible Region

COMPOUNDS	REFS.
Substituted phenols	408, 318, 1285, 2090
Salicylaldehyde and derivatives	2089a
Acetylacetone	1696
Hydroxypyridines	230
Anthraquinones	1617
Phenylpyrimidines	1765
Dihydroxyacetophenones	2089
Substituted benzoic and naphthoic acids	196

*Intra*molecular H bond formation can cause optical rotation (650, 1523) by giving the molecule a helical shape and hence "form rotation." Robinson and Bott (1734) show the large increase in rotation resulting from ring forming H bonds in a copolymer resembling proteins. A thorough discussion of the topic is not available.

Phototropism, a color change resulting from irradiation with UV light, seems to be connected with *intra*molecular H bonding. This topic is discussed in Section 4.2.3.

5.3.8 Reaction Mechanism and Kinetics. Either *intra*- or intermolecular H bonds can be an important factor in determining both reaction rate and mechanism. Since their effects are similar, the intermolecular cases will be considered as well as the *intra*molecular cases. Knorre and Emanuel have reviewed this field (1120).

The effect of chelation on reaction rates is clearly indicated by data of Vavon and Montheard on the speed of several reactions of aldehydes and ketones (2108). Some of their data are shown in Table 5-IX. The chelated aldehydes often react much more rapidly than their associated isomers, and the nonsubstituted aldehydes react at an intermediate rate. This order is changed for other reactions such as hydrogenation on platinum and oxidation by chromic acid.

TABLE 5-IX Rates of Phenylhydrazone and Oxime Formation of Aldehydes as Related to Internal H Bonding

	PHENYLHYDRAZONE		OXIME	
ALDEHYDE	HALF-TIME[a]	RATIO[b]	HALF-TIME	RATIO
Benzaldehyde	9	Reference	0.7	Reference
o-Hydroxybenzaldehyde	0.7	0.078	0.7	1.0
p-Hydroxybenzaldehyde	200	22	9	13
1-Naphthaldehyde	195	Reference	5	Reference
2-Hydroxy-1-naphthaldehyde	0.7	0.0036	1	0.20
4-Hydroxy-1-naphthaldehyde	370	1.9	120	24

[a] Time in minutes for half completion of reaction.

[b] Half-time divided by half-time for reference aldehyde.

E. C. Wagner and collaborators have published a series of papers (1759, 1682, 1760, 1406) that show the influence of *intra*molecular H bonding in isomeric compounds such as 4(7)-nitrobenzotriazole.

Because of the H bond in the 4(7) compound, there is a restricted tautomerism. The conjugated double bond arrangement is to some extent "frozen" in the 7-nitro tautomer shown in Fig. 5-5. The results

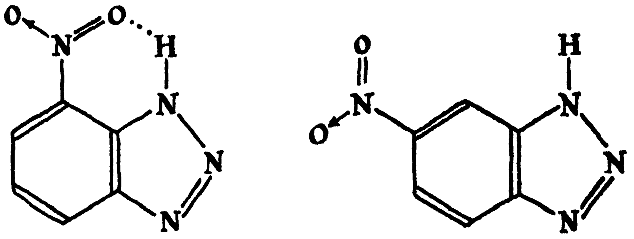
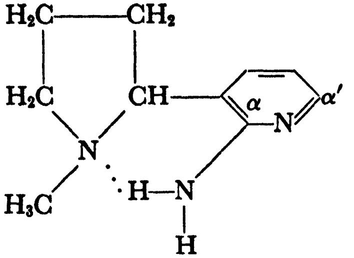


FIGURE 5-5 Isomeric nitrobenzotriazoles.

are high volatility, lower acidity, less association in solution—the typical properties of chelated molecules. In addition, the internally bonded form is more easily reduced polarographically.

Gol'dfarb and Kondakova (789) describe the different paths that reactions can take. They report that alkyl iodides substitute in the pyridine part of α-aminonicotine (internally H bonded),



but with α'-aminonicotine the same reagents give alkiodides.

Astle (81, 80, 79) studied the polarographic reduction potentials of a number of nitrophenols, nitrocresols, and nitroresorcinols. In all cases he found reduction easier when internal H bonding was present. Indeed, the reduction stopped at hydroxylamines in acid solution where *intra*molecular H bonds could stabilize this product but went on to amines in basic media. Similar results were found in hydroxyacetophenones (2088). (See Section 11.2.2 for additional comments on polarography.)

As another example, Knorre and Emanuel (1121) give the following rate constants, (k), for the reaction of hydroxylamine hydrochloride with hydroxybenzaldehydes at 28°C:

ortho: $k = 42.8 \cdot 10^{-3}$/sec
meta: $k = 15.8 \cdot 10^{-3}$/sec
para: $k = 5.9 \cdot 10^{-3}$/sec

The corresponding three nitrobenzaldehydes all have practically the same reaction constant, so the high value for the *ortho* isomer is attributed to the chelate H bond weakening the C=O bond.

Consider another set of results, this from Pekkarinen's work (1604) on hydrolysis of esters (Table 5-X), which shows the lower reaction rate in the chelated ester and the higher activation energy required to overcome this restraint.

Shaw and co-workers (1838) have finished a series of papers on the decomposition of thioureas. They suggest an ionized, H bonded intermediate (Fig. 5-6) and note that the tetramethyl compound does not

TABLE 5-X Rates of Hydrolysis and Activation Energies of Some *cis-trans* Isomeric Esters

ESTER	*k* (liter mole/sec at 25°C)	*k* (*trans*) / *k* (*cis*)	ACTIVATION ENERGY (kcal)
Diethyl fumarate	4.47	11	11.6
Diethyl maleate	0.407		11.5
Monoethyl fumarate ion	0.158	32	11.1
Monoethyl maleate ion[a]	0.00486		13.4

[a] Only case where inner H bonding can occur.

react at all—presumably because of inability to form the necessary H bond.

Next, consider reactions in which H bonds between molecules may affect the rate of reaction by taking part in the reaction itself or by altering the properties of a reactant. Palit (1570) has formulated a general principle in terms of H bonding helping or working against the electron shift necessary for the reaction, and has analyzed several cases. He makes the point that the rate can change in either direction as the H bond covers or opens the "active center" (see also 1284). Some reactions in which H bonds in the activated complex have been proposed are: (1) the self-condensation of polyglycine esters (1703); (2) acetal formation from vinyl alcohols (747); (3) formation of cyanohydrins (1981); and (4) inhibition of phenol alkylation by dioxane (881). This list is illustrative but by no means complete.

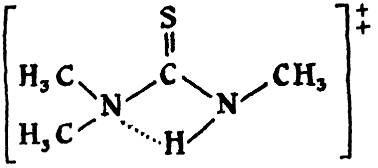
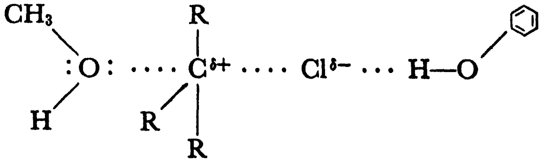


FIGURE 5-6 A H bonded intermediate in the decomposition of thioureas. [From Shaw and Walker, *J. Am. Chem. Soc.* **79**, 4329–31 (1957).]

We may examine particularly the displacement reaction of methyl halides as discussed by Swain (1981a, 1982). He showed that the reaction is termolecular and depends in part on H bonding. The transition state is envisioned as



Szwarc and Smid (1986) suggested the possibility of intermolecular H bonding of the radicals from benzoyl peroxide to trifluoroacetic acid, in order to explain the different products from this reaction and that of the acid with propionyl peroxide.

The sensitivity of reaction mechanism and rate to H bonding is probably not as well known as are some other effects. Many questions concerning the form of intermediates or reaction complexes, the thermodynamic changes taking place and the effects of solvents and adjacent groups are, as yet, unanswered. In this section we have shown that H bonds influence a wide variety of reactions, that this influence is directionally unpredictable by general rules, and that often it is important.

5.3.9 Viscosity. The best summary of the effect of inner H bonds on viscosity is that of Friend and Hargreaves (722). They show in conclusive fashion that the viscosity of *ortho*-substituted aromatics is lower than that of associated *meta* and *para* forms and essentially the same as that of similar non-H bonded compounds—another reflection of the tendency toward normalcy resulting from internal satisfaction of H bonding capacity. Figure 1-2 shows the structure of *ortho*- and *para*-hydroxybenzoic acid.

As sample values of viscosity, compare the data in Table 5-XI. Notice the substituted anilines. Here, even though an *intra*molecular H bond may form in the *ortho* isomer, the second amino hydrogen gives intermolecular association, and *ortho*- and *para*-chloroaniline have similar viscosities. Both values are larger than that shown for the nonassociated *o*-chlorotoluene. Dihydroxybenzenes and derivatives provide similar data (721) as do nitroanilines, although these compounds are further complicated by intermolecular H bonding. They show "mixed association."

5.3.10 Density and Molar Volume. It is to be expected that compounds with intermolecular H bonds would have higher densities (and lower molar volumes) than internally bonded isomers. Of course, a meaningful comparison can be made only if data are available for similar compounds at the same temperature and in the same physical state. Some data are presented in Table 5-XI. In each case the *ortho*- isomer has lower density than those of the *meta*- and *para*- isomers. Furthermore, the H bonded compounds are more dense than similar non-interacting substances, a point made earlier in Table 2-XVI.[a]

---

[a] The densities of the hydroxybenzaldehydes are below those of the methoxybenzaldehydes because of the large temperature difference.

TABLE 5-XI Viscosity and Density of *Intra*- and Intermolecular H Bonded Compounds[a]

COMPOUND	VISCOSITY (millipoises at 150°C)	DENSITY, d_4^{20} (g/cc)	MELTING POINT (°C)	H BONDING TYPE
o-Hydroxybenzaldehyde	4.91	1.0343 (150°)	−7	*intra*
p-Hydroxybenzaldehyde	30.8	1.129 (130°)	115	inter
o-Methoxybenzaldehyde	5.42	1.1326	36	none
p-Methoxybenzaldehyde	—	1.123	0	none
o-Nitrophenol	6.23	1.447	45	*intra*
m-Nitrophenol	—	1.485	97	inter
p-Nitrophenol	20.80	1.468	114	inter
o-Nitrophenylmethyl ether	7.00	1.2540	10	none
m-Nitrophenylmethyl ether	—	1.373 (18°)	38	none
p-Nitrophenylmethyl ether	—	1.233	54	none
o-Hydroxyacetophenone	5.02	1.1307	oil	*intra*
m-Hydroxyacetophenone	20.0	—	96	inter
o-Methoxyacetophenone	—	1.0849	—	none
m-Methoxyacetophenone	—	1.0993 (15°)	oil	none
o-Chloroaniline	3.40 (210°)	1.2125	0	*intra*
m-Chloroaniline	—	1.2225 (15°)	−10	inter
p-Chloroaniline	3.91 (210°)	1.427 (19°)	70	inter
o-Chlorotoluene	2.3[b] (210°)	1.0817	−34	none
m-Chlorotoluene	—	1.0722	−48	none
p-Chlorotoluene	—	1.0697	7	none

[a] See Fig. 2-17 for a comparison of *o*-, *m*-, and *p*-chlorophenol viscosities.

[b] Extrapolated 50° beyond measured range.

5.3.11 Other Properties. A number of *intra*molecular H bonded substances have been studied by x-ray and electron diffraction; for example, glycols (146), maleic acid (1834), and proteins (e.g., 1432, 883). Since this type of bond does not present any special problems in structural determinations there is no need for special treatment here, and such molecules are discussed in Chapter 9.

Certain discussions in Chapter 2 have treated other properties of *intra*molecular H bonds. See especially:

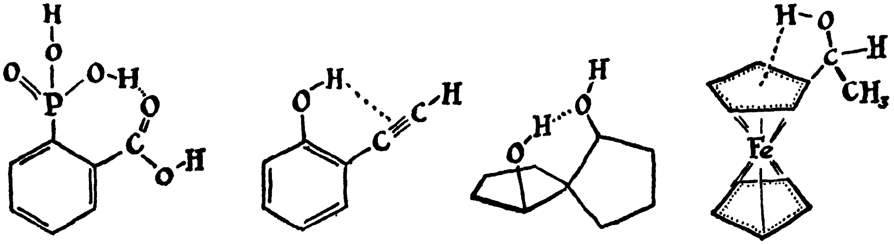
Parachor, Sec. 2.4.8, p. 54.
Thermal Conductivity and Thermal Expansion, Sec. 2.4.10, p. 56.
Surface Tension, Sec. 2.4.13, p. 63.

5.4 New Directions

We have restricted the examples presented to simple compounds with well established internal H bonds. Some more complex or more controversial *intra*molecular H bonds are shown in Fig. 5-7.

The examples in Fig. 5-7 deserve some comment, since they are newer proposals of *intra*molecular H bonds. Several, notably (b), (d), and (g), involve π electrons as the "base"; (e) is included in order to point out that large molecules can show chelation (often with multiple H bonds, as in this example); (f) exhibits a large, internally bonded *ion;* (k) is a very unusual case which may not be a H bond at all—as proposed, it places the hydrogen atom in one tetrahedral face where it may have some similarity to a bifurcated H bond.

Only recently have measurements been made of the effect of H bonding on nonaromatic stereo-conformation. The molecules shown in (c),

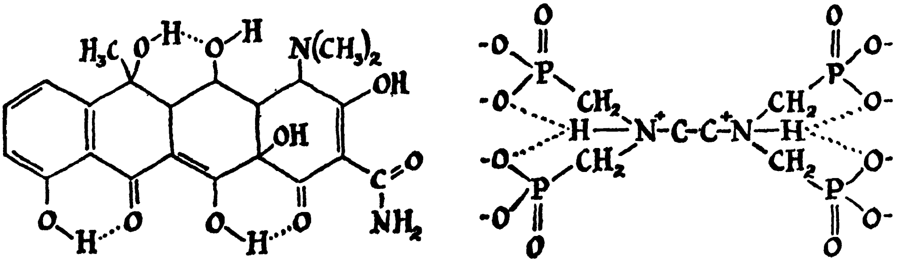


o-carboxybenzenephosphoric acid (1030) a

o-hydroxyphenylacetylene (1667) b

spiro(4,4) nonanediol(1,6) (323) c

α-hydroxyethylferrocene (2033) d



Terramycin (1952) e

ethylenediamine-tetra (methylene-phosphonic) acid ion (2162) f

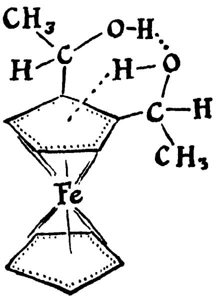
FIGURE 5-7 Some unusual *intra*molecular H bonds. *This page: o*-carboxybenzenephosphoric acid; *o*-hydroxyphenylacetylene; spiro(4,4) nonanediol(1,6); α-hydroxyethylferrocene; Terramycin; ethylenediamine-tetra (methylene-phos-

(i), and (j) of Fig. 5-7 exemplify compounds that are influenced to some degree by *intra*molecular bonding. For other discussions, see 145, 281a, 414, 1161, 1162, and 1504.

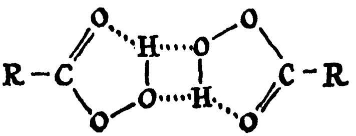
Cole and Jefferies list some "rules" regarding IR spectra studies, two of which are:

1. In *cyclo*hexane-*trans* 1:2 diols, a secondary equatorial O—H group H bonds in preference to a tertiary O—H group.
2. In *cis* 1:2 diols, an axial O—H group H bonds in preference to equatorial groups, regardless of the number of other attachments on the carbon atom.

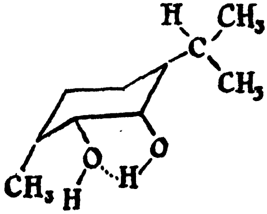
These rules predict which O—H will act as proton donor in H bond formation; of course, in a broad sense they both H bond to some extent.



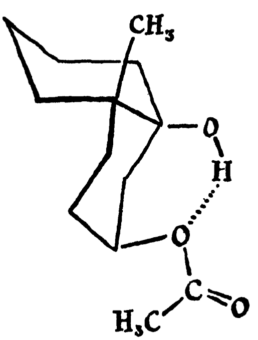
1,2-di-α-hydroxyethylferrocene
(2033) g



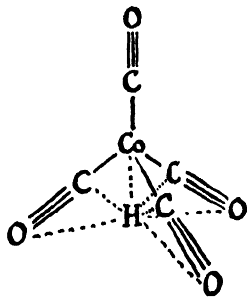
peracids (mixed association)
(1953) h



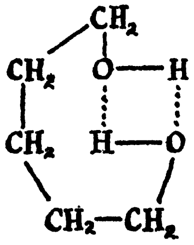
***cis*-2-hydroxyneoisomenthol**
(414) i



coprostane-3β, 5β-diol-3-acetate
(1504) j



Co(CO)$_4$H
(578) k



pentamethylene glycol
(645) l

phonic) acid ion. *Shown above:* 1,2-di-α-hydroxyethylferrocene; peracids (mixed association); *cis*-2-hydroxyneoisomenthol; coprostane-3β,5β-diol-3-acetate; Co(CO)$_4$H, pentamethylene glycol.

Nickon finds H bonds (i.e., IR shifts of about 50 cm^{-1} for O—H stretch), for 1,2-halohydrins, when the halogen and O—H groups are in positions that permit interaction. This means that for *cis* (e, a) or *trans* (e, e) groups internal H bonds occur; for diaxial groups they do not.[a]

In some cases (small groups such as methyl), the H bonding apparently can overcome the normal tendency for alkyl groups to be equatorial. For *iso*propyl or *t*-butyl this is not true. Perhaps "conformational tendency" can be determined more easily by IR spectra than by electron or x-ray diffraction. Also, there are some interesting geometric relations that would be worth working out. In the diols discussed by all of the above authors, the H bonds are probably nonlinear and nonplanar.

5.5 Conclusions

From the discussions in this chapter we can list the following principal characteristics of *intra*molecular H bonds.

1. They are common and generally occur in 5, 6, or 7 atom rings.
2. The formation of an *intra*molecular H bond does not cause abnormal behavior such as deviations from idealized laws of gases and solutions. This difference from intermolecular H bonds is due to the absence of association.
3. Generalization 2 provides a criterion for identification of *intra*molecular H bonds. When H bonding groups are present but the usual evidence for association is lacking, we may infer that the H bonding capacity has been used internally. This test is even more convincing if the characteristic IR spectral changes are observed but are unaccompanied by indications of association.
4. The most direct and readily obtainable test to distinguish *intra*molecular H bonds from association is the observation of changes in the IR and Raman spectra at low concentration and pressure. Intermolecular H bonding (and its spectral characteristics) disappear at low concentrations in an inert solvent, whereas *intra*molecular H bonds do not.

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[a] The nomenclature is that of Barton and Cookson (145); "e" meaning equatorial and "a" meaning axial.

CHAPTER **6**

What Groups Form Hydrogen Bonds?

> *A class must be defined in terms of observable properties, and this often introduces difficulties of two kinds. The first difficulty is . . . that most properties can vary continuously . . . so that clean-cut separations . . . are often somewhat arbitrary. . . . The other difficulty . . .* [*is*] *that it is often necessary to amend definitions many times in order that the class may continue to be useful.*[a]
>
> E. B. WILSON, JR. *Harvard University, 1952*

A survey of any concept must be made within bounds selected by the authors of the survey. Such a selection of bounds implies, indeed it *constitutes*, a working definition of the concept. Hence the usefulness of the survey is enhanced by a clear and explicit statement of this definition.

Unfortunately, a precise definition often evokes criticism from two directions, as noted by E. B. Wilson, Jr.[a] First, different workers may disagree on the optimum placement of the bounds of the concept, since lines of demarcation in science are rarely sharp. Second, the growth of human experience may cause an evolution of the concept—a movement of the lines of demarcation. Anticipating this evolution, some scientists prefer to remain unfettered by sharply drawn lines. They wish to avoid the danger that study of the concept will be inhibited by a definition solidified in a mold formed by inadequate information. Davies has, for

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[a] E. B. Wilson, Jr., *An Introduction to Scientific Research*, McGraw-Hill Book Co., Inc., New York (1952), p. 151

example, made a clear and forceful statement of this danger with reference to the H bond (479). We, however, feel it is necessary to state the criteria we have found useful in fixing the topical limits of this book. These criteria are needed in this chapter which is devoted to exploration of the peripheral examples of H bonding.

6.1 Defining the Hydrogen Bond

6.1.1 Purpose of a Definition. A definition of the H bond enables us to sort hydrogen-containing compounds into two groups, one containing compounds that do form H bonds, and one containing compounds that do not form H bonds. Without such a sorting we could not claim a comprehensive coverage in this book. However, we offer an overt discussion of this sensitive issue for another and more crucial purpose—to place in focus a discussion of the reasons for the existence of H bonds, i.e., the theory of the phenomenon. Perhaps this advantage can be enjoyed without loss if we state that our definition is offered with no hope or desire that it will possess immortality.

6.1.2 The Definition. There are those who would lay down a definition of the H bond in terms of the chemical principles which govern its existence. This may be possible two or three decades hence, but with the present use of quantum mechanics, we cannot treat such a weak interaction in a predictive way. Hence the bounds of the subject must be determined with the aid of operational criteria. Before listing these criteria, however, it is well to be reminded of the meaningful definition of the chemical bond given by Pauling (1585). He notes that chemists talk about bonds when convenience dictates identifying a group of atoms as an entity, as a stable aggregate. In that context, then, it is quite correct to call the H bond a "bond," since convenience *does* dictate recognizing the existence of aggregates such as dimers of formic acid and polymers of methanol. Thus, our operational definition shall be based in part on criteria for detecting molecular aggregates.

However, there is more to the definition, just as there is more to the name. The word "hydrogen" in the name "hydrogen bond" conveys the belief that at least one H atom in the aggregate has a specific and unique role. *The H bond specifically involves a hydrogen atom already bonded to another atom.* This provides the basis for completing our definition. We will be convinced that a given molecular aggregate contains a H bond when operational criteria pertaining to the specificity of this unique type of hydrogen atom interaction have been satisfied.

A hydrogen bond is said to exist when:

1) there is evidence of a bond, and

2) there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom.

The evidence called for by criterion (1) can be drawn from a wide range of types of measurements. All of the classical methods for detecting chemical bonds have been cited as providing evidence for H bonds. Methods which can be grossly classified as molecular weight determinations are important; cryoscopic, vapor pressure, and vapor density measurements are typical. Of course any measurement that can satisfy criterion (2) may also suffice for criterion (1).

For the label of specificity, criterion (2), we must appeal to a more limited area of study, to spectroscopic and diffraction data. The most definitive data are, no doubt, those which indicate atom positions in the molecular aggregate. Thus, x-ray diffraction, neutron diffraction, and certain nuclear resonance studies of solids can provide more or less direct evidence that there are H atoms which occupy positions of close approach (hence bonding distance) to two other atoms. Electron diffraction spectra can yield the same information for gaseous species. More easily obtained, however, are IR and Raman spectra, which reveal specific involvement of H atoms by peculiarities in their vibrational degrees of freedom in the molecular aggregate. Finally, high resolution proton magnetic resonance studies provide a sensitive index of the electronic environment of the H atoms.

With this ground work established, we shall examine briefly the well known H bonding systems, then deal with the less well recognized types.

6.1.3 Well Recognized H Bonding Systems. The H bond, A—H· · ·B, is usually considered to be a bond in which a hydrogen atom lies between two closely spaced electronegative atoms, A and B. The atoms A and B are usually identified as oxygen, nitrogen, or fluorine, and occasionally chlorine (e.g., see 1585, 1643, 447). This identification certainly includes the well recognized H bonding systems. The compounds generally accepted as H bonding acids or bases are listed in Table 6-I. The properties of any combination of a compound from the acid column with a compound from the base column will be affected by H bond formation. These properties furnish norms of behavior which can be used to test other systems.

TABLE 6-I Well Recognized H Bonding Compounds

H BONDING ACIDS		H BONDING BASES	
A	EXAMPLES	B	EXAMPLES
F	HF	F	F$^-$, HF
O	Carboxylic acids Water Alcohols Phenols Oximes	O	Carboxylic acids Water Alcohols Phenols Amides Ketones Aldehydes Ethers Esters
N	Amides Pyrrole Amines Ammonia	N	Amines Pyridines Ammonia Pyrrole[a]

[a] Concerning the H bonding of pyrrole, see 2062, 2060, 1055, 1059, 1413, and 979.

6.1.4 Operational Criteria for H Bond Formation. In these well recognized systems the formation of a H bond, A—H···B, is accompanied by some or all of the following measurable effects.

1. Changes occur in the vibrational spectra of A—H and B:
   a. The frequency of the A—H stretching mode decreases.
   b. The band width of the A—H stretching mode increases.
   c. The intensity of the A—H stretching mode increases.
   d. The frequencies of the A—H deformation modes increase.
   e. There are new low frequency modes associated with stretching and bending of the H bond itself (ν_σ and ν_β in Fig. 3-1).
2. The proton magnetic resonance moves toward lower field.

3. The A····B distance is short, compared to the sum of the van der Waals radii.

4. Electronic transitions of either the acid or the base may be shifted.

5. The molecular weight is larger than the formula weight, as shown by cryoscopy, vapor pressure, and vapor density data.

6. Various properties indicate association: dielectric behavior, solubility, heat of mixing, molar volume, viscosity, etc.

Of these effects, the IR intensity (1c) and the proton magnetic resonance (2) are probably the most sensitive to H bond formation, whereas the IR frequency (1a) is probably the most easily measured.

We shall examine a series of systems which are not universally accepted as H bonding systems. Rather than appeal to chemical intuition or to a table of electronegativities, we shall decide whether an H bond forms on the basis of the criteria defined by the well recognized H bonding systems.

6.2 Do C—H Groups Form Hydrogen Bonds?

6.2.1 Chloroform. The properties of chloroform dissolved in basic solvents furnish a most interesting example. There is a body of opinion on the side that the relatively weak interactions of chloroform should not be classified as H bonds but rather should be attributed to the less specific effects of a "polar" solvent (e.g., see 349, 347). With reference to the theory of H bonding the case is important because C—H compounds are not usually listed as H bonding acids.

The most generally accepted criterion of specific interaction, the frequency shift of the C—H stretch (ν_s), furnishes ambiguous evidence. No systematic frequency shift is observed when chloroform is dissolved in oxygenated bases (1510a, 1510, 980, 1259, 175, 861). On the other hand, with two nitrogen bases, pyridine (1259) and triethylamine (980, 142), distinct frequency shifts are observed for the C—D stretch of $CDCl_3$ (36 and 80 cm^{-1}, respectively). For triethylamine, even the C—D bending mode shifts upward as usual with H bonding. These nitrogen bases are the two strongest bases studied (see Table 3-II), and two possibilities arise. Either H bonds form only for the strongest bases (as indicated by ν_s), or the smaller frequency shifts for the weaker H bonds are masked by solvent effects. Exactly the same conclusion results from examination of the band widths.

These infrared spectral studies do provide a separate basis, however, for concluding that H bonding occurs. The characteristic increase in intensity of ν_s with H bond formation is more sensitive than frequency shift as an indicator of an interaction specifically involving the hydrogen atom. Intensity measurements have been made for sixteen chloroform-base systems. In every case, ν_s of chloroform is intensified several-fold, as compared to ν_s in more inert solvents such as CCl_4 (980, 1259, 861). Furthermore, the factor of intensification correlates nicely with other measures of base strength, e.g., heat of mixing (980) and IR frequency shifts of stronger acids (see Tables 3-II and 3-VII). Certainly the absorption coefficient measurements are consistent with the proposal that chloroform acts as a H bonding acid. (Early IR studies of chloroform-base systems are 333, 799.) Temperature dependence studies of $CHCl_3$ by Liddel and Becker are less directly interpretable but also suggest H bonding (1229). (See also 868.)

Proton magnetic resonance is extremely sensitive to H bond formation. Hence Huggins, Pimentel, and Shoolery turned to this technique as an aid in deciding whether chloroform interactions involve H bonding (982). For both acetone and triethylamine bases, the chloroform NMR spectra show the characteristics of H bond formation.

Turning to the less specific methods, there is ample verification of association. For example, equilibrium constants have been measured for the association of chloroform with acetone by vapor pressure measurements (184, 1818) and by NMR (982). Moelwyn-Hughes and Sherman calculate $-\Delta H$ of formation of the 1:1 chloroform-acetone complex to be $+4.1$ kcal/mole (1441), whereas Huggins *et al.* obtain $+2.5$ with about ± 1 kcal/mole uncertainty (982). For the chloroform-triethylamine association the equilibrium constant has been measured by IR (142) and NMR (982). Barrow and Yerger find an association constant smaller by a factor of eight than that for association of ethanol-triethylamine (implying $-\Delta H$ of formation is less by about 1 kilocalorie) (142). Huggins *et al.* find $-\Delta H = +4$ kcal/mole for chloroform-triethylamine (982). (See also 572, 1259, 1306a.)

Related to these thermodynamic quantities are the determinations of heat of mixing. Searles, Tamres, and co-workers found that the heat of mixing of chloroform with many bases correlates smoothly with the shift of the O—D stretch of CH_3OD in these same bases (1823–1826, 1995, 1996) [as did Gordy and Stanford much earlier (812)]. Since there is no question that the O—D frequency shift in alcohols is related to H bonding, the correlation is indirect evidence that the chloroform heat of mixing is also caused by H bonding. Other studies of heats of mixing of chloroform with bases reveal association (see 1348, 1347, 84, 1173, 1135).

Staveley, Tupman, and Hart found that volume-change as well as the thermodynamic effects, on mixing acetone and chloroform, show the large deviations characteristic of association (1940). Different types of data which have been offered as evidence of $CHCl_3$-base association include: solubility (438, 2236, 436, 1349), vapor pressure (628), PVT behavior (1182a), dielectric polarization (572, 777), diamagnetism

(2112), freezing point diagrams (1705), osmometry (1944), ultrasonic absorption (1577, 1833), dielectric relaxation (660), parachor (209), and solvent shift of other H bonding equilibria (684, 1117). (See also 681, 735, 1510.)

In summary, the evidence in favor of association of chloroform with bases is conclusive. The evidence that this association is of the H bonding type is substantial, and it is consistent with the statement that chloroform forms H bonds, at least with such strong bases as pyridine and triethylamine. Thus it must be concluded that, in this instance, a C—H group can serve as a H bonding acid.

6.2.2 Hydrogen Cyanide. The investigators of hydrogen cyanide seem to agree that it forms H bonds. Dulmage and Lipscomb determined the crystal structure of HCN, and found infinite linear chains and rather short carbon-nitrogen distances (3.18 Å) along the C—H···N direction (562). Hoffman and Hornig found unusual changes in the IR spectrum of HCN on solidification of the vapor, and concluded that structural changes accompany the formation of H bonds in the crystal (943). Dielectric measurements also reveal a specific orienting effect in liquid HCN (400, 1164). From PVT data (470, 749) there is further evidence of association in gaseous HCN. In summary, the evidence for H bonding in HCN is strong if not conclusive.

6.2.3 Acetylenes. Evidence for H bonding of acetylenic C—H bonds is good, but it is not voluminous. Stanford and Gordy found systematic frequency shifts of the acetylenic C—H stretching mode of phenyl acetylene dissolved in bases (1932). Another type of evidence concerns the solubilities of acetylenic compounds in many bases.[a] McKinnis, for example, presumes that the solubility of acetylene is dominated by the H bond interaction, and is able to correlate the solubility with electronegativity of the base atom B (1308). (See also 563.)

6.2.4 Aldehydes. There remains uncertainty concerning H bonding by the aldehydic C—H bond. Schneider and Bernstein found no evidence for H bonding in the IR spectra of solid formaldehyde and acetaldehyde (1813). In contrast, IR data have been cited as evidence of H bonding by the aldehydic C—H by Pinchas (1638, 1639) and earlier by Freymann and Freymann (706). Vrazovskiĭ and Shchipkova attributed the existence of α and β modifications of *o*-methoxybenzaldehyde to inter- and *intra*molecular H bonding of the CHO proton (2079). Vavon and Scandel explained the rate of reaction of *ortho*-substituted

[a] 433, 1351, 2125, 945, 1308, 1115.

aldehydes in terms of "chelation" (2109). Terenin, Yakovkin, and Volobuev have interpreted the fluorescence of benzaldehyde adsorbed on metals as evidence for such CHO H bonding (2015).

6.2.5 Halogenated Alkanes. The work of Zellhoefer, Marvel, and Copley on the solubilities of partially chlorinated hydrocarbons has been mentioned in Section 2.4.2. These workers measured the solubilities of various halogenated methanes and ethanes in a number of oxygen-containing compounds (438, 1347, 1348, 1349). A small portion of their data is shown in Table 6-II. Marvel *et al.* interpreted the higher solubility in the basic solvents as evidence of H bonding, in agreement with Glasstone's then recently published suggestion (777) that a hydrogen attached to carbon could form H bonds. In an IR study of more limited scope, Klemperer *et al.* reached the same conclusion (1117). They found that bromoform and methylene chloride are about as effective as chloroform in inhibiting polymerization of *N*-ethylacetamide. In contrast, methyl chloroform is much less effective despite its high dielectric constant. Evidence that a specific interaction is involved is provided by the shift of the carbonyl frequency compared to CCl_4: $\Delta\nu_s(CO)$ in $CHBr_3$ is 24 cm^{-1}; in $CHCl_3$, 20 cm^{-1}; in CH_2Cl_2, 16 cm^{-1}; in CH_3CCl_3, 2 cm^{-1}. Klemperer *et al.* concluded that the solvent interactions must be attributed to H bonding between the C—H and the carbonyl groups.

TABLE 6-II Solubility of $CHFCl_2$ in Various Solvents (T = 32.2°C)

SOLVENT	MOLE FRACTION SOLUTE
Decahydronaphthalene	0.272
Decane	0.324
Anisole	0.415
Dioxane	0.479
Benzaldehyde	0.436

Other evidence of H bonding of halogenated methanes is available for $CHBr_3$ and CHI_3 (784a), for CHF_3 (2024), for $CHCl_2F$ (435, 438, 1347), for CH_2Cl_2 (628, 1348, 435), for $CHCl_2CCl_3$ (801), and for $CHCl_2CHCl_2$ (861).

6.2.6 Other C—H Compounds. A number of workers have postulated that C—H bonds in the α position to an ether, an oxygen, or a carbonyl group can form *intra*molecular H bonds; methyl pyridines-1-

oxides (1014); dimethyl oxalate (546); dioxanes (1968); nonadecanone (940); cyclopentanone (1971); butyric acid (701).

Syrkin and Shott-Lvova attribute the high dipole moments of fluorene and triphenylmethane in dioxane (compared to benzene) to H bonding of the C—H bond to the dioxane oxygen (1985).

Dippy, in 1939, reviewed the evidence for C—H participation in H bonds (525), as did Huggins, in 1943 (987).[a]

6.3 Do Sulfur Compounds Form Hydrogen Bonds?

6.3.1 Mercaptans. There are a number of articles in the literature suggesting that thiols do not form H bonds. Giacomo and Smyth conclude that the dielectric dispersion of mercaptans is consistent with the interpretation that H bonding is very weak or absent (523). Plant, Tarbell, and Whiteman found that the IR spectra of a series of amino thiols give no indication of H bonding (1647). After summarizing other conclusions of this type, Gordy and Stanford proceed to report distinct IR evidence that mercaptans form H bonds with strong nitrogen bases such as pyridine, α-picoline, and dibenzylamine (813). The S—H stretching mode shifts to lower frequency, broadens, and becomes much more intense. More recently, IR evidence has been offered for H bonding of the S—H groups of H_2S in base solutions (1067), halobenzenethiols (1056), benzenethiol in solutions (1058, 1057), benzenethiol and sulfoxides (2128), and dithiophosphoric acids (1388, 27). The UV absorption of cysteine suggests H bonding of the S—H group and a carbonyl or amine, according to De Deken *et al.* (511). Hoyer detects *intra*molecular H bonding in 1-mercaptoanthraquinone by chromatographic separations (969). The solubility and heat of mixing studies of benzenethiol reveal some H bonding (1351, 434). It is clear that the S—H group does show the specific H bond association behavior with strong bases, and it seems likely that the relative weakness of the S—H as a proton donor accounts for the absence of H bonds in some systems. (See also 343, 737, 896, 1795, 1470.)

6.3.2 Sulfur as a Base. Evidence that the sulfur atom can act as a base in H bonding has been offered for diethylammonium diethyldithiocarbamate (238), ethylenethiourea (2165), thioamides (668), thiocarbamic acids (325, 955), disulfides (359), and 2-thiopyridone (1607).

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[a] See also 2184, 561, 55, 761, 126, 322, 1941, 56, 1942, 261, 1474, 1932, 799, 333, 802, 2236, 804, 777.

6.4 Do Aromatics Form Hydrogen Bonds?

Whether aromatics can act as H bonding bases has great practical as well as theoretical interest. There have been many experimental studies of H bonding substances dissolved in benzene with the apparent implication that the solvent is considered inert. The theoretical interest stems from the proposal that the H bonding base need not be a highly electronegative atom.

The evidence relative to H bonding obtained from IR and Raman studies is voluminous. The correlation of base strength with $\Delta\nu_s$ presented in Table 3-II typifies this evidence: enumerating individual references would but add weight to Table 3-II. [It is ironical that the workers who first demonstrated systematic base strength-$\Delta\nu_s$ correlations used benzene as an inert reference solvent (Gordy *et al.*, 801, 809, 812).] Among the acids not listed in Table 3-III for which frequency shifts have been observed in aromatic bases are phenol (979, 1290, 1292), water (823), amides (1117), amines (386), alcohols other than CH_3OD (979, 1049, 1670, 1671, 2062a), HCl (1068, 1069), and pyrrole (1055).

Of course, H bonding affects band intensities and band widths as well as frequencies. The measurements of the IR spectral properties of a variety of H bonding systems by Huggins and Pimentel are informative (979). Their work shows that benzene, though quite a weak base, has behavior which correlates very well with the criteria for well recognized H bonding systems. Additional data which show that the characteristic intensification of ν_s results from interaction with the aromatics is provided by the $CDCl_3$-aromatic systems (980).

Proton magnetic resonance studies offer ambiguous support for H bonding. At first consideration, the data seem to oppose the H bond postulate, because the interaction with aromatics shifts the proton resonance of $CHCl_3$ (1705) and H_2O (412) to higher fields. The H bond interaction usually shifts the resonance to lower fields. However, it seems quite definite that the anomalous shift has been correctly interpreted in terms of the unique diamagnetic anisotropy of the aromatic π-electrons (1705, 1658, 202). This interpretation inherently involves a specific orientation of the proton relative to the π-electrons. In addition, then, to explaining the unexpected direction of the NMR shift, this interpretation offers evidence that the proton position in the complex is appropriate for H bonding.

There are numerous types of data indicating association of some type which could be H bonding. Solubility data for HCl in aromatics (298) and H_2O in benzene (1935) reveal association, as do freezing point diagrams of HCl with aromatics (424, 1705) and of $CHCl_3$ with aromatics (1705). The distribution coefficients listed in Table 2-XIV suggest that benzene has greater base strength than CCl_4, as do IR studies of the association of *N*-ethylacetamide in various solvents (1117). Heats of mixing of $CHCl_3$ and aromatics are consistent with H bonding association (1995). Tuomikoski has interpreted dipole measurements of pyrrole in benzene as indicating H bonding (2059). (See also 1814.)

In conclusion, the data support strongly the existence of complex formation between acids and aromatics acting as bases. Since there is ample evidence that the proton of the acid is specifically involved in the interaction, it can properly be called a H bond. An important implication of the conclusion that the base B can be aromatic is that the base must be a good electron donor but *not necessarily a highly electronegative group*. Clearly, this conclusion must influence a discussion of the theory of H bond formation.

6.5 Do Boranes Contain Hydrogen Bonds?

Pauling assigned to boron an electronegativity of 2.0, and to hydrogen 2.1 (1585). This implies that the B—H bond does not have the charge distribution conventionally ascribed to H bonding acids. Furthermore, the boranes are electron deficient compounds, and they do not seem to meet normal requirements of a good base. Consequently, the proposal that the bonding in boranes might be compared to H bonding is a startling idea to most chemists. Nevertheless we shall examine the data concerning the boranes with hope of heuristic benefit.

In keeping with the spirit of this chapter, we shall examine the properties of the boranes in the light of each of the operational criteria listed in Section 6.1.4. We begin with number 5, the comparison of molecular and formula weights. This test reveals some sort of association, since the simplest borane, BH_3, dimerizes to B_2H_6 so completely that BH_3 itself has never been detected spectroscopically. Furthermore, the evidence that this association involves a specific interaction with a proton already bonded to another atom is unequivocal.[a] The structure of diborane has been shown, by a variety of techniques, to have the bridge configuration shown in Fig. 6-1. In this structure two hydrogen atoms occupy unique positions equidistant from the two boron atoms. (The data establishing this structure are reviewed by Lipscomb, 1243.) The association equilibrium $2BH_3 = B_2H_6$ is estimated by Slutsky and Bauer to have $-\Delta H^\circ = +28$ kcal (1893). This B—H—B bridge, or "three center

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[a] Only that literature of direct use in the current discussion is quoted, with no attempt to be comprehensive. For additional references, see, for example, 1643 (p. 192), 1243, 974.

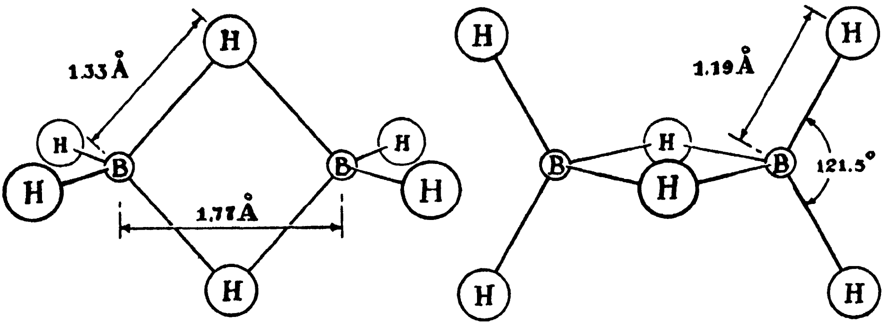

FIGURE 6-1 The Hydrogen Bridge Structure of Diborane, B_2H_6.

bond" (see 573), is a common structural unit in the boranes, having been definitely located in B_5H_9, $B_{10}H_{14}$, B_4H_{10}, and B_5H_{11} (see 1243 for individual references). Thus the boranes *usually* involve atom arrangements in which it is necessary to draw two bonds to some of the hydrogens. These bonds are long (1.33 Å) compared to the normal B—H bond lengths in which the H atom has only one boron neighbor (1.19 Å), and the boron-boron distances are shorter than van der Waals contact distance. Criterion number 3 (Section 6.1.4) has been satisfied.

Since the boranes satisfy criteria 3 and 5, they meet the general requirements of H bonding. Despite this positive verification that the boranes involve structural units which resemble "bent" but symmetrical H bonds, it may be that the similarity is only superficial. Perhaps the bonding is very different in character and, if so, other properties can be expected to differ from the usual H bond behavior.

The most obvious property to examine is the vibrational spectrum of the bridge arrangement. Shapiro, Wilson, and Lehmann (1836a) studied the IR spectra of several alkyldiboranes and have identified the IR active bridge B—H stretching mode. This absorption occurs in the region 1500–1610 cm^{-1} and is the most intense feature in each of the spectra examined.[a] This frequency range is to be compared to that of the normal B—H stretch, which is near 2500–2600 cm^{-1}. The large frequency shift of about 1000 cm^{-1} is appropriate for a centrally positioned hydrogen atom. Thus criterion (1a) of H bonding (Section 6.1.4), a frequency shift of ν_s, is satisfied. Two other criteria are offered by IR

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[a] This assignment corrects the earlier proposal of Hrostowski and Pimentel that the stretching frequencies of borane bridge hydrogens are found in the region 1800–2140 cm^{-1} (974). The full impact upon the assignments of the other boranes is not yet clear, but Shapiro *et al.* (1836a), suggest that the spectral range in which the higher borane bridge modes may be found is large, extending into the region given earlier (974). The present discussion is restricted to the diborane case for which the assignment seems well substantiated.

spectra: intensification and broadening of ν_s. The diborane spectra of Shapiro *et al.* do not suggest extreme band width. On the other hand, the relatively high intensity of the bridge ν_s is consistent with familiar H bond behavior.

Another interesting technique is the proton resonance measurement. Ogg has identified the resonances characteristic of the two types of protons of diborane, and finds the resonance of the bridge protons at higher magnetic fields (1538). Ogg offers the interpretation that the shift signifies that the bridge protons are "more hydride-ion like" than the terminal H atoms. Whether this is correct or not, the shift is in the opposite direction to the usual H bond effect.

To summarize, most of the evidence available is in favor of calling the borane bridge a H bond interaction: the borane structures positively involve hydrogen atoms multiply bonded; the bridge B—H bonds are long; the stretching frequency is lowered, and its intensity is high compared to normal B—H bonds; the proton resonance supports the conclusion that the bridge proton is specifically involved in an unusual bonding situation. There is but slight evidence in support of the conventional view that the electron deficient borane structures cannot involve the same bonding situation as the H bond. This evidence is provided by the normal band width of ν_s and the direction of the NMR chemical shift. Despite these deviations, the pattern of similarity between the borane bridge bond and the H bond certainly encourages the expectation that a single theoretical framework for boranes and H bonds will suffice (see Section 8.2.4).

6.6 Summary

This chapter opened with concern that a definition of the H bond might limit the growth of knowledge. We shall close with another glance in the direction of the future. An operational definition of the H bond permits an objective examination of evidence for H bonding in systems not generally considered to involve this interaction. Such an examination suggests that the concept of the H bond can be usefully employed over a broader area. It seems that the older view that the atoms A and B must be highly electronegative is undesirably restrictive. The requisites of a suitable acid should be extended to include the halogen-activated C—H, the acetylenic C—H, and the S—H groups. H bonding bases apparently include aromatic systems, possibly even the electron-deficient boron atom. Accepting these as members of the H bonding family will aid in the recognition of other new examples and, more important, will guide us in formulating a useful theory of the H bond.

CHAPTER 7

Thermodynamic Properties of Hydrogen Bonds

> *The fascination of a growing science lies in the work of the pioneers at the very borderland of the unknown, but to reach this frontier one must pass over well travelled roads; of these one of the safest and surest is the broad highway of thermodynamics.*[a]
>
> G. N. LEWIS and M. RANDALL *University of California, 1923*

7.1 Introduction

Having defined the H bond and presented the qualitative evidence for its occurrence, we may now consider quantitative behavior. Since a H bond is formed in an equilibrium reaction, the thermodynamic equations are applicable. Fortunately, many cases involve fairly simple equilibria in a temperature range which is readily available (usually between 0 and 200°C).

7.2 Thermodynamic Relations

Reliable values of thermodynamic functions of H bonds are derived from the equilibrium constant, K, and its variation with temperature. The experimental techniques vary only in their approach to finding the concentration or pressure values needed to determine K. The basic relations are

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[a] By permission, from the dedication in *Thermodynamics and the Free Energy of Chemical Substances*, by G. N. Lewis and M. Randall. Copyright, 1923. McGraw-Hill Book Company, Inc.

$$K = \frac{\text{activity of product}}{\text{activity of reactants}} = \frac{[\text{A—H} \cdots \text{B}]}{[\text{AH}]\,[\text{B}]} \tag{1}$$

$$\Delta F = -RT \ln K \tag{2}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2} \tag{3}$$

$$\Delta F = \Delta H - T\Delta S \tag{4}$$

In equation *(1)* it is common to use concentration or pressure and to adjust the experimental conditions such that these quantities are nearly equal to activity and fugacity; then no appreciable error is involved. It is important to remember that the units of K influence both ΔS and ΔF, and that values of K (or ΔS and ΔF) are not directly comparable unless the units are the same (25, p. 269).

7.3 Experimental Methods

The most widely used experimental methods are IR (providing 35 percent of the values in Appendix B), UV, PVT, vapor density, second virial coefficient, and distribution (each accounting for about 10 percent of the values in Appendix B). These techniques are discussed in Chapters 2 and 3, but we will recapitulate the relevant features. In all cases, pure compounds and accurate temperature (and, for gases, pressure) control are required.

7.3.1 Infrared Spectra. The concentration of the associated and non-H bonded species are determined from the intensities of both the monomeric and associated ν_s band as a function of concentration and temperature. A usual assumption in calculating K is that no polymeric species absorb at the monomeric frequency. This assumption, which implies cyclic polymeric forms, seems to be valid, as shown in Section 3.3.6. It is necessary to use a concentration range sufficiently low that only monomer and one polymer (usually taken to be dimer) are important species, a condition difficult to meet in some cases. Another assumption is that the absorption coefficient does not change with temperature. Section 3.3.1 discusses the recent criticism of this assumption. Despite these necessary simplifications and the major experimental difficulty of making reliable IR intensity measurements, the IR method probably is the most useful method for measuring K in solutions.

7.3.2 Ultraviolet Spectra. In general, the same procedure and assumptions are used here as in the IR method. Because there is smaller separation of monomer and polymer bands, UV techniques usually cannot be applied in cases where multiple species exist. For solutions of compounds with appropriate chromophoric groups in monomeric and a single H bonded species the UV method ranks with the IR method in utility.

7.3.3 **PVT, Vapor Density, and Virial Coefficient.** In these three techniques the pressure (of a known volume and weight of gas) is measured over a temperature range. The data may be treated in two ways: by assuming that the real gas is a mixture of perfect "gases" (each "gas" being one of the species), or by describing the behavior of the real gas by a virial equation.

In the first case (PVT) it is most common to assume that only one polymeric species occurs (normally the dimer). More can be assumed, but the addition of adjustable constants tends to make the interpretation ambiguous. The PVT method is a reasonably good one, particularly when the assumption of a single polymeric form is valid.

Sometimes the density of the vapor is calculated from P, V, m, and T, and authors speak of a "vapor density method." There are also a few cases in which the vapor is actually weighed. The general treatment and usefulness of these procedures are the same as those described for PVT.

In the third kind of treatment (virial coefficient) the data are used to define a virial equation containing constants expressing the non-ideal behavior of the gas. Generally, the second virial coefficient is used; higher ones are sometimes included. The virial coefficient is related to K, usually by assuming that the non-H bonding part of the gas imperfection is expressed by the second virial coefficient from the Berthelot equation. The difference then is presumed to be equal to $-RTK$ (see Section 2.2).[a] Higher virial coefficients can be used, but the problem of multiple constants mentioned above recurs. The method is not completely trustworthy, and the separation of the imperfection caused by H bonding is not universally accepted. See Section 2.2 for additional comment.

None of these vapor measurements distinguish the H bonding interaction specifically but combine it with the intermolecular attraction. In general, this means they have an additional deficiency relative to the spectral methods.

[a] Note that here, as in Section 2.2, we have altered Lambert's notation by using K for association instead of for dissociation.

7.3.4 Distribution or Partition. The concentration of an associating material can be measured in both layers of a binary, immiscible solvent mixture. Then, if the species are known in the two solvents, an equilibrium constant can be related to the measured concentrations. The shortcomings of this technique have been mentioned (Section 2.4.5). The basic problem is knowing what species is really formed and allowing for the multiple equilibria which may occur. These limitations make distribution probably the least useful of the major methods.

7.4 Theoretical Calculations

There have been many attempts to calculate ΔH independent of the equilibrium constant. The difficulty of a complete theoretical treatment of the H bond unfortunately requires approximations. The uncertainties thus introduced deprive the calculations of predictive value. Briefly, the usual approximations are based on some sort of electrostatic model, with computation of electrostatic, dispersion, and repulsive contributions by the methods of classical physics. Of course, the calculations require knowledge or estimation of such quantities as molecular arrangement, charge distribution, potential function, etc. Only a few systems have been treated. Reference 1327, for HF dimers; 25, for carboxylic acids; and 1561b, for ice furnish illustrative examples. Many other references are listed in Section 8.3, where a more complete discussion of the theoretical treatments is given.

7.5 Experimental Values

No comprehensive collection of H bond thermodynamic values has been available, although Allen and Caldin (25) did publish a review on carboxylic acids, and recently Lindberg (1232) covered some hydroxyl-containing materials. Appendix B is a lengthy tabulation of ΔH and ΔS values, and Appendix C lists K values.

The appendixes do not include every published value. First, they are limited to values derived from experimental data (excluding calculations based only on theory). Second, they do not include properties derived by comparison with molecules of supposed equivalent structure (although these methods are taken up later in this chapter). Third, some values were excluded because they are in extreme discordance with other work of good quality, because they involve systems for which the associated species cannot be specified, or because they are based on scanty experimental evidence. The listings in Appendixes B and C do not coincide because many K's are determined at a single temperature, and, in a few cases, because thermodynamic properties are given without the underlying K's. See the introduction to the appendixes for a description of their arrangement.

To organize the rather voluminous data of Appendix B for the general view that we wish here, we consider first the pure substances (in each of the phases), then solutions, and finally certain miscellaneous cases (adsorbed material, monolayers, etc.).

7.5.1 Pure Compounds. One homologous series, the carboxylic acids, has been studied so much that it deserves separate mention. It also illustrates the variation and conclusions that might be expected when other series are investigated more thoroughly. There are about 40 published values for some measured or calculated thermodynamic property (most frequently ΔH) of these acids—over half of these on formic and acetic acids! Figure 7-1 shows a histogram of the data, and Table 7-I lists some selected values to illustrate the present state of affairs.

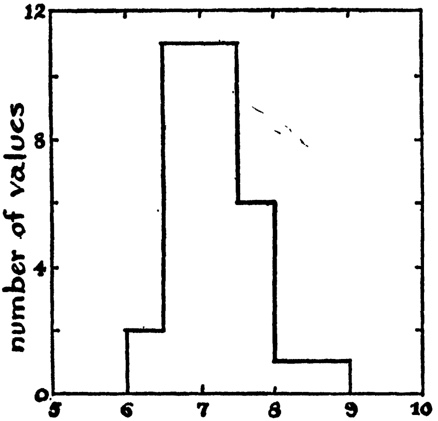


FIGURE 7-1 $-\Delta H$ per H bond in dimeric carboxylic acids (gaseous).

We may summarize by saying that $-\Delta H$ is essentially constant at 7 ±0.5 kcal/mole-H bond, and $-\Delta S$ at 18 ±0.5 e.u./mole-H bond, regardless of length or branching of carbon chain, substitution of strong electronegative groups, or, in the few cases studied, converting the H bond to a deuterium bond. These data do not furnish support for the proposal that the deuterium bond is stronger (see 2136, 2137). There is so little work with liquid and solid acids that these conclusions cannot be extended to those phases except by assumption. The most reliable result on a liquid acid (stearic acid, 1789) gives $-\Delta H = 6.7$ kcal/mole, within the generalized value. The acoustical absorption method seems to give low values (by 2–4 kcal) which, for the present, must be considered as being outside the error of other techniques. Allen and Caldin (25) concluded that ΔH values from the vapor density method have a precision of ±0.1–0.2 kcal/mole, whereas spectroscopic values are less

TABLE 7-I Some Selected Values of K, $-\Delta H$, and $-\Delta S$ per H Bond in Dimeric Carboxylic Acids (gaseous except where noted)

ACID	K (atm^{-1}) (at 300°K)	TEMP. RANGE (°C)	$-\Delta H$ (kcal/mole-H bond)	$-\Delta S$[a] (e.u./mole-H bond)	METHOD[b]	REFS.
Formic	260	50–150	7.05 ± 0.2	18.0	PVT	2009
		—	6.95		IR	1866
		75–185	7.25		2VC	689
	267	10–150	7.05	18	VD	428
Formic-*d*		50–150	6.4 ± 1		IR	908
Acetic		95–270	7.52 ± 0.05	18.1	CAP, IR	2155
		75–185	6.9		2VC	689
	539	50–150	6.8	18	VD	1661
	680	80–200	6.9 ± 0.1	16	VD	1044
Acetic-*d*		24–139	8.0		IR	244
Acetic-d_3 acid-*d*	685	80–170	7.05	17.0	VD	1661
Trifluoroacetic	177	30–150	7.0	18.3	PVT	2010
Trifluoroacetic-*d*	161	30–150	7.0	18.1	PVT	2010
Acetic (liquid)	43.6 (mf^{-1}) (303°K)	20–50	3.1	12	AA	699
Propionic	1258	50–150	7.6	18.2	PVT	2009
			8.6		AA	699
Propionic-*d*	996	25–125	7.0 ± 0.5	18	IR	909
Propionic (liquid)	868 (mf^{-1}) (304°K)	20–50	4.6	14	AA	699
Butyric		140–200	6.9	16.5	VD	1272
Butyric-*d*		50–150	6.9		IR	908
Trimethylacetic	1296	133–200	7.0	16.2	VD	1044
Heptanoic	17 (l/m) (479°K)	190–227	6.7	14	VD	1272
Stearic (liquid)	400 (mf^{-1}) (365°K)	40–220	6.7 ± 0.3	14	IR	1789

[a] Based on K in atm^{-1} units.

[b] AA = Acoustic absorption
CAP = Heat capacity
IR = Infrared spectra
PVT = Pressure, Volume, Temperature
2VC = Second virial coefficient
VD = Vapor density

precise, varying by ±1 kcal/mole. Various experimenters do not agree as well as these figures would cause one to assume. Entropy estimates are more variant, few being more precise than ±0.2 e.u. and most probably nearer ±1 e.u.

Clearly, there are many gaps even in this most studied area. There are few data on unsaturated or aromatic acids, and few values for acids with four or more carbon atoms or with substituents other than halogens.

In addition to the work on acids, there are perhaps 50 values of thermodynamic functions for other substances in the pure state. Alcohols (17 cases) and HF (7 cases) account for a good fraction of these.

TABLE 7-II $-\Delta H$ of Various Kinds of H Bonds in Pure Compounds[a]

	$-\Delta H$ (kcal/mole-H bond)			
TYPE AND COMPOUND	GAS	REFS.	LIQUID	REFS.
1. O—H···O				
Water	4.4–5.0	(1753, 1182)	3.4	(836, 1801)
Alcohols				
Methanol	3.2	(2156)	4.7	(1670)
	3.2–7.3	(1183)		
	4.0	(1149)		
	4.6	(1753)		
	6	(1709)		
Ethanol	4.0	(1149)	~4	(1555)
Propanol			6	(1218)
*Iso*propanol	4.0	(1149)		
2. N—H···N				
Ammonia	3.7	(1753)		
	4.4	(1182)		
Methyl- and ethylamines	3.1–3.6	(1182)		
3. F—H···F				
HF	6.7	(1034, 1882, 1897a)		
	6.8	(1253, 694)		
	7.0	(1924a)		
DF	6.8	(1253)		
4. C—H···N				
HCN	3.3	(749)	4.6	(415)

[a] The temperature range and method for each value are given in Appendix B. See Table 7-I for carboxylic acid values and Table 7-IV for values derived from heats of sublimation.

Another segment (perhaps 20 cases), derived from heats of sublimation, is of questionable worth. Table 7-II presents most of those values not based on heat of sublimation.

From the values in Table 7-II, we see that the enthalpies of two important H bonds fall within the ranges given:

O—H···O 3–6 kcal/mole (other than gaseous, carboxylic acids)
N—H···N 3–5 kcal/mole

Further, we may note that there is no particular trend (with molecular size) among the values for alcohols. Without doubt, there is room for careful, systematic work in this entire area.

The ΔH values from heat of sublimation are segregated because there is considerable skepticism about their derivation. The procedure used is to select a reference compound, either a hypothetical "non-H bonded" structure of the H bonded material, as Pauling (1585) and others (1990) did for ice, or an isoelectronic structure, following the Japanese workers (1977, 1828). Considering the ice case first, there are serious reasons to doubt this procedure and the $-\Delta H$ of 4.5 kcal/mole found for ice. Searcy (1822) suggests two objections: the coordination number is fixed by the H bonding at a value different from the non-H bonded homologues (H_2S, etc.), and the molecules are much closer together in real ice than in similar non-H bonded substances. The second objection is equivalent to saying the van der Waals forces are influenced by H bonding. Searcy derives a value of 6.4 kcal in good agreement with Verwey's 6.8 (2116) from calculating repulsive and London energies. Table 7-III lists the calculated values and shows a wide spread of values with those around 4.5 and 6.5 being most common. "Calculated" values are those based entirely on theory or on a hypothetical model of structure, for example, non-H bonded water.

Experimental values do not decide the question of the validity of the calculational methods. Actually there are only a few data available, and they vary from one to another (3.4–6.6).

One group of workers (86) find 13.2 kcal/mole as the activation energy for dielectric absorption in water. They interpret this as breaking three H bonds having 4.5 kcal/mole each. The answer is clearly dependent on the average number of bonds presumed to be broken per water molecule. This average might well be closer to two than three, so the activation energy might be nearer 6.6 kcal/mole.

For the many organic compound ΔH's calculated in this manner (Table 7-IV), the same objections are valid when the calculations are

TABLE 7-III $-\Delta H$ Values of the H Bond in Ice

METHOD	$-\Delta H$ (kcal/mole-H bond)	REFS.
Calculated		
Raman	3	465
Work of cohesion	3.23	836
Heat of sublimation	4.25	1990
Heat of sublimation	4.5	1585
Dispersion, dipole, and induced dipole forces	4.3–4.9	1752
AC conductivity	5.17	1468
Heat of sublimation	5.8	1561b, 682
Heat of sublimation	6.1	519, 1752
Dispersion and repulsive forces	6.4	1822
Dispersion and repulsive forces	6.8	2116
Heat of sublimation	7.7 ± 1	879
Experimental		
Vapor pressure	3.4 (liquid)	1801
Second virial coefficient	5.0, 5.7 (gas)	1753, 1182
Conductance	5.75	1469
Dielectric absorption	4.4[a] (or 6.6[b]) (solid)	86
Self-diffusion	>4.6[a] (liquid)	2138

[a] Activation energy; see text.

[b] Our estimate from their data.

based on an isoelectronic compound. As an example, consider the values of oxamide, oxalic acid, and rubeanic acid in Table 7-IV. These materials are themselves isoelectronic to a single reference material, 2,3-dimethylbutane. The values derived for $-\Delta H$ are N—H···O, 4.2 kcal/mole; S—H···S, 3.8 kcal/mole; and O—H···O, 3.1 and 3.3 kcal/mole. The O—H···O values seem low but, more significant, the S—H···S value is much too high to reconcile with the demonstrated weakness of the H bonding of the thio acids.

Bondi and Simkin presented a similar calculation for liquids, using the heat of vaporization (ΔH_v) (241, 242). The purpose was to obtain an estimate of ΔH_v but in the process a value of the "H bond increment, δ(OH)" is derived. This increment is ". . . a measure of (but not identical with) the heat of formation of the H bond, . . ." Values for δ(OH) *are* very similar to enthalpy values, though they are not intended as thermodynamic functions. Bondi gives an extensive discussion of their use with simple and polyhydric alcohols and a few other compound classes. Table 7-V compares δ(OH) and ΔH values.

A somewhat different and more meaningful approach is that of Davies (1, 480), in which he plots ΔH of sublimation against c, the number of carbon atoms in the alkyl chain. The linear plot permits an easy extrapolation to zero chain length, giving a value for the terminal group. This method has not been used widely, but it is free of the objections given above. Some values derived in this way are:

TABLE 7-IV $-\Delta H$ of H Bonds in Solids Derived from Heats of Sublimation ($-\Delta H_s$)

COMPOUND	ISOELECTRONIC COMPOUND	$-\Delta H$[a]	REFS.
H_2O	Non-H bonded H_2O	4.25	1990
		5.8 ± 0.2	682
		7.7 ± 1	879
Acetic acid	*Iso*butane	7.6	379
Oxamic acid[b]	2,3-Dimethylbutane[f]	3.9	258
Rubeanic acid[b]	2,3-Dimethylbutane[f]	3.8	
α-Oxalic acid[b]	2,3-Dimethylbutane[f]	3.3	
β-Oxalic acid[b]	2,3-Dimethylbutane[f]	3.1	
2-Furoic acid[c]	*Iso*propylcyclopentane	7.0	
2-Thenoic acid[c]	*Iso*propylcyclopentane	4.3	
NH_3	Non-H Bonded NH_3	1.31	1990
Urea	*Iso*butene	3.5	1977
Oxamide	2,3-Dimethylbutane	4.2	
Acetamide	*Iso*butene	3.0	
Acetamide[d]		3.1	10
ε-Caprolactam	Methylcyclohexane[e]	7.0	1977
δ-Valerolactam	Methylcyclohexane	7.2	
Diformylhydrazine	Hexane[f]	6.1	
Dimethylglyoxime	3,4-Dimethylhexadiene	5.3	1828
Diketopiperazine	1,4-Dimethylcyclohexane	6.9, 7.0	1828, 379
Cyclohexanol	Methylcyclohexane	7.3	379

[a] Calculated by what Suzuki *et al.* (1977) call "method ii." The isoelectronic compound does not have approximately the same dipole moment as the test substance. Thus the ΔH_s includes some attraction of the dipoles present.

[b] Calculated by the present authors using the same isoelectronic value that the original authors used for oxamide (1977).

[c] Calculated by the present authors.

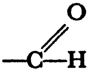
[d] Original author calculated on a different basis—used Slater-Kirkwood dispersion formula instead of isoelectronic compound.

[e] This ΔH_s was corrected by adding the ΔH_s increment for a CH_2 group.

[f] This ΔH_s was corrected by adding 0.6 kcal to account for conjugated π-electrons.

N-methyl amides[a]	$7.95 + c(1.66)$ kcal/mole
C_2–C_6 amides[a]	$16.42 + c(1.05)$ kcal/mole
$>C_7$ amides[a]	$19.80 + c(0.55)$ kcal/mole
Paraffinic alcohols[b]	$10.0 + c(2.2)$ kcal/mole
Paraffinic hydrocarbons[b]	$1.1 + c(1.7)$ kcal/mole

TABLE 7-V $-\Delta H$ and δ(OH) Values for Some Common Functional Groups

	δ(OH) (kcal/mole-H bond)		$-\Delta H$ (kcal/mole-H bond)	
FUNCTIONAL GROUP	LIQUID AT 100°C	NO. OF CASES	GAS NEAR 25°C	NO. OF CASES
—OH	4.4–4.8	>10	3.2–7.0	7
$—NH_2$	1.4–1.8	5	3.4–3.6	2
=NH	0	3	3.1–3.3	2
—C≡N	1.7–2.5	10	3	1
$—NH_2$ (aromatic)	2.4–2.8	3	—	—
 $—C(=O)—H$	1.2–1.6	9	4.6	1

The magnitudes of these numbers, compared to the much smaller values (in the range 3–5 kcal/mole) obtained in solution studies, dictate a pause to consider their significances. Possibly, certain energy contributions are included in the heats of sublimation which are not measured in the solution studies. For example, surely some fraction of the van der Waals attraction toward the solvent is lost when the H bond is formed. This serves to reduce the measured heat of dissociation of the solution dimer compared to a value measured in the vapor state; but heats of solutions are such that this could not account for more than several tenths of a kilocalorie. There is, of course, the possibility that the heat of formation of a H bond in the solid is simply larger, almost by a factor of two, than in solution. This possibility is suggested by quite another sort of information furnished by the x-ray crystal structure data of formic and acetic acids. The H bond lengths are much shorter in either of these crystals than in the gaseous dimers. The shortened lengths are good evidence of stronger interactions (see Section 3.3.5). It may be that the same situation exists for amide H

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[a] Only amides with an even number of carbon atoms have been studied.

[b] This equation is for the latent heat of evaporation at absolute zero, as derived by Moelwyn-Hughes and quoted by Davies.

bonds (the requisite bond length data are not available for the gaseous, H bonded amides).

On the other hand, there are data suggesting that amides have a rather high value for association as pure liquids. Trifan and Terenzi measured IR spectra of several polyamides and polyurethanes from 25°C to 300°C. They deduce an average $-\Delta H$ of 8.5 ±1.2 kcal/mole for the polymers.[a] Until more data are available we must draw the provisional conclusion that $-\Delta H$ for amide N—H···O bonds in crystals (and possibly in pure liquids) may be much larger than in solutions. Under any circumstances, however, we are reminded that the data of Davies establish empirically the substantial contribution of the amide groups to the stability of the amide crystal structures.

Davies also presents the interesting data reproduced in Fig. 7-2 (1).

These differences are interesting, and it is surprising that the difference, for example, between ΔH_s of benzoic acid and benzene should be the same as that between *p*-hydroxybenzoic acid and phenol. Surely it is tempting to attribute the difference to the extra enthalpy of disrupting H bonds formed by the carboxylic acid group (which contradicts the reservations we have expressed about the validity of the ΔH estimates given in Table 7-IV).

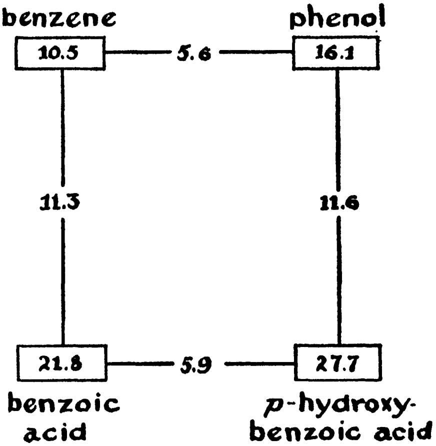

FIGURE 7-2 Some interesting heats of sublimation, and differences between them.

7.5.2 Solutions. A very large number of values of thermodynamic functions are available for solutions, but any critical selection quickly exhausts the reliable data. Common problems are the use of a solvent which enters the H bonding equilibrium, too short a temperature range, or lack of real knowledge of the species present. Davies (487) discussed some of these experimental limitations on H bond enthalpies.

Appendix B lists about 200 values for H bond enthalpies determined in solution. The emphasis is quite uneven, about a third (55 cases) of these measurements are for acetic acid, methanol, or phenol. Again, there is ample room for careful work on a series of compounds. The

[a] 2032a and Abstracts, 134th ACS meeting, p. 7T.

studies of Mecke (phenols) and Davies (acids and amides) are probably outstanding.

Binary Solutions. From the 200 reported values we have selected a few to illustrate some general features. Table 7-VI quotes some K values for solutions—arranged to show the effect of different solvents, S—H groups, and two dimer arrangements.

TABLE 7-VI Some Association Equilibrium Constants in Various Solvents[a] (K in l/m at 25°C)

	SOLVENT	
SOLUTE	CCl_4	BENZENE
Acetic acid	1000–4000	170–550[b,c]
δ-Valerolactam	280[c]	—
Propionamide	45	2.4 (30°C)
Phenol	0.7–2.3	0.57
Ethanol	0.64	—
Ethanthiol	0.021	—
Thiophenol	0.019	—

[a] See Appendix C for references.

[b] K for acetic acid in $CHCl_3$ is about the same, 100–420.

[c] Interpolated to t = 25°C.

Several points become apparent from a study of Table 7-VI. Equilibrium constants have not been determined with great accuracy—three- to four-fold variation between determinations is common. Solvent disturbances of the acid dimerization is clearly detected in the equilibrium constants. In benzene and $CHCl_3$, K may be only 1/10 its value in CCl_4. The two values available for ethanthiol and thiophenol show the weaker interactions of S—H groups: K_{assn} is about 1/25 that of comparable O—H compounds. The acid dimer is a more favorable arrangement than the dimers of alcohols and phenol.

Passing on to enthalpy data, Fig. 7-3 gives histograms to compare the frequencies of ΔH values reported for O—H···O bonds in binary solutions. The figure also compares data for O—H···O bonds in pure compounds in various states. Although the carboxylic acid value from 6.5–7.5 kcal/mole-H bond is well established, it is not typical of other O—H···O bonds. Most of the latter range from 3.5–5.0 kcal/mole-H bond, with the largest number between 4 and 4.5 kcal/mole-H bond.

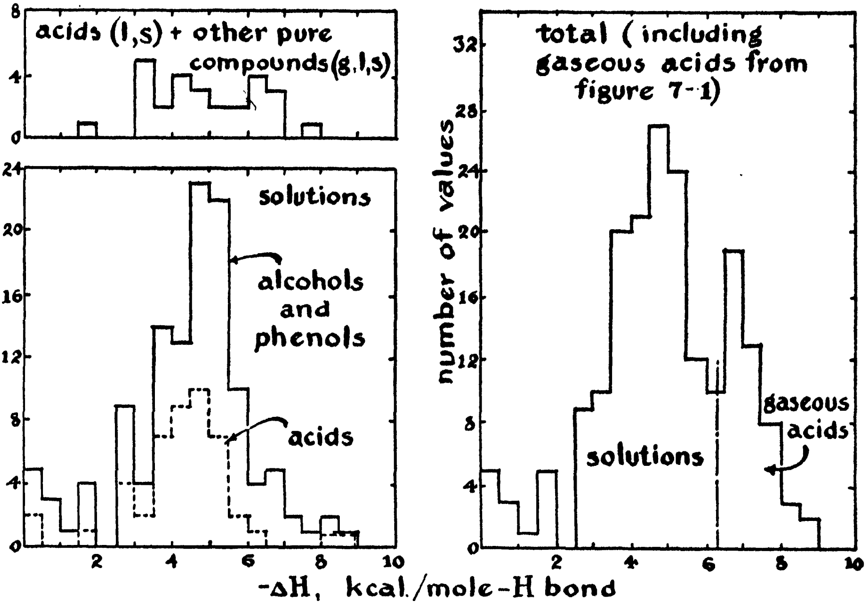

FIGURE 7-3 Histogram comparison of $-\Delta H$ values for O—H···O bonds.

In Table 7-VII, the effect of solvent on ΔH is illustrated for acetic acid, phenol, and some amides. In the lower part of the table, the series of amides in benzene shows a rather constant heat of interaction for a variety of structural changes.

The absence of a clear dependence of ΔH on the solvent dielectric constant is suggested by the identical values of ΔH for phenol in benzene and in chlorobenzene (with dielectric constants of 2.25 and 6.37, respectively). The change of ΔH for *N*-methylacetamide in $CHCl_3$ suggests an enthalpy of interaction between $CHCl_3$ and amides near 2 kcal/mole. The data for benzoic acid are not consistent, but there may be a complication of cyclic and noncyclic species. If so, a change of solvent might alter the species present as well as the fraction of the monomer. The presence of open dimer of carboxylic acids has been proposed to explain the high "atomic polarization" deduced from polarization studies (see Section 2.1.2), as well as the difference between ΔH values from gas and solution work. An alternate explanation based on higher polymeric forms is also possible (495).

In Figs. 7-4 through 7-6, ΔH *vs.* ΔS is plotted for acids, other O—H···O bonds, and amides (499). This presentation reveals a monotonic relationship between these thermodynamic properties for

TABLE 7-VII Some Selected Values for $-\Delta H$ of H Bonding in Binary Solutions

	$-\Delta H$ (kcal/mole-H bond[a]) SOLVENT		
SUBSTANCE	CCl_4	BENZENE	$CHCl_3$
Benzoic acid	5.0[b]	4–8[b]	6.3[b]
Phenol	4.3	3.5	—
		3.5[c]	—
Acetamide	—	3.6	—
N-Methylformamide	—	3.5	—
N-Methylacetamide	3.9	3.6	1.6
N-Methyltrichloroacetamide	—	3.6[b]	—
Trichloroacetamide	—	3.6	—
N-Methylbenzamide	—	3.6	—
Acetanilide	—	3.0	—

[a] See Appendix B for references.

[b] For each H bond in an assumed cyclic dimer.

[c] The solvent here is chlorobenzene.

acids and hydroxyl compounds. Included in the figures are equations for least square lines and the standard errors of estimate, σ, for each. The relation is intuitively reasonable: a higher value of $-\Delta H$ implies stronger bonding, with a more restricted configuration in the polymer,

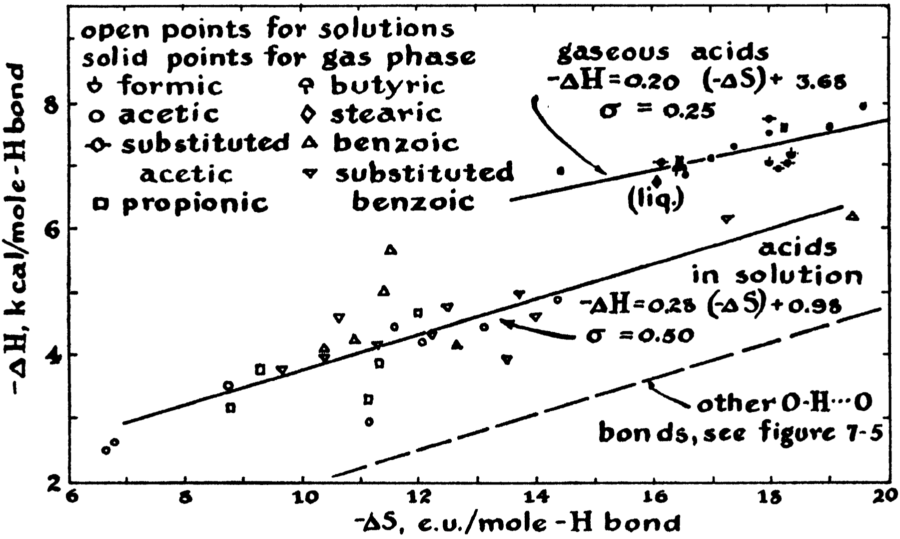

FIGURE 7-4 $-\Delta H$ *vs.* $-\Delta S$ for carboxylic acids. $-\Delta S$ from K in atm^{-1}.

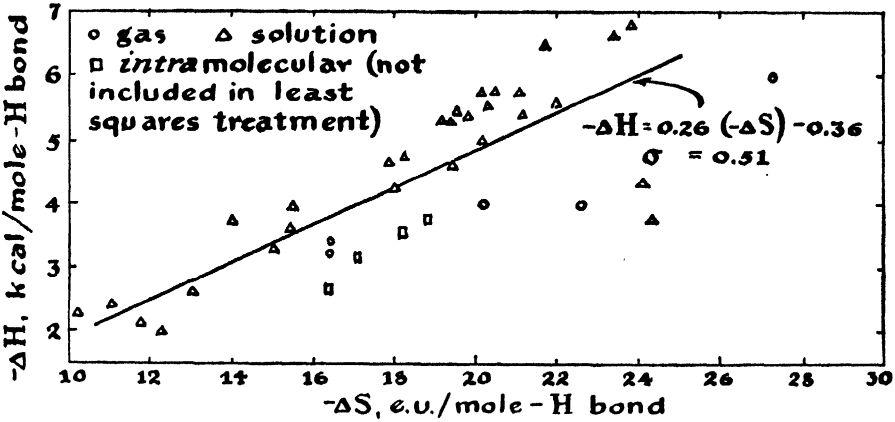

FIGURE 7-5 $-\Delta H$ *vs.* $-\Delta S$ for O—H···O bonds other than in acids. $-\Delta S$ from K in atm^{-1}.

hence greater order leading to a larger value of $-\Delta S$. It is of importance that these two effects tend to work against each other in ΔF, since a change in ΔH is partially compensated for by an accompanying change in ΔS [see equation *(4)*]. The result is that the equilibrium constant is not particulary sensitive to change in the ΔH of H bond formation.

Ternary Solutions. The thermodynamic properties of this group of solutions are probably the least well documented of all those discussed. They exemplify all the problems mentioned at the beginning of the section on solutions. In addition, this region has had the least amount of good systematic work.

Again, individual values of interest may be found in Appendix B. Tables 7-VIII and 7-IX show some trends. For phenol-ester combinations, hydrocarbon solvents appear to give a slightly higher enthalpy and entropy than does CCl_4 (Table 7-VIII). The effects of alkyl and chlorine substitutions are shown in Table 7-IX. The drastic effect of *ortho*-chloro substitution is distinctive, obviously caused by *intra*molecular H bonding.

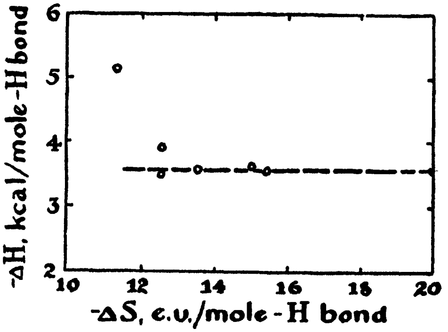

FIGURE 7-6 $-\Delta H$ *vs.* $-\Delta S$ for amides (N—H···O). $-\Delta S$ from K in atm^{-1}.

The remainder of the data on ternary solutions is on systems too diverse to allow comparisons.

TABLE 7-VIII Thermodynamic Values of Phenol Solutions in CCl_4 and Hydrocarbon Solvents[a] ($-\Delta S$ from K in l/m)

	CCl_4 SOLVENT		HYDROCARBON SOLVENT		
COMPOUNDS	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$	SOLVENT
Phenol-dioxane	4.7, 3.8	11.5, 18	5.4	13.1	Pet. benzene
Phenol-ether	3.7	7.6	3.8	18	Hexane
Phenol-ethyl acetate	4.8	11.9	5.7	13.7	Pet. benzene

[a] Data from 1478, 1480, 1481, 2047.

TABLE 7-IX The Effect of Substituents on $-\Delta H$ and $-\Delta S$ for Phenol-Ester Combinations ($-\Delta S$ from K in l/m)

COMPOUNDS	SOLVENT	$-\Delta H$	$-\Delta S$	REFS.
Phenol-methyl acetate	*n*-Heptane	5.3	12.8	1478
Phenol-ethyl acetate	Pet. benzene	5.7	13.7	
Phenol-methylchloro acetate	Pet. benzene	5.0	13.7	
p-Chlorophenol-methyl acetate	*n*-Heptane	6.7	16.9	
m-Chlorophenol-methyl acetate	*n*-Heptane	6.5	15.2	
o-Chlorophenol-methyl acetate	*n*-Heptane	1.4	3.5	
α-Naphthol-methyl acetate	*n*-Heptane	5.7	13.7	1479

7.6 Theoretical Values of Solution Thermodynamic Functions

There have been several approaches to the expression of thermodynamic quantities of solutions. Scatchard published a series of papers (see 1801 and previous papers, especially 1802) based on the classical approach via chemical potential. Barker (130, 128, 131) applied the theory of conformal solutions (1254) to some H bonding systems after modifying it to allow for dipole attractions or, more generally, molecular orientations. The curves are similar in both cases.

Scatchard's procedure is the basis for calculating "excess" thermodynamic functions (ΔH^E, ΔS^E, ΔF^E)—the difference between the function for the ideal solution and actual solution of the same composition. The excess functions can be calculated from accurate vapor pressure-composition data. They are usually plotted in a diagram such as Fig. 7-7.

It should be emphasized that the method is not limited to H bonding solutions. It is useful, for instance, in studying the thermodynamic consequences of mixing molecules of very different molecular size, as is done in polymer solutions. However, it is instructive to consider the results that are available for associated solutions in which ΔH^E is usually an order of magnitude larger than it is for non-H bonded systems.

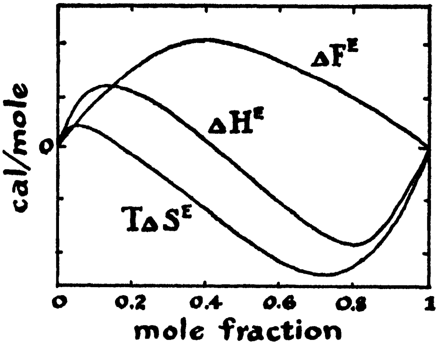

FIGURE 7-7 Schematic diagram of excess thermodynamic properties as a function of solution composition (various properties can be negative, depending on the system).

In general, we can say that ΔH^E curves with a maximum result from breaking of H bonds, and the reverse is true for forming of H bonds. These generalities are hard to apply in those cases where H bonds are both made and broken. Presumably the observed curve is the net result of these two tendencies, and we might expect examples to be found for both forms of curve within each solution type.

Various authors have commented on the effect of H bonds on heat of mixing at a single concentration—usually 0.5 mole percent. This gives a single value for the heat of mixing, and its sign can be predicted fairly well. One of the most extensive studies of this type (1313) was discussed in Section 2.4.4 and illustrated by Table 2-XII where the actual trends are compared with those predicted from Table 2-X.

Here is another occasion to remember that there are no sharp boundaries to the definition of H bonds—weak interactions involving hydrogen atoms will have properties like "strong" interactions of the normally weaker, less specific causes.

7.7 Conclusions

Despite the large number of entries in Appendixes B and C, the most striking conclusion is that there are few systems which have been thoroughly studied. Even for the heavily investigated carboxylic acids, the solvent effect is not clear. Probably the most important reason for this is the difficulty of determining the species present (e.g., as in alcohols, phenols, and amides). In addition there remain several possible difficulties which require clarification: IR absorption coefficients may vary with temperature; ΔH may vary with temperature; H bond enthalpy probably depends upon polymer size. Some method of expressing the multiple nature of the associated ensemble and its change with temperature is needed. Perhaps some help will come from polymer theory, since at least a part of this problem is common to both areas. Nuclear magnetic resonance has some potentiality for the determination of thermodynamic properties. It may prove to be a powerful method.

A selected list of "best" values for ΔH of some representative H bonds is given in Table 7-X. For individual values, refer to Appendix B.

TABLE 7-X Selected Values of $-\Delta H$ (kcal/mole-H bond)

H BOND TYPE	COMPOUND	DIMER GAS	DIMER IN CCl_4	PURE LIQUID
O—H···O	CH_3COOH	7.0	5.4	5.8
	H_2O	5.0	—	3.4
	CH_3OH	4.5 ±1.5	4.6 ±1.2	4.7
	C_6H_5OH	—	4.3 ±0.2	—
N—H···O	$CH_3CONHCH_3$	—	3.9	—
N—H···N	NH_3	4.4	—	—
	CH_3NH_2	3.4	—	—
F—H···F	HF	6.8	—	—
C—H···N	HCN	3.3	—	4.6

Although in some specific series (acids, phenols) there seems to be a variation of ΔH with solvent or phase change, there is, as yet, as much disagreement between individual determinations for a specific compound as there is change from these factors. The result is that the effects are not well understood, and predictions of change of ΔH with solvent or phase change are not possible.

Equilibrium constants for about 250 compounds or systems are available (see Appendix C). Yet, there is rarely more than a single study of a given system. Even in the more thoroughly studied cases (acetic and benzoic acids, phenol, and HF) values from various methods disagree sometimes by a factor of 2 or 3. Once again the most outstanding conclusion is that additional accurate and systematic studies are needed.

CHAPTER **8**

Theory of the Hydrogen Bond

For the best and safest method of philosophizing seems to be, first diligently to investigate the properties of things and establish them by experiment, and then to seek hypotheses to explain them. For hypotheses ought to be fitted merely to explain the properties of things and not attempt to predetermine them except in so far as they can be an aid to experiments.[a]

ISAAC NEWTON *Cambridge University, 1689*

8.1 Introduction

The development of a "theory" of a chemical behavior usually passes through three evolutionary stages. At first, as data are collected, the scientist attempts to find correlations. Then, as the structure of the phenomenon becomes clear, he tries to fit the phenomenon into existing theory. Finally, the theorist gains confidence in a particular model of behavior (a new theory) which agrees with the facts sufficiently well that the model has qualitative and preferably quantitative predictive power. It is at this point that a new theory can significantly influence and aid the growth of our knowledge of chemical behavior.

The development of the theory of the H bond chemical interaction entered this last phase about two decades ago. Yet, in 1957 Coulson said, "the most that can be expected is that calculations will give us indications as to those explanations which are most likely to be correct,

[a] Isaac Newton, *Principia*, Motte's Translation Reviewed by Cajori, University of California Press (1934), p. 673.

and which are unlikely" (446). Today the theory remains a subject of considerable controversy, its qualitative predictive power is limited, and it has almost no quantitative predictive power. It seems certain that the full impact of the H bond upon our general theory of the chemical bond has not yet been realized.

8.1.1 Reviews of the Theory of Hydrogen Bonding. Reviews of the theory of the H bond are numerous.[a] Inasmuch as the Russian literature is not always readily accessible, it is of special note that two such reviews concern Russian contributions: that of Sokolov (1913, in German) and that of Magat (1317, in French).

Discussion of the H bond theory is divided into two portions in this chapter. First, the nature of the bond itself is considered, together with the relevant and informative data. Second, theoretical treatments of individual properties of H bonded systems (such as heat of formation, vibrational perturbations, NMR shifts, dielectric effects) are considered in the light of the first part. Before proceeding with the discussion, however, it will be helpful to review certain aspects of modern theory of the chemical bond.

8.1.2 Ionic and Covalent Bonds. In this chapter much is said on the question of whether the H bond is electrostatic in character. In this use, the term "electrostatic" denotes that the bond forms as a result of attractive coulombic interactions of charge separations existing prior to bond formation. It is important to note that the valence rules play no role in the explanation of the bonding.

To justify such a description within quantum mechanics we are led into a consideration of ionic and covalent contributions to an approximate wave function. If covalent contributions are minor, the bond is said to be ionic in character, and the electrostatic model is considered to be applicable. Unfortunately, the terms "ionic character" and "covalent character" are used with various meanings. This is so, in part, because the rapid development of chemical bond theory has caused a drift of the meanings of these terms over the past two decades. Pauling's definitions, as presented in his book (1585, p. 48), no doubt represent the intent of most workers as of 1940. He concluded that there is a covalent bond between two atoms X and Y if the dissociation energy of X—Y is the mean of the dissociation energies of X—X and Y—Y. If the dissociation energy of X—Y exceeds this mean, the excess is attributed to "additional ionic character of the bond." This criterion furnishes the basis for his scale of electronegativity, and ionic character is inter-

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[a] 446, 1913, 1914, 1910, 1317, 171, 1755, 1004, 1006, 172, 989.

preted as being associated with charge separation in the bond, yielding a permanent dipole moment. This definition of ionic character is an operational one since it is fixed by measurable dissociation energies.

As the chemist has gained his sea legs in the use of wave mechanics he has attempted to define covalent and ionic character in terms of wave functions. The new point of view is presented, for example, by Coulson, who maintains, "there are two distinct definitions of a covalent bond" (447, p. 145). He proceeds to describe the bond wave function, first by a molecular orbital type approximation, and then by a valence bond type approximation. In either case the approximate wave functions consist of linear combinations of atomic orbitals. Partial ionic bonding is revealed by the magnitudes of coefficients which imply asymmetry of electron distribution.

Regardless of preference, we are faced with three definitions of the term "ionic character," in terms of: electronegativity, molecular orbitals, or valence bond wave functions. Any paper on the nature of the H bond must be evaluated in the light of what the *writer* meant *when he wrote that paper.*

There is one more question we need to ask of quantum mechanics: What can it tell *positively* about chemical bonds? What can be said which is quite free of the reservations that the usual approximation procedures imply?

Let us consider the joining of two atoms X and Y to form a stable bond X—Y. The potential terms in the exact wave equation describing X—Y *are* precisely known, and they can be written without *any* knowledge or consideration of the electronegativities of X and Y. Every potential term is either an attractive coulombic term between unlike charges, a repulsive coulombic term between like charges, or a term depending upon the interaction of electron spin and electron orbital angular momentum. The chemical bond occurs when there is an electronic distribution which has a net gain of attractive interactions over repulsive interactions compared to the separated atoms. The point we have made is not meant to be profound but is intended to help maintain perspective in discussing the nature of the H bond: quantum mechanics tells us that *all bonds have their origin in the same wave equation.* Applying this conclusion to H bonds, the wave equation for the interaction of A—H (i.e., X) with B (Y) does *not* contain special terms when the unperturbed A—H bond has an unsymmetrical charge distribution. Even if experience were to indicate that H bonds are not found unless A—H has an unsymmetrical charge distribution, we could be certain that this is *not* because there are extra potential terms resulting from the asymmetry. Hence we can look forward to the disappearance of the ionic bond when the millennium of chemical theory begins. In that age of exact wave functions, all molecular structure problems will be solved on a computing machine with but one program of calculational instructions. There will no longer be a need to segregate molecules into classes suitable for different approximation methods.

8.2 Theories of Hydrogen Bond Formation

We are fortunate in having a current and authoritative review of the theoretical treatment of the H bond by Coulson (446). This review was presented at the 1957 Ljubljana Conference, and it was well received by that critical audience as a representation of the status of the theory. Coulson's first point was a warning against the hope for quantitative agreement with experiment. With current approximations, quantum mechanics is barely able to estimate the energies of normal bonds to an accuracy of ±20 kcal, an uncertainty about four times as great as the entire H bond energy. Coulson does propose, however, that it is now "possible to say with some confidence just what are the really significant factors." With this introduction, we shall turn to the now classical theory of the electrostatic nature of the H bond.

8.2.1 The Electrostatic Model. The *electrostatic* model of the H bond inevitably and properly brings to mind the name of Pauling (1590). In his book, *Nature of the Chemical Bond*, he states that the bonding properties of the hydrogen atom depend upon the 1*s* orbital. With a single orbital, the hydrogen atom cannot form more than one pure covalent bond. Hence he concludes that the H bond formation must be due to ionic forces. This argument, which was presented in 1928 (1590), is based upon the Pauli exclusion principle, the valence bond representation of the chemical bond, and the classical valence rule that the H atom bonds solely through the 1*s* orbital. (See also 1589.) It is still advanced by proponents of the electrostatic theory, and is found in modern textbooks (e.g., 447, p. 302; 1643, p. 197). This argument is empirically supported by the fact that the strongest H bonds are formed when A and B are fluoride ions, the H bonds involving oxygen atoms are next strongest, and N—H acids usually form relatively weak H bonds. As additional evidence there have been cited calculations based on point charge

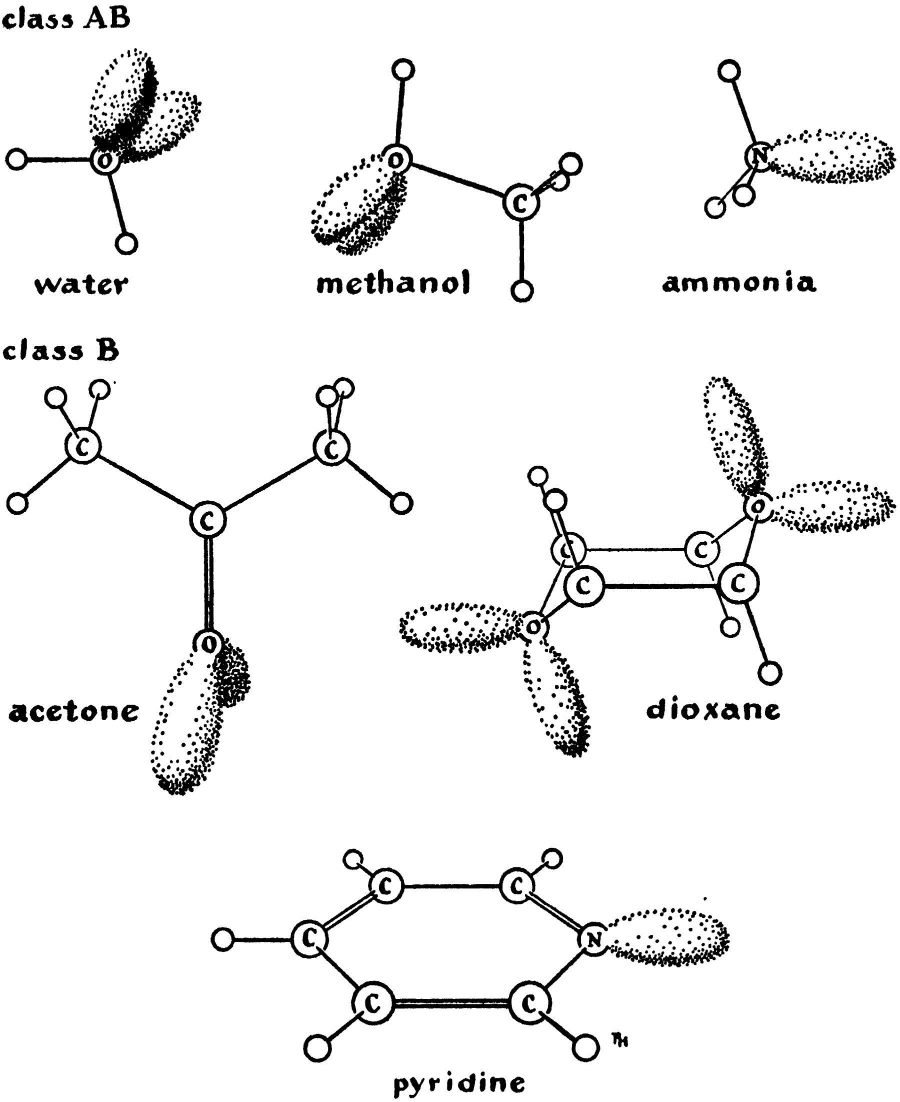
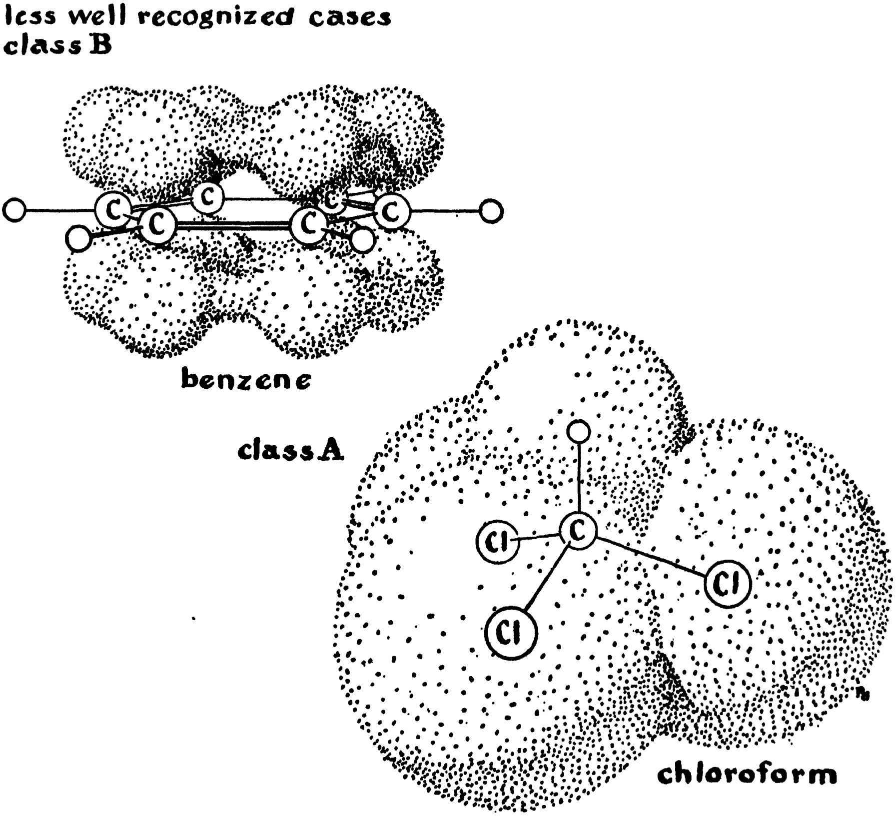


FIGURE 8-1 Proposed spatial distributions

models of H bond energy (see footnote *a*, Section 8.3.1), dielectric properties (199, 172), and spectroscopic properties (1084, 199, 1767, 1327, 407, 1849).

Modern discussions of an electrostatic model of the H bond are more sophisticated than the earliest point charge calculations. Theorists believe that the charge distribution of the nonbonded electrons must be explicitly included in the calculation. Furthermore, the concept of orbital hybridization provides a basis for deciding this charge distribution. Figure 8-1 shows the structures of some H bonding substances, including the popularly accepted electron distributions for nonbonding electrons. With an assumed orbital hybridization, the point charge model can be modified to specify the approximate spatial position of the electrons of the base in a H bond. Such a treatment is considered as giving a more



of electrons important in H bonding.

accurate estimate of the H bond energy and a reliable prediction of the H bond orientation relative to other bonds of the base molecule.

For example, Lennard-Jones and Pople proposed that the electrostatic description of the H bond of water should be as shown in Fig. 8-2 (1210, 1659). The charges were placed so as to give the correct dipole moment, and then the electrostatic energy was calculated. The resulting energy, 6 kcal, was sufficiently reasonable to encourage the use of the model. Fyfe applied the model to a variety of systems, including HF_2^- (737), and proposed that there is no sharp transition between elements forming or not forming H bonds. The approach is amplified in a paper by Schneider on the role of the lone pair electrons (1812). He begins with the premise that "the H bond is known to be primarily electrostatic in nature," and that the point charge model used by Bauer and Magat (172) is unsatisfactory "on the basis of more recent knowledge of the structure of the water molecule." Schneider proceeds with a detailed treatment based on point charges placed at the centroids of charge of hybridized nonbonding orbitals. (See also 1470a.)

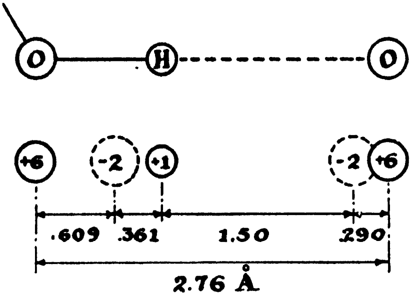


FIGURE 8-2 Lennard-Jones and Pople electrostatic model for H bonded water (as applied by Schneider, 1812).

Of course, this model depends upon the reliability with which the orbital angles and charge distributions can be predicted. Calculations of H bond energies do not offer a severe test because there is parametric freedom in the placement of the point charges. The bond angle expectations are less arbitrary and not specifically dependent on the electrostatic model of the H bond. The structure of ice presents a notable success. Presuming sp^3 hybridization for each oxygen atom, the model places each pair of nonbonding electrons precisely on the line of centers of two oxygen atoms. For carbonyl bases the H bond should make an angle of 120° to the C=O bond direction. In crystalline formic acid this angle is 122°, but in crystalline acetic acid the angle is 144° (see Fig. 9-4). The deviation from 120° is also observed in the crystal structures of amides. In Table 10-I the data show that the angle between the C=O bond and the N····O line varies from 95° to 164°. Finally, Table 9-XI shows a variety of examples in which the acid is an alcohol.

For carbonyl bases the angle of interest falls in the range 99–120°. When the base is the oxygen in an hydroxyl group, the angle varies from 90° to 135°.

Two conclusions can be drawn from these data. First, any prediction of the orientation of the H bond must be assigned an uncertainty of about 20°. On the other hand, the bond angles display a tendency which reassures us in using the concept of orbital hybridization, whether in an electrostatic or a covalent description of the H bond.

8.2.2 Deficiencies of the Electrostatic Model. At the 1957 Ljubljana Conference one of the important points of fairly general accord was that the electrostatic model does not account for all of the phenomena associated with H bond formation. Toward this conclusion, Coulson (446) lists the following types of evidence.

1. The increase in intensity of IR absorption of ν_s in many-fold excess of that explainable by the electrostatic model. (See 693, 979, 2097.)
2. The absence of correlation between H bond strength and dipole moment of the base (812, 2055, 1792).

Other experimental data which have been cited as evidence against a purely electrostatic description of the H bond are:

3. The lowered IR intensity of ν_b (979, 2097).
4. The angular orientation sometimes found between the dipoles of A—H and B—Y in crystals involving H bonds A—H···B—Y [for example, the molecules in the hydrogen halide crystals take a zigzag arrangement in preference to the parallel orientation preferred by a dipolar array (957, 82)].
5. Frequency shifts in electronic transitions (2053).
6. The relative stabilities of the *cis-* and *trans-* forms of the *ortho-*halophenols (1748).

Of these, probably the most decisive are type 2 and the combination of types 1 and 3. It is difficult to rationalize the weak H bonds formed by acetonitrile as a base (molecular dipole moment of 3.44 D) and the strong H bonds formed by trimethylamine (molecular dipole moment of 0.7 D) together with the interpretation that an acid A—H forms H bonds with these bases because of the electrostatic interaction of the A—H dipole with point charges on the nitrogen atoms. Another interesting comparison is afforded by the approximately equal H bond properties of acetone, diethyl ether, and dioxane, with dipole moments of 2.85 D, 1.15 D, and 0.4 D, respectively. These qualitative discrepancies can be backed by a substantial body of quantitative data. Table 8-I collects some of these data, and verifies the absence of any systematic dependence of enthalpy of H bond formation upon the molecular dipole moment. Compilations of $\Delta\nu_s$ (814) and of ΔF show that these properties are similarly unrelated to μ. Certainly these data show that the strength and behavior of a H bond are not determined in a direct way by the dipole moment. This lack of dependence is not easily reconciled with

TABLE 8-I ΔH of H Bond Formation and Dipole Moment of Various Acid-Base Pairs[a]

ACID	BASE	$-\Delta H$ (kcal/mole)	μ (acid) (Debyes)	μ (base) (Debyes)
Phenol	Benzyl acetate	3.3	1.7	1.8
	Diethyl ether	3.7		1.2
	Acetonitrile	4.2		3.4
	Dioxane	~4.5		0.4
	Ethyl acetate	4.8		~1.8
	Trimethylamine	5.8		0.7
	Dimethylformamide	6.4		3.85
	Hexamethylene tetramine	6.9		0
Benzyl alcohol	Dioxane	2.1	1.7	0.4
Phenol		~4.5	1.7	
p-Cresol		5.3	4.4	
o-Cresol		5.4	3.7	
m-Cresol		5.7	4.2	
Benzoic acid		6.2	1.0	

[a] The dipole moments were collected from a variety of standard reference sources such as 1206a and 2160. The values of ΔH are from Appendix *B*.

the electrostatic model of the H bond. Turning to the intensity of absorption of the A—H bending mode, it would surely be expected to increase, not decrease, if the enhancement of the stretching mode is properly attributed to increased ionic character of the A—H bond (as suggested by Barrow, 139). The alternate explanations which have been offered for these behaviors may be classed together in that they all impute some covalent character to the H bond. This opens the next topic for consideration, estimates of the relative importance of ionic and covalent contributions to the H bond interaction.

ψ_a	A———	H	B	covalent A—H bond
ψ_b	A^-	H^+ ··········	B	ionic (no charge transfer)
ψ_c	A^-	H—————	B^+	covalent H—B bond (with charge transfer)
ψ_d	A^+	H^-—·—·—·—·—	B	ionic (no charge transfer)
ψ_e	A	H^-	B^+	covalent A—B bond (with charge transfer)

$$\Psi = a\psi_a + b\psi_b + c\psi_c + d\psi_d + e\psi_e$$

FIGURE 8-3 Possible valence bond structures for the H bond.

8.2.3 Estimates of Covalent Character. Coulson (446) reviews attempts to determine the amount of *covalent* contribution to the H bond by the variation approximation scheme. Five valence bond structures which might be considered are shown in Fig. 8-3. Coulson and Danielsson (448) utilized variation trial functions appropriate to structures ψ_a, ψ_b, and ψ_c, together with the assumed exponential relation between bond length, r, and bond order, p:

$$p = \exp\{\bar{c}[\mathrm{r}(1) - \mathrm{r}(p)]\} \qquad (1)$$

$\bar{c}$ = constant for all elements

r(1) = bond length of a normal single bond ($p = 1$)

In Coulson and Danielsson's treatment the coefficients a, b, and c were estimated with additional assumptions. The coefficients a and c were taken to be proportional to the bond orders of the A—H and H—B bonds. This assumption with equation *(1)* leads to the relation

$$\frac{a}{c} = \exp\{-\tfrac{1}{2}\bar{c}[\mathrm{r(A—H)} - \mathrm{r(H—B)}]\} \qquad (2)$$

One more assumption which determines the coefficient b relates the molecular dipole moment to the contribution of the ionic structure ψ_b. The relation presumes that ionic character does not change when the H bond forms. Even within this complex of assumptions we can proceed to calculate the importance of ψ_c, the covalent H bond term, only after the proton position in the H bond is specified. For the particular case of both A and B taken to be oxygen atoms, Coulson and Danielsson assumed a constant A—H bond length of 1.0 Å (448). This leads to their conclusion that "the long bond [2.8 Å] is essentially electrostatic, the covalent contribution . . . amounting only to a few percent." Even so, they add, "With the short H bond [2.5 Å] . . . covalency is beginning to be appreciable."

Aside from the assumptions not open to direct test [e.g., equations *(1)* and *(2)*], there is a serious weakness in the assumption of constant A—H distance. Experiment shows that a H bond of over-all length 2.5 Å would have an O—H bond length near 1.07 Å (see Fig. 9-1). Because equation *(2)* is extremely sensitive to a change in r(A—H), this raises the estimate of the amount of covalent character to 22 percent, double the value obtained by Coulson and Danielsson. Since this is in fair agreement with a second estimate (based on a Morse potential curve) by Coulson and Danielsson, it would seem that the appropriate conclusion of this paper should not be that the H bond is essentially ionic but rather that the covalent contribution is quite important for short H bonds (see comments in 1488). Of course, the uncertain validity of the assumptions remains to becloud either conclusion.

The treatment just outlined might be described as semiempirical. Although the essence of the procedure is quantum mechanical, coefficients in the variation trial function are determined through the empiricisms represented by equations *(1)* and *(2)*. A less empirical procedure is to write explicit functions considered to represent the structures in Fig. 8-3, and to determine the coefficients by use of the variation method secular determinant. This procedure requires the evaluation of complicated integrals, and tractability dictates simplifications which result in new uncertainties. Coulson and Danielsson attempted such a more rigorous calculation (448a), but that paper will not be described because Coulson (446) indicates that Tsubomura's treatment based on all five structures in Fig. 8-2 is a substantial improvement (2055). Tsubomura finds that the addition of structures *c* and *e* lowers the energy by 8.1 kcal, an amount larger than the 5.95 kcal calculated with an electrostatic model by Pople (1659). Tsubomura refers to this energy as "delocalization energy," and concludes that "the delocalization energy is of the same order of magnitude as, or rather larger than, the electrostatic energy."[a] (See also 1529.)

Sokolov made early calculations based on wave functions ψ_a, ψ_b, and ψ_c (1919, see 1913). His focus of attention included the behavior of the IR stretching frequency, ν_s, (1919) and proton transfer processes (1912, 1918, 1920). He concludes that the electrostatic conception of the H bond is inadequate in explaining these phenomena. In contrast, the electron donor-acceptor point of view provides a useful model for clarifying these behaviors (1913).

8.2.4 Molecular Orbital Description. The *molecular orbital* description of the H bond has received surprisingly little attention. Pimentel considered HF_2^- qualitatively with molecular orbitals composed of linear combinations of atomic orbitals (1634). (See also 1529.) Using only fluorine *p* orbitals directed along the bond (p_A and p_B) and the hydrogen atom 1*s* orbital (*s*), three molecular orbitals result. These are shown in the second column of Fig. 8-4. Since the H bond involves four electrons,

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[a] The calculation yields the following percentage importances of the several trial functions: ψ_a, 70 percent; ψ_b, 8 percent; ψ_c, ~1 percent; ψ_d, 19 percent; ψ_e, ~1 percent. This result, which applies to an oxygen-oxygen length of 2.70 Å with an O—H bond length of 0.96 Å, is recognized by Tsubomura to be intuitively shocking. It indicates that ψ_d is twice as important as ψ_b, although ψ_d places a negative charge on the hydrogen atom and a positive charge on the oxygen atom whereas ψ_b has the expected charge distribution. In spite of Tsubomura's discussion of the significance and cause of this result (2055), it must be remarked that these coefficients provide no reassurance of validity of the calculations.

	Symmetrical H Bond	Unsymmetrical H Bond	No H Bond
ψ_3 (antibonding)	$(p_A - p_B) - a_3 s$	$(p_A - b_3 p_B) - a_3 s$	$p_A - a_3 s$
ψ_2 (nonbonding)	$p_A + p_B$	$b_2 p_A + p_B$	p_B
ψ_1 (bonding)	$(p_A - p_B) + a_1 s$	$(p_A - b_1 p_B) + a_1 s$	$p_A + a_1 s$

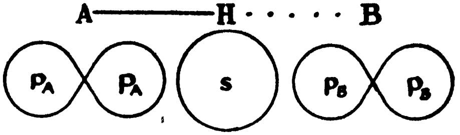

FIGURE 8-4 Molecular orbitals for H bond formation (not normalized).

the ground state $\psi = \psi_1^2\psi_2^2$ involves the bonding orbital ψ_1 and the nonbonding orbital ψ_2. Thus the molecular orbitals provide a concise though qualitative description of the bonding in HF_2^-. Since only one pair of electrons formally takes part in bonding in an orbital extending over two bonds, each bond is expected to be relatively weak. This is in accord with the long bonds in HF_2^- which are about 25 percent longer than the bond in gaseous HF. The other electron pair occupies a nonbonding orbital which places the excess charge on the fluorine atoms, the location dictated both by electronegativities and by one's chemical intuition.

The appeal of this uncomplicated description makes further examination worthwhile. It can be extended to unsymmetrical H bonds by varying the coefficients as shown in the third column of Fig. 8-4. In each orbital the coefficient b decreases from unity to zero as the atom B is moved away from a symmetrical position. When the distance is sufficiently large that no H bond exists, the pair of electrons in ψ_1 forms the A—H bond, and the other pair of electrons is located on the base atom B. In this picture, the H bond formation results from participation of p_B in ψ_1, the bonding orbital. No issue of violation of the Pauli principle is raised, though only the 1s orbital of the hydrogen atom is in use. The bonding orbital simply extends to the region on either side of the H atom giving bonding on either side. The importance of the electronegativity of A and B appears in the nonbonding ψ_2 where the second pair of electrons must be housed. If A and B are electronegative, ψ_2 represents a favorable repository for these electrons. Thus the electronegativity plays a rather passive role in this molecular orbital discussion.

If this is the role of electronegativity, we might expect that the H bond would be formed to atoms of low electronegativity, provided the number of electrons in the system does not require occupancy of ψ_2.

This is, of course, the situation in the electron deficient boranes.[a] Hence it is interesting to find the striking similarity of the three center orbitals proposed by Eberhard, Crawford, and Lipscomb for the borane B—H—B bridges (573) to Pimentel's three-center orbital ψ_1 of HF_2^-. The principal difference in the descriptions is that the bifluoride ion case involves four electrons, and hence the nonbonding orbital ψ_2 must be utilized. Since this implies high charge on the terminal atoms, the bond will be most stable if these atoms are highly electronegative. In the electron deficient boranes, however, there are too few electrons to permit occupancy of ψ_2, and the low electronegativity of the boron atoms is well adapted to the optimum electron sharing between hydrogen and boron. We see that the molecular orbital treatment provides a qualitative basis for understanding both the H bond and the boranes.

8.2.5 Empirical Potential Functions. There is one more type of treatment which is properly classified as an empirical model of the H bond. An explicit form is assumed for the potential function associated with the movement of the H atom within the H bond. Nordman and Lipscomb have proposed such a model based upon a Morse function (1521). This proposal will not be explored, however, in favor of the similar and more completely developed *potential function* model of Lippincott and Schroeder (1242, 1815). The potential function is written as a sum of four terms, the first of which has the form

$$V_1 = D_o\{1 - \exp[-n(r - r_o)^2/2r]\} \tag{3}$$

where

r = A—H internuclear distance (with force constant k)
r_o = A—H equilibrium distance in absence of the H bond (with force constant k_o)
D_o = A—H bond dissociation energy
n = parameter

The second term, V_2, has the same form as V_1 but applies to the H···B bond. It involves the quantities r^*, r_o^*, D_o^*, k_o^*, and n^*, which have the same meanings for the H···B bond as do their unstarred counterparts for the A—H bonds. The remaining terms, with arbitrary coefficients $\bar{A}$ and $\bar{B}$, represent van der Waals repulsion and electrostatic attraction between atoms A and B.

$$V_3 + V_4 = \bar{A}\exp(-bR) - \bar{B}R^{-m} \tag{4}$$

R = A ··· B distance

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[a] The hydrogen bridge structure of diborane is shown in Fig. 6-1.

The potential function contains, in addition to the spatial variables r and R, ten parametric variables. All but three of these are related to observational data, with the aid of such relations as $(\partial V/\partial r)_{\text{equilib.}} = 0$. With the two assumptions that $r_o = r_o^*$ and $k_o = k_o^*$, only one parameter remains and that one is selected to obtain optimum fit to certain data. Lippincott and Schroeder have used this potential function in attempting to correlate such experimental behavior as the dependence of frequency shift, $\Delta\nu_s$, on R, of $\Delta\nu_s$ on H bond energy, and of r on R.

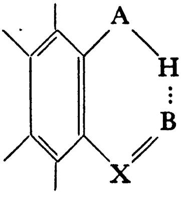
The usefulness of this function, like that of the Morse function for diatomic molecules, depends upon its applicability to observational data and upon its convenience. Unfortunately it does not possess the virtue of simplicity, a substantial deficiency from the standpoint of convenience. Whether its applicability to data will stimulate general acceptance of the function remains to be seen. Nevertheless, the goal of discovering an empirical potential function which expresses the energetics of the vibrational degrees of freedom of the H bond is one of considerable interest and value. (See also 989, 2070, 1792, 112, 1951, 1078.)

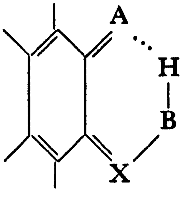
8.2.6 Mesohydric Tautomerism: Resonance. For completeness, brief reference should be made to proposals on the nature of the H bond which have not won general acceptance.

The term *mesohydric tautomerism* was proposed by Hunter to describe the sharing of a tautomeric H atom by two atoms of oxygen, nitrogen, or sulfur (but not carbon) (1006). His review (1004) indicates that this terminology describes a model based on belief in a resonance description of the H bond. Hunter describes an associated substance B—A—H···B—A—H in terms of the two structures *(a)* and *(b)* below.

··· H—A—B ··· H—A—B ··· H—A—B ··· H— *(a)*
—H ··· A—B—H ··· A—B—H ··· A—B—H ··· *(b)*

Hunter asserts that "the chemical and . . . physical properties . . . are intermediate between those expected of *(a)* and *(b)*, . . . although neither of these tautomers has a real existence." The same type of resonance is considered to account for H bond chelation, as shown by the example:





"The main tenet of the conception . . . is the nonexistence of the individual tautomers."

Hunter proposes that this main tenet is verified by a number of crystallographic determinations (1011).

Any evidence that the individual tautomers *do* exist discredits one basic notion of mesohydric tautomerism. Surely the relatively small perturbations of the A—H vibrational bending modes indicate that the H atom remains "attached" to A though H bonded to B. (See Section 3.4.1.) Possibly more obvious evidence is that offered by spectroscopic measurements which locate the H atom. Both neutron diffraction and proton magnetic resonance studies show that the proton is usually nearer one atom than the other. (See Section 9.3.)

The *resonance* implicit in the concept "mesohydric tautomerism" has been specifically proposed by a number of authors both prior and subsequent to Hunter's proposal (Sidgwick, 1871; Sherman, 1844; Coates, 399; Wirtz, 2187; Vand, 2091). Coulson disposes of models based on resonance of a covalent character between two structures on the grounds that "(i) . . . it does not provide enough resonance energy unless the protons are central to each O···H···O region and (ii) . . . in order to get them there it would be necessary to expend too much energy on stretching the normal O—H bonds." (446). (See also 275.)

8.2.7 Subclassifications of H Bonds. *Subclassifications* among H bonds have been proposed since the earliest studies of the H bond. For a time there were proponents of a distinction between a hydrogen and a "hydroxyl" bond (200). This distinction was no doubt stimulated by the incorrect belief that the IR absorption of the O—H stretching mode disappears in some cases (707) and not in others. When it was found that the apparent disappearance was in fact due to broadening of the band, the hydroxyl bond lost favor (103). (See also 2067, 920, 919.)

Later, Hunter and Marriott defined two kinds of H bonds: A—H···B, "homogeneous" H bonds where A and B are identical functional groups; and "heterogeneous" H bonds where A and B are different (1009). This terminology is rarely used.

Oshida, *et al.*, distinguish three types of H bonds, the type occurring in alcohols in which the H atom moves from one O atom toward another; a type occurring for example among amides and involving resonance; and another type involving a symmetrical H bond (1551). Sobczyk has a similar classification into four types: (1) the van der Waals' type, where the proton remains strongly attached to A; (2) the shortened bond type, in which quantum mechanical forces enhance the van der Waals forces; (3) the symmetrical bond type; and (4) the polar-bond type, in which the proton becomes strongly attached to B (1909).

Cannon tries to distinguish between dipole interaction and H bonding (349). In a more recent paper (347) he proposes criteria for H bond formation:

1. Asymmetry of the nonbonding orbital of the proton acceptor
2. Partial ionic character of the A—H bond of the donor
3. "Proton transfer can occur and a broad $[\nu_s]$ absorption band results."

The first two of these criteria are, unfortunately, accessible only through indirect and sometimes heavily intuitive interpretation of observational results. Nevertheless, Cannon is led to the conclusion that "the tendency of the N—H [of amides] to form a hydrogen bond will be very small." He recognizes the association of amides, of course, and attributes it to dipole-dipole interaction. (See also 345a, 346, 1194.)

Whether any of these periodically recurring subclassifications will prove to be useful remains to be seen. As suggested by a variety of data (e.g., see Tables 2-IV, 2-VIII, 2-XVII, 3-II, 3-VII, Figs. 3-7, 3-13, 3-14) the qualitative similarities of the properties of different H bonded systems are every bit as striking as the differences.

See also 899, 1849, 1854, 1340, 1141, 709, 167, and 1781.

8.2.8 Summary. There are two basic reasons for the substantial support enjoyed by the electrostatic model of the H bond. First, it avoids the clash of the H bond extravalency with our classical theory of the chemical bond. Second, it offers the possibility of quantitative calculation of H bond behavior. Unfortunately, some phenomena are not amenable to this model. Furthermore, the most recent electrostatic calculations are based on complicated charge distributions which differ sufficiently from the earlier naive point charge models to detract from the earliest successes.

The covalent description has appeal from the standpoint of explaining some behaviors not readily handled by the electrostatic model. On the other hand, it leaves the difficulty of fitting extravalency into our present valence bond understanding of the covalent bond. This difficulty emphasizes the importance of clarifying the theory of the H bond, and it may foreshadow changes in the theory of the chemical bond, possibly including a turn toward the molecular orbital approach.

8.3 Theory of the Properties of Hydrogen Bonded Systems

8.3.1 Heat of Formation. As mentioned earlier in this chapter, the approximations currently in use prevent reliable quantum mechanical calculations of the energetics of H bond formation. Many estimates have been made on the basis of the electrostatic model,[a] a simple calculation if point charges are assumed. This model substitutes, however, arbitrariness for intractability since it is necessary to select positions and magnitudes of the charges. Nevertheless, this model has enjoyed continued popularity as a model "accounting for most of the energy of formation of the H bond." A basis for such acceptance can be seen in Fig. 8-5, which is applicable to the linear distribution of charges shown there. Reasonable values of q_1 and q_2 give attractive energies over a range encompassing normal heats of formation of H bonds. For example, attributing all of the dipole moment of H_2O to O—H bond dipoles implies $q_1 = 0.32$ electron charges, and for the H bond length in ice, 2.76 Å, the calculation yields about 3.8 kcal, quite a satisfactory estimate of the H bond energy. The calculation can be refined slightly by using a lengthened O—H bond. However, even for a short H bond of 2.50 Å, the use of the experimental O—H length of 1.07 Å modifies the energy only about 1 kcal or so.

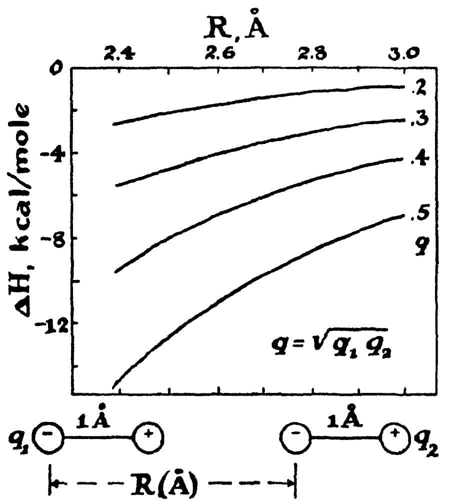


FIGURE 8-5 Electrostatic energy of point charge dipoles.

Another quantity of interest is the energy of the H bond as a function of O—H···O bond angle. Using the same model and a variable angle θ between the two bonds, the plot of Fig. 8-6 is obtained, applicable to the selection of $\sqrt{q_1 q_2} = 0.30$ electron charges. Figure 8-6 shows that the bent model at 30° is only a few tenths of a kilocalorie less stable than in the linear configuration. In contrast, the energy is more sensitive to the angle designated ϕ.

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[a] See 199, 200, 1439, 172, 873, 277, 1671, 840, 486, 1327, 1326, 1343, 407, 1517, 1210, 1659, 737, 1812.

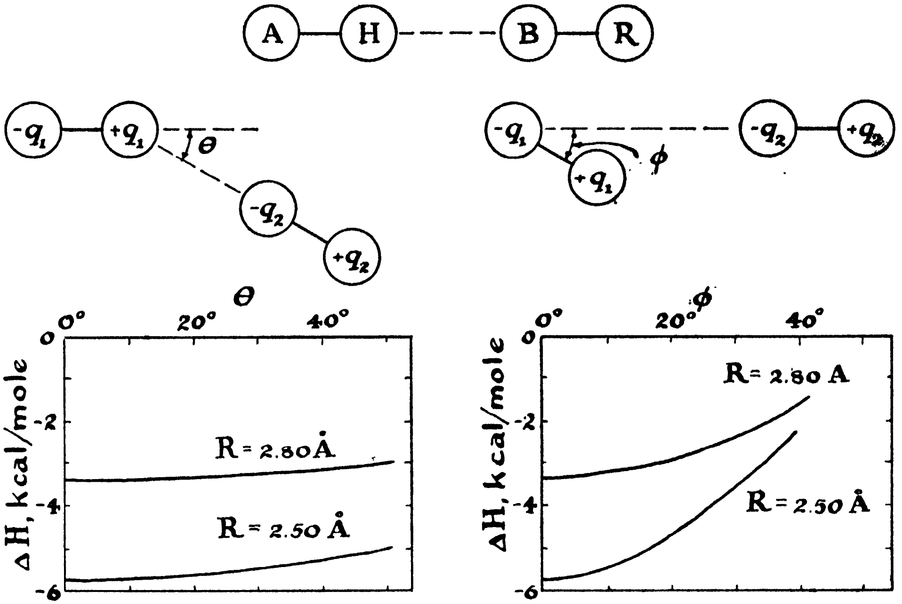

FIGURE 8-6 Electrostatic energy of the point charge model, bent configurations. R(A····B) = 2.80 Å, r(A—H) = 0.99 Å; R(A····B) = 2.50 Å, r(A—H) = 1.07 Å; $\sqrt{q_1 q_2}$ = 0.30 electron charges.

The satisfaction that these acceptable energies might yield is immediately dulled when one considers that the model predicts that the equilibrium distance R will be such that the H···O length is zero. Surely the experimental values of R imply that other repulsive terms must be added to the potential function. These new terms contribute repulsive energies which must be subtracted from the calculated values given in Fig. 8-5. If the repulsive energies are large, the electrostatic model gives too low an estimate. In fact, if the repulsive energies can be estimated to be at least as large as the electrostatic attractions, there remains no basis for claiming that this simple electrostatic model "accounts for most of the energy." It is necessary to find another attractive potential term just as large. This consideration lends importance to the controversy over the magnitude of the repulsive terms. Verwey has estimated a value near 8.4 kcal, using potential functions of either the r^{-n} or $\exp(-r/p)$ types (2116). Sokolov, on the other hand, suggests that the repulsive energy may be as high as 60 kcal (1919, 1913), a figure which suggests that the electrostatic model is not at all applicable. Coulson feels that Sokolov's estimate is "impossibly large" (446). Batuev also objects, claiming that Sokolov's basic assumption—that hydrogen in the

H bond keeps its normal van der Waals radius—is incorrect (154). For our purposes we need not await the resolution of this disagreement, since even the lower figure for repulsion, 8.4 kcal, indicates that the attractive energies calculated with the simplest electrostatic model are too small by at least a factor of two.

Coulson (446) accounts for the additional attractive energy in terms of dispersion forces and delocalization energy. The first of these has been estimated to be about 3 kcal in magnitude (e.g., see 2116), and is a term which might be considered to be a legitimate refinement of an electrostatic model. The delocalization energy, on the other hand, is specifically derived from the inclusion of covalent type functions in the wave function. Any importance assigned to this term tends to detract from the electrostatic model of the H bond. Coulson (446) offers as the best estimate of this term Tsubomura's calculation (2055) of 8 kcal. Even with the large uncertainty Coulson assigns (±4 kcal) the delocalization energy is comparable to, possibly larger than, the electrostatic energy.

An answer to this challenge is the more sophisticated point charge model mentioned in the preceding section (1210, 1659). The charge distribution pictured in Fig. 8-2 brings the negative charge of the base much closer to the proton and substantially increases the attractive energy. What has not been pointed out, however, is how far this refinement of the electrostatic model carries the model toward the covalent description. Indeed, the model might be described quite aptly as a "point charge covalent bond model." It is to be remembered that the stability of the covalent bond reflects the fact that electrons can preferentially occupy space simultaneously near two positive atomic centers, the resulting extra attraction more than compensating for the nucleus-nucleus and electron-electron repulsions.[a] The charge distribution of Fig. 8-2 has exactly these characteristics. The electron pair of the base atom occupies a region of space which can be brought geographically near the proton, so that these electrons are simultaneously near two positive atomic centers. The resulting attraction more than counterbalances the additional nucleus-nucleus and electron-electron repulsive terms.

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[a] This can be seen in the valence bond description by examining the "exchange" term, the term said to give rise to the covalent bond. This term has an integrand which involves products of trial functions centered on two different atoms, and it is largest in spatial regions where *both* trial functions are large. These spatial regions are called "overlap" regions, and their importance is that electrons which occupy this space are simultaneously near two atomic centers.

In summary, calculations of the heat of formation by the simplest electrostatic point charge model have long been considered to have some predictive value and, more important, to verify the electrostatic model of the H bond. When the necessary repulsion terms are added, the agreement with experimental values is lost. When other attractive terms are sought, "delocalization energy" seems to offer some improvement, suggesting that the covalent description must be invoked. As an alternative, the electrostatic model can be modified by attempting a more intimate description of the electron distribution of the base atom (i.e., of its nonbonding electrons). With this refinement which restores agreement with experiment, the electrostatic model approaches a point charge description of the covalent bond. The situation at present seems to be that the models now being used in calculations of heats of formation of H bonds do not have either of the assets once claimed; neither can we predict with reliability an unknown heat of formation of a H bond, nor can we use these calculations in verifying the electrostatic character of the H bond. (See also 1748, 1051.)

8.3.2 Electronic Spectral Shifts. Treating in a theoretical way the shift of electronic transitions accompanying H bond formation requires calculation of the energy of H bond formation for ground and excited states. This formidable task is even more complicated if the results are to be compared to shifts of the peak of absorption. Then the Franck-Condon principle must be considered (1633), thus requiring even more intimate knowledge of the energetics of H bond formation. In view of the difficulties already discussed in calculating the energy of the ground state, success will be hard won in treating the excited state.

There is one theoretical treatment which deserves mention. The "electron migration" theory of Sklar has been applied by Baba and Nagakura (1483, 92, 91), Miyasaka (1418), and Tsubomura (2056). Miyasaka (91) considered an H bond system R═N—H· · ·O—X where the migrating electrons resonate between the unoccupied jth orbital ϕ_j of the conjugated system R and the π orbital ζ of a nonbonding electron of the substituent N. The final result of this perturbation treatment is a rather simple expression involving some quantities difficult to evaluate:

$$\Delta\nu_m = (\alpha - \beta)\{(\mu_o\nu_o/2xe) - \Delta\nu_o\}/(w_o - w_{o2})$$

where

$\Delta\nu_m$ = frequency shift caused by H bond formation
μ_o = dipole moment assigned to H bonding substituent
ν_o = absorption frequency without H bond formation
$\Delta\nu_o$ = frequency shift due to H bonding substituent

w_o = ionization potential of unperturbed substituent
w_{o2} = electron affinity of the excited level
$\alpha = \int \zeta H' \zeta \qquad \beta = \int \phi_j H' \phi_j$
H' = perturbation terms in Hamiltonian due to H bond
x = parameter of the order of the length of the conjugated system R

Calculations of shifts in acceptable agreement with experiment have been made. Whether this treatment will have general applicability remains to be seen.

See also 1159, 2046.

8.3.3 Vibrational Spectral Behavior. Possibly the most unique manifestation of the H bond is the perturbation of the A—H stretching mode, ν_s. Each of the three changes that occur—frequency shift, increase in band width, and enhancement of intensity—is unusual and characteristic. Since these effects are so unusual they must contain interesting information about the nature of the H bond. Despite a great deal of study, this information has not yet been extracted.

Band Width. The structure of ν_s has been discussed at length in Chapter 3 (Section 3.3.8). As indicated there, one of the currently popular theories is based on the assumption of extreme mechanical anharmonicity of ν_s (268, 724, 1). The theory is well described (268), and will not be reproduced here in view of the experimental evidence concerning the anharmonicity presented in Section 3.3.9. Of particular interest are the remarks in that section referring to the absence of odd power terms in the potential function for the IR-active ν_s mode of a cyclic carboxylic acid dimer. The implication which can be drawn is that the anharmonicity of this vibration may be quite low. Since an explanation of the extreme band widths must encompass the carboxylic acids (see Fig. 3-20), anharmonicity does not seem to be a likely one. The weight of evidence suggests that ν_s is not unusually anharmonic.

A related proposal based on presumed change of the potential function is the "double minimum" explanation. The presence of the base introduces the possibility that a second minimum energy position exists with the proton nearer B than A. Such a double minimum would have a complicated set of energy levels for ν_s, in extreme cases giving two rather widely separated absorptions for ν_s. Detoni and Hadži have so assigned absorptions in the spectra of aromatic selenates and of selenic acid (520). Barrow and Yerger made a systematic search for such cases and concluded that acetic acid-alkyl amines may have such potential functions (143, 2221). It is quite reasonable that some acid-base pairs may have double minimum potential functions. Yet, it does not seem likely that such an explanation will span all of the examples of unusual ν_s band width and structure. The apparent absence of mechanical anharmonicity already mentioned is one piece of contradictory evidence. The erratic displacements expected for overtones of energy close to the central energy maximum have not been observed.

An entirely distinct explanation of the band width is the "predissociation theory" of Stepanov (1950, 1948) and Volkenstein (2122). For example, Stepanov proposes a continuous sequence of energetically unstable states for the excitation of ν_s. The proposal is interesting, in view of the magnitude of the energy for excitation of the fundamental A—H stretching mode (near 8 kcal) as compared to normal H bond energies of a few kcal. Any obvious interpretation must, however, be compatible with the basic similarity of the band structures of the first, second, and higher harmonics of ν_s to that of the fundamental.[a,b] Bratož and Hadži offer further arguments against the predissociation theory, based on fine structure sometimes observed in ν_s (268).

Another of the interpretations is that the extreme width is to be explained in terms of combinations. The references are listed in Section 3.3.8. Although the data are somewhat ambiguous, the proposal is most reasonable. In particular, combinations involving the low frequency motions of the H bond could be important. Batuev refers to this theory as "frequency modulation," the low frequency modes ν_σ modulating the A—H mode ν_s, resulting in the appearance of the succession of combinations $\nu_s \pm n\nu_\sigma$ (159, 155). Bratož and Hadži feel that this represents but a rough solution to the anharmonic problem (268).

For a review of the earliest attempts to explain the breadth of ν_s, see 268.

Frequency Shift. The frequency shift of ν_s reveals the change brought about in the potential function for the A—H stretching mode when it participates in a H bond. Despite theoretical interpretation from several points of view, the frequency shifts have not provided definitive support for any particular model of the H bond. For electrostatic model estimates of $\Delta\nu$, see Section 8.2.1. For quantum mechanical calculations of $\Delta\nu$, see 407, 1915–1919, 465.

Intensity. The effect of the H bond on the intensities of ν_s and ν_b does

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[a] Batuev, attempting to marshal every argument in favor of his own frequency modulation theory in preference to the predissociation theory, observes that the predissociation theory ignores the fundamental principles of Marxism-Leninism (155). Neither Marx nor Lenin seems to have published any work on the H bond.

[b] In his review, Cannon presents brief but useful summaries of the theories of Stepanov and of Batuev (345a).

offer some information about the nature of the H bond. As mentioned earlier in this chapter, the many-fold increase of intensity of ν_s without corresponding increase in intensity of ν_b is not readily explained with the electrostatic model. [In contradiction to this statement is Barrow's interpretation of the intensity behavior of ν_s of alcohols in bases (139). He proposed that increased ionic character of the A—H mode is responsible for the ν_s intensity.] Tsubomura proposes that the intensity of ν_s is to be attributed to charge transfer forms (ψ_c in Fig. 8-3) in the wave function (2053). Huggins and Pimentel draw attention to the slight decrease of intensity of the bending modes (980, 2097), and suggest that polarization of the base on H bond formation accounts for the intensity behaviors (979). Figure 8-7 shows how such polarization provides a charge movement which can increase $d\mu/dr$ for the stretching mode (since the induced negative charge, q_i, oscillates in a direction opposite that of the proton) while providing a contribution to $d\mu/d\theta$ of sign opposite that of the unperturbed A—H bond. Thus the IR intensity behaviors draw attention to the movement of charge on the base toward the proton of the H bond, and provide a basis for favoring the covalent (or charge transfer) over the ionic model of the H bond.

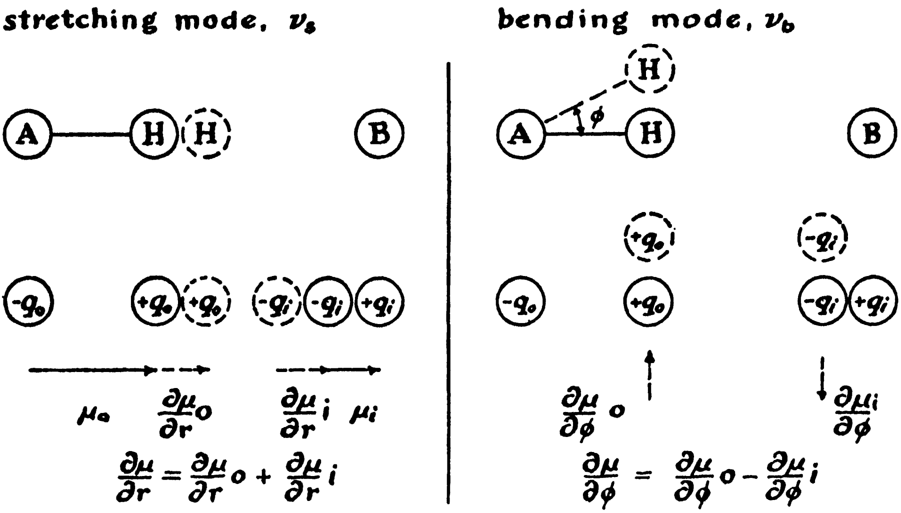


FIGURE 8-7 Dipole changes of stretching and bending modes as influenced by polarization in the base.

8.3.4 Proton Magnetic Resonance. The proton resonance shift accompanying H bond formation is toward lower fields (except when the base is an aromatic pi electron system). This implies a shift in the direction "toward" the resonance of a bare proton, and has been interpreted to mean that the proton in the H bond is more "bare" (1863). The supposed movement of charge away from the proton can be attributed to repulsion by the base electrons. This conclusion is of great interest because it implies that the H bond stability is *not* derived from electron sharing—the proton actually "sees" *less* electron density after H bond formation.

Before accepting these interpretations we must ask if they have the conventional chemical meanings. When a chemist concerns himself with electron distribution near a nucleus, he is almost always interested in the energy of the system or in properties determined by the energy. He is concerned, then, with the electron distribution as manifested by properties depending upon the inverse first power of the distance, ρ, from the nucleus. But the proton magnetic resonance chemical shift depends upon the magnetic shielding caused by the electronic environment, a property with a more complicated dependence upon spatial distribution. Possibly the reduced shielding, which is deduced from the H bond shift toward lower fields, does not at all imply that the proton "sees" fewer electrons insofar as energy is concerned.

In fact, a convincing argument to the contrary can be framed, that the proton undoubtedly resides in *higher* electron density after H bond formation if the density is integrated with a ρ^{-1} weighting factor. The argument is based on the absolute statements that could be made if we knew the *exact* wave function before and after H bond formation. Knowing the exact wave functions we could evaluate precisely all of the contributions to the potential energy before and after H bond formation. These contributions are enumerated below, e_1 and e_2 designating the two most important pairs of electrons.

$$A^+ \text{—} e_1 \text{—} H^+ \cdots\cdots e_2 \cdots B^+$$

	Attractive	Repulsive
Before H bond formation	H^+-e_1	H^+-A^+
	A^+-e_1	e_1-e_1
	B^+-e_2	e_2-e_2
After H bond formation	Above terms and also	
	H^+-e_2	e_1-e_2
	A^+-e_2	B^+-H^+
	B^+-e_1	A^+-B^+

By the distances of approach we see that the largest of the new terms is necessarily the attractive H^+-e_2 term. The electron pairs are somewhat farther apart but furnish the next larger term, the repulsive e_1-e_2 term. The other new terms must be of much smaller magnitude, the largest of these again being a repulsive term, B^+-H^+. Hence the most obvious explanation of the H bond stability is the addition of the new H^+-e_2 term.

Turning to the question of the electron density near the proton, we must consider also the H^+-e_1 term. If we propose that H bond formation reduces the electron density near the proton, then the H^+-e_1 term must decrease even more than the H^+-e_2 term increases. The net effect would then be that the proton interaction with all of the electrons is *repulsive* with respect to H bond formation, a most unreasonable proposal. One of the other terms would have to account for the H bond stability, though the next largest new terms are also repulsive. We can hardly suggest that the reaction to the addition of all these repulsive terms is an even larger increase in the A^+-e_1 term. We must discard the premise and return to the conclusion that the net proton-electron interaction *is* attractive with respect to H bond formation, which implies that the proton must "see" *more* electrons insofar as the ρ^{-1} weighting factor is concerned.

What, then, *can* the decrease in magnetic shielding mean? It must mean that the magnetic shielding depends upon the electron distribution in a different way than does the energy. If this is so, it is not so readily evident that direct interpretation of a chemical shift is meaningful in terms of chemical concepts such as electronegativity, ionic and covalent character, base strength, etc. The most vivid case in point is, no doubt, the H bond to the aromatic bases for which the extremely anisotropic diamagnetism of the base results in chemical shifts in the direction opposite the more usual H bond shift.

There is a theoretical treatment, by Ramsey (1684), of the diamagnetic shielding expressed in an expansion in inverse powers of ρ. Considering only the functional dependence upon ρ, Ramsey's expression has the form

$$\delta = f_1(1/\rho) - f_3(1/\rho^3) + \cdots \qquad (5)$$

If the first term in equation *(5)* dominates δ, it implies that the magnetic shielding is determined by the electronic distribution in the same way as is the energy. In this case there should be good correlation between chemical shifts and chemical concepts such as electronegativities. This seems to be the situation for fluorine magnetic resonances, a fact which has led to the expectation of the same result for proton magnetic resonance shifts. That this is not true for protons is shown by the data of Fig. 4-2 (1811). Further, the argument just presented concerning the energy of H bond formation indicates that the leading term in equation *(5)* is not dominant.

Using equation *(5)*, we cannot proceed much further except to note the negative sign of the second term. This sign implies that a *higher* electron density (evaluated with a $1/\rho^3$ weighting factor) would produce a shift toward *lower* fields, that is, toward lower shielding.

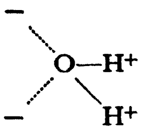
An alternate approach is presented in the model used by Buckingham and Pople (313). The theory, which is discussed clearly by Pople, Schneider, and Bernstein (1659a), takes as a premise the electrostatic model of the H bond. The perturbing effect of a uniform electric field on the diamagnetic susceptibility of a proton is considered as describing the effect of H bond formation. An electric field may reduce the diamagnetic shielding of the proton if the orientation removes or reduces the axial symmetry of the A—H bond. The proposal is checked by an order of magnitude calculation of the chemical shift caused by a reasonable charge placed a reasonable distance from an isolated hydrogen atom (313).

Buckingham and Pople refer to the effect of the electric field as a "paramagnetic" term, and it has the ρ^{-3} dependence of the second term in equation *(5)*. Although equation *(5)* has the virtue of attempting to describe the true electronic environment of the proton, it has the disadvantages of intractability. The electric field perturbation model is mathematically simple but an extreme approximation. Since these two treatments lead to the same functional dependence on ρ, perhaps the electric field model provides a useful approximation to the more complete description of equation *(5)*. Whether this proves to be true or whether the characteristic arbitrariness of the electrostatic model will deprive the model of more than qualitative predictive value is not yet clear. In any event, the two treatments do concur in shifting attention from the ρ^{-1} term to the ρ^{-3} term with its opposite sign.

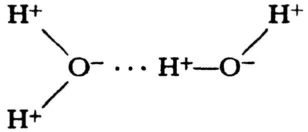
In summary, the proton chemical shift seems to have a complicated interpretation in terms of electron distribution, probably requiring more detailed description of the electron distribution, including the angular as well as the radial distribution. Nevertheless, it is possible that the shift toward lower field implies increased electron density near a proton in proximity to a base because of the domination of the ρ^{-3} term in equation *(5)*. Hence the direction of the H bond shift does not give clear evidence in favor of the electrostatic character of the H bond.

8.3.5 Dielectric Constant. Because of the emphasis on electric dipoles by workers in this field it is not surprising that electrostatic models have dominated the explanations of dielectric effects of H bonds. Perhaps the models used for water will be instructive. Section 2.1.2 contains a general discussion of various treatments.

Bernal and Fowler (199) presented an early theory of H bonded water. For dielectric constant discussions they used a tetrahedral charge distribution of this kind



For energy calculations a simpler charge distribution was used.



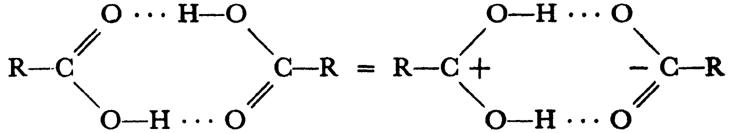
The exact location of the charges in the first scheme was not given. One important part of their model was the appreciable fraction (0.75–0.80) of the molecules which were *not* free to rotate—a departure from previous theories.

Onsager (1546) did not draw a specific diagram of the charges in a "proton bond" but did indicate that his equation based on a generally electrostatic picture would apply *if* the H bond caused an increased moment of the group containing the hydrogen atom.

More recently there have been some modifications in the model, and the mathematical treatments have been considerably improved. Kirkwood (1111) used the Bernal-Fowler model and devised a statistical method to allow for near neighbors. Pople (1659) allowed for bending H bonds of the type shown in Fig. 8-1. Harris and Alder applied to Pople's model a statistical mechanical treatment which attempts a precise evaluation of distortion polarization (877). The calculated results are shown in Table 2-III, and in Fig. 2-1 they are compared with experimental values. These changes correct for failures of the simplest dipole picture, and as more of them are added the principal appeal of the electrostatic model—simplicity—tends to be lost.

These same workers mentioned other associated substances, alcohols in particular, without treating them as thoroughly. The models above were designed primarily for substances which build infinite chains or networks of H bonds. Less extensive interactions (cyclic dimers, solvent-solute complexes, chelates) are, perhaps, somewhat simpler. They are generally treated as either a simple charge distribution in the H bond or in terms of the more complex distribution of Fig. 8-2.

Self-ionization has been proposed by Harris and Alder (876a) as a significant factor in the dielectric polarization of carboxylic acids. (See also 158.) An equilibrium concentration of ion pairs is postulated:



Infrared spectral data furnish a critical test of this model. The existence of the ion pair species implies a second minimum in the potential function for the movement of the hydrogen atoms toward the ion pair structure. This is, however, the movement appropriate to the IR active asymmetric O—H stretching mode. Such a double minimum in the potential function would imply a considerable frequency disturbance of some of the overtones of the stretching mode—a disturbance which has not been reported.

Frank has taken a new tack by considering the effect of covalency of the H bond in water on dielectric constant and dielectric relaxation (694a).

8.3.6 Conductance. Conway, Bockris, and Linton (423) have made a thorough study of proton conductance in water and alcohols. (See Section 2.1.5 for a general description.) Their model was basically that of Lennard-Jones and Pople (Fig. 8-2). However, to account for the rate of transfer, some molecules must rotate. This created some "doubly filled H bonds," causing further rotation. These steps are pictured schematically in Fig. 8-8.

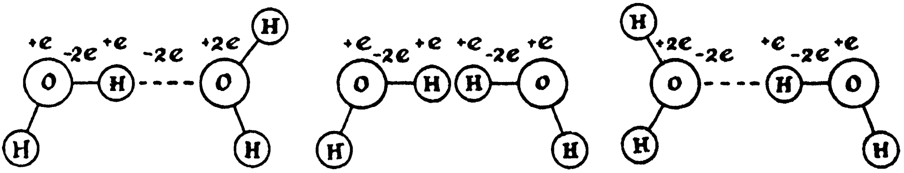


FIGURE 8-8 Proposed proton conductance mechanism (423). Left, before rotation. Middle, "doubly filled H bond." Right, after rotation.

In this model the ionization step is pictured as a "tunneling" of protons between two potential energy minima symmetrically located. Conway and co-workers used the Morse equation, although Lippincott and Schroeder's might be more suitable (see Section 8.2.5).

On these ideas a structure of equations is built to calculate the rates of the various steps. The equations are electrostatic (for bending H bonds) and statistical mechanical (for the tunneling). The success enjoyed by the model is mentioned in Section 2.1.5. (See also 1076, 223.)

Quite another treatment of electrical conductivity in H bonded systems is based upon an assumed double minimum potential function for movement of the hydrogen atom along the H bond. Cannon, in his review (345a), summarizes well the several types of data which have been offered as evidence of such a potential function. Gierer and Wirtz (753) have attributed the large mobilities of the H^+ and OH^- ions in aqueous solutions to proton transfer through a double minimum barrier. Riehl (1719) has treated the electrical conductivity of ice in terms of a two-step process. First a proton is transferred from one molecule to a neighbor, forming an H_3O^+, OH^- ion pair, with an activation energy of 8 or 9 kcal/mole separating the two assumed potential minima. This step is followed by a turning movement (similar to that discussed earlier in this section) with an activation energy of 12–13 kcal/mole. Pollock and Ubbelohde (1655) have adopted the proton transfer explanation of conductance for a number of H bonded crystals. Some of their data and calculated activation energies are presented in Table 9-XXIX.

CHAPTER 9

Hydrogen Bonds in Crystals

The structures of the crystals cited . . . reveal the rather remarkable fact that only in very exceptional cases does a hydrogen atom bonded to nitrogen or oxygen occupy a position such that hydrogen bond formation is impossible.[a]

J. DONOHUE *California Institute of Technology, 1952*

9.1 The Importance of Hydrogen Bonds in Crystals

The importance of H bond formation as a factor determining crystal structures can hardly be overemphasized. As Donohue indicated in his review of the role of H bonds in crystals (537), one can predict with confidence that a substance containing both acidic and basic functional groups crystallizes in a lattice involving H bonds. Since this useful fact has been recognized by crystallographers for some time, it is not surprising that there are many reviews.[b] Of particular importance are those by Donohue (537) and, more recently, by Ubbelohde and Gallagher (2068).

It is possible to understand this dominance of the H bond in terms of the energy of molecular interactions. The heats of sublimation of most organic crystals are determined by van der Waals interactions with energies of the order of several hundred calories per carbon atom. But if a H bond can be formed, the stability of a molecular crystal can be

[a] From *J. Phys. Chem.* **56**, 502-10 (1952).

[b] **1724, 1723, 1525, 1585, 281, 1524, 1867, 537, 1000, 403, 2068, 1316, 1641, 1488, 1637, 1035, 2154.**

raised by a few kilocalories per mole merely by orienting the molecules to bring H bonding groups into proximity. Since this gain does not sacrifice the van der Waals energy, it is safe to expect that Nature will select this energetically economic arrangement. Table 9-I lists substantiating heats of sublimation and melting points of some molecular crystals. Equally convincing are the relations found by Davies and coworkers (480) between carbon numbers and heats of sublimation of homologous aliphatic amides. These data are well represented by the linear relations given in Section 7.5.1. The linearity shows that successive additions of carbon atoms add to the heat of sublimation without noticeable detraction from the constant term. This has the obvious interpretation that the constant term is to be attributed to the terminal amide group with its H bond interaction. Even the extreme change in molecular shape implied by the lengthening of the hydrocarbon chain does not alter the terminal group packing.

TABLE 9-I Heats of Sublimation and Melting Points of Some Molecular Crystals

COMPOUND	HEAT OF SUBLIMATION (kcal/mole)	MELTING POINT (°K)	MOLECULAR WEIGHT
H_2O	12.2[a]	273	18
H_2S	8.8	190	34
Acetic acid	31.3	290	60
Urea	21.0[b]	410	56
Acetamide	13.6[b]	354	59
*Iso*butene	7.6[b]	133	56
δ-Valerolactam	17.8[b]	313	99
Methylcyclohexane	10.6[b]	147	98

[a] 1585; [b] 1977.

A final bit of evidence strongly suggestive of the importance of H bonding in crystal formation is the collection of heats of sublimation presented in Fig. 7-2. These data, also compiled by Davies (480), display differences which invite an obvious though possibly deceptively simple interpretation.

Of course the strong interactions present in H bonded crystals are reflected in other physical properties, such as melting point, dielectric behavior, electrical conductivity, and piezoelectric behavior. The effect on melting point, for example, may be the most widely recognized effect of H bonding because of its importance in regard to ice. The difference in melting point between H_2O (273°K) and H_2S (190°K) is attributed to the extra lattice strength contributed by the stronger H bonds of water. The heats of sublimation shown in Table 9-I indicate that this interpretation is correct.

9.2 Experimental Techniques

There are three important methods of finding the atomic positions in a crystal lattice: x-ray diffraction, neutron diffraction, and nuclear magnetic resonance. (For a discussion of electron diffraction studies of H bonded crystals, see 2083; also 2081a, 2082, 2084.) Most of the information known on crystal structures has been accumulated through x-ray studies. Yet, the other two techniques are of paramount importance because they are capable of locating the hydrogen atoms. At present, practically all of the definite information concerning hydrogen atom positions comes from neutron diffraction and proton magnetic resonance studies.

The reason that neutron diffraction is so much more effective than x-ray diffraction as a means for locating hydrogen atoms can be seen in the atomic scattering amplitudes given in Table 9-II (taken from reference 94, except for the neutron diffraction scattering factor for deuterons).

TABLE 9-II Scattering Amplitudes for X-rays and Neutrons

	X-RAYS ($Å^{-1}$)			
$\sin\theta/\lambda$	0	0.2	0.4	NEUTRONS
f_O	8.26	5.60	3.10	$0.58\cdot10^{-12}$ cm
f_C	5.89	3.20	1.99	0.66
f_H	1.00	0.50	0.14	−0.38
f_D	1.00	0.50	0.14	+0.65

In comparison with carbon and oxygen, hydrogen scatters neutrons much more effectively than x-rays. In fact, there are few x-ray studies of H bonded systems in which H atom positions have been reliably determined (see 403, 1880, 2169, 1933).

Some workers feel that polarized IR spectra can be interpreted unambiguously in terms of bond angles. The discussion of Section 3.3.10 gives a basis for doubt.

Neutron Diffraction. We shall not discuss the details of the now classic x-ray method (for which there are many standard references), or the neutron diffraction method [which has been reviewed by Wollan and Shull (2193)]. But there is one experimental aspect of neutron diffraction which deserves special mention. The scattering factors of H and D, shown in Table 9-II, differ in sign as well as in magnitude. Because of this sign difference, a partially deuterated sample with a mole ratio $H/D = 0.650/0.378 = 1.72$ is of unique value. With the H/D concentration ratio exactly the inverse of the ratio of the scattering factors, the two isotopes scatter to the same extent but in opposite phase. Hence the hydrogen scattering exactly cancels the deuterium scattering by destructive interference. And thus the diffraction pattern of the partially deuterated compound differs from that of the normal compound by the loss of the scattering of the partially deuterated hydrogen atom positions. The ease of deuterating the acidic protons which form H bonds makes this method ideal for locating protons in H bonds.

Nuclear Magnetic Resonance Band Widths. In 1949 Gutowsky, Kistiakowsky, Pake, and Purcell (849) pointed out that band width measurements might be used to estimate distances between protons. Applying the theory of Van Vleck, they calculate the proton-proton distance 1.71 ± 0.02 Å in the $—CH_2Cl$ group of 1,2-dichloroethane, and an N—H distance of 1.025 ± 0.005 Å in solid ammonium halides (F, Cl, and Br). (See also 850, 203.) This proposal has particular importance in the study of the H bond because of the difficulty of locating proton positions by other techniques. Several laboratories have investigated H bonded crystals in this fashion. Richards and his colleagues have been particularly active (1715, 512, 1714, 673, 1606, 672). A series of N—H compounds has been studied by Kromhout and Moulton (1153, 1459). All of these results are listed in the following section.

9.3 Hydrogen Atom Positions in Hydrogen Bonds

Only lately have data on hydrogen atom positions become numerous. Many of these are listed in recent compilations (O—H···O, 1488, 2154; N—H···O, 1459). We can look forward to many more such measurements in the next few years, and a more complete understanding of the factors which determine the hydrogen atom positions. Only for O—H···O bonds is there enough information to give a reliable picture at this time.

9.3.1 O—H Distances in Hydrogen Bonded Crystals. The known O—H distances in O—H···O bonds are listed in Table 9-III. The O····O distances are listed for comparison, but the references are not given since they appear in other tables in this chapter. In Fig. 9-1 the measured O—H bond lengths are plotted against the O····O distances, as was done with fewer data by Nakamoto, Margoshes, and Rundle (1488) and later by Welsh (2154). The solid curve in Fig. 9-1, drawn according to a visual best fit, has a standard error of estimate[a] of r equal to ±0.02 Å. In addition, Fig. 9-1 displays the asymptotic behaviors. For extremely long H bonds the asymptote is taken to be the 0.96 Å bond length of gaseous water (monomer). For short H bonds the asymptote must be the dotted line representing

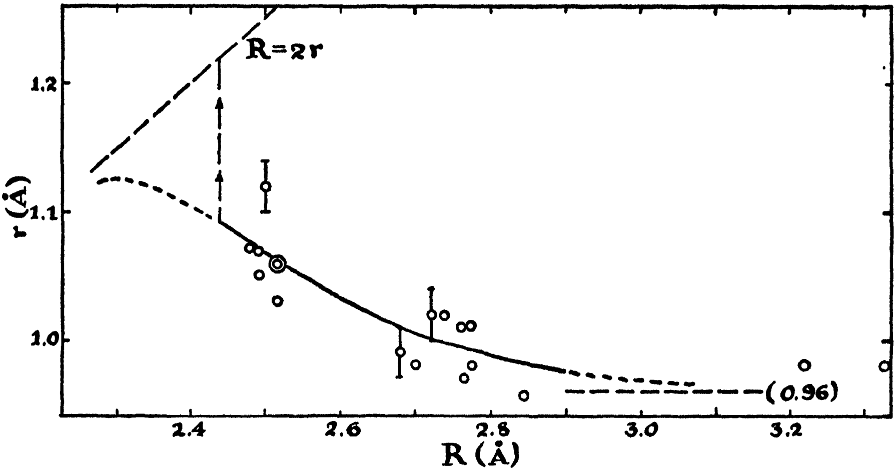


FIGURE 9-1 r(O—H) *vs.* R(O····O) for O—H···O bonds. (Data from Table 9-III.)

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[a] We use the statistician's term "standard error of estimate" with a meaning exactly analogous to that of the familiar "standard deviation." For each compound of known R and r, the smooth curve predicts a value of r, r_p, from the experimental value of R. If the difference between r_p and the experimental value of r, r_e, is called e, the goodness of fit can be measured by

$$\sigma = \left(\sum_{1}^{n} e_i^2/n - 2\right)^{1/2}$$

$$e_i = |r_p - r_e|_i$$

where

n = number of compounds for which both R and r are known.

R = 2r, corresponding to a H bond with H atom centrally located between the oxygen atoms.

TABLE 9-III O—H Bond Lengths in H Bonded Crystals: O····O Bonds[a]

COMPOUND	r (O—H)	R (O····O)	REFS. (O—H length)
Oxalic acid·$2H_2O$	0.955 Å	2.85 Å	740
H_2O (cubic)	0.97	2.76 ±.01	1835, 951
$Ca(OH)_2$	0.98	3.33	326, 1615, 1488
$CaSO_4 \cdot 2H_2O$	0.98	2.70	1563
$Mg(OH)_2$	0.98 ±.02	3.22	586
α-HIO_3	0.99 ±.02	2.69 ±.01	740
D_2O	1.01	2.76	1762, 1561a, 1623, 1620, 1619
$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	1.01 ±.02	2.77 ±.02	95
α-Resorcinol	1.02 ±.04	2.72 ±.03	94, 96
H_3BO_3	1.02, 1.05	2.73–2.70	450, 451
KD_2AsO_4	1.03	2.52	740
KH_2PO_4 (77°K)	1.05	2.49	97
KH_2AsO_4	1.06	2.52	740
Oxalic acid·$2H_2O$	1.06	2.52	740
	0.98, 1.41[b]	2.88, 2.52	1019
KH_2PO_4 (R.T.)	1.07 ±.01	2.48 ±.005	97, 1623
KH_2PO_4 (113°K)	1.07 ±.01	2.50	1223
$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	1.12 ±.02	2.50 ±.02	95

[a] See also 1466, 1077.

[b] This length corresponds to a symmetrical H bond.

Two interesting aspects of Fig. 9-1 deserve mention. First, the clusters of data suggest there are two "regions" of H bond formation, one with R = 2.74 ±0.06 Å and r = 1.00 ±0.02 Å, and the other with R = 2.50 ±0.02 Å and r = 1.07 ±0.05 Å. This clustering is no doubt fortuitous and due to the small amount of data as indicated by the distribution of the more numerous measurements of O····O distances. Figure 9-9 shows that a continuous range of O····O distances is observed. The second interesting feature of Fig. 9-1 relates to the controversy over the O····O bond length corresponding to a symmetrical H bond. Some authors have felt that H bond lengths near 2.45 Å would have a centrally located H atom (e.g., Rundle *et al.*, 1764, 1488). Speakman has proposed that potassium hydrogen bisphenylacetate has a symmetrical H bond with R = 2.55 Å (1927), but Davies and

Thomas disagree, basing their view on results from IR studies (505). (See also 229a.) Figure 9-1 suggests that a symmetrical position would be obtained only at O····O bond lengths shorter than 2.30 Å. Yet, it is possible that a symmetrical position will be indicated experimentally at bond lengths in the range 2.45–2.55 Å. The smoothed curve of Fig. 9-1 shows how the minimum of the potential function depends on R, but there is in many of these solids a symmetry requiring a double minimum. For these cases the approach of r to $\frac{1}{2}$R is accompanied by a decrease of the potential barrier separating the two minima. If this barrier is sufficiently low, discussing the ground state in terms of a proton localized in one of the minima is no longer of value. Instead, the proton occupies both minima equally, and there is substantial probability of finding the proton midway between the heavy atoms (as suggested by the vertical dotted line in Fig. 9-1). The discovery of such behavior would give information about the potential function for H atom movement. Hence it remains a problem of some interest to seek experimental evidence of the proton positions for the shortest H bonds. Neutron diffraction and proton resonance studies are two suitable techniques. Spectroscopic methods are applicable also, since the double minimum potential function has characteristic band splittings (analogous to the inversion doubling of ammonia). [Features in the IR spectrum of some benzselenic and benzsulphuric acids have been interpreted by Blinc and Hadži (1) as the doublet splitting of a double minimum potential function.]

9.3.2 A—H Distances in Hydrogen Bonded Crystals. There are a few scattered data for A—H···B bonds where either A or B is not oxygen. Most of these cases were studied by proton magnetic resonance and, in some, proton-proton distances were determined rather than A—H distances. Table 9-IV shows the data available.

The data for other types of H bonds are insufficient for developing curves of r *vs.* R. We can, however, compare the scattered data in Table 9-IV for the various A—H···B bonds with the curve of Fig. 9-1. To do so we must observe that an experimental value of R(A····B) can be converted to an equivalent $R_{eq.}$(O····O) by subtracting from R the sum of the van der Waals radii of A and B and adding double the van der Waals radius of oxygen. This $R_{eq.}$(O····O) plus the curve of Fig. 9-1 define an equivalent $r_{eq.}$(O—H). Finally, $r_{eq.}$(O—H) can be converted to a predicted r(A—H) by adding to $r_{eq.}$(O—H) the covalent radius of A and subtracting that of oxygen. This procedure (using Pauling's values of van der Waals and covalent

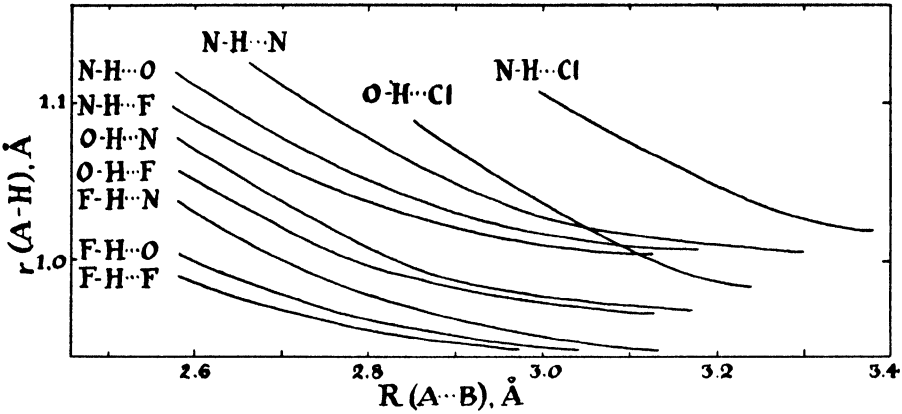

FIGURE 9-2 Predicted r(A—H) *vs.* R(A····B) for A—H···B bonds.

radii, 1585) leads to the predictions of Table 9-V. Since these predictions are sufficiently close to the experimental values to be of use, the curves of Fig. 9-2 are presented to aid in estimating r(A—H) for a variety of A····B systems. Each of these curves is established by slid-

TABLE 9-IV NMR Band Width Measurements of Proton Positions

CRYSTAL	H BOND TYPE	SEPARATION REPORTED	DISTANCE (Å)
Formamide	N—H···O	N—H	1.036 ±.025[a]
Oxamide	N—H···O	N—H	1.039 ±.013[a]
Cyanamide	N—H···O	N—H	1.05[a]
Glycine	N—H···O	N—H	1.074[b]
Urea	N—H···O	N—H	1.077[b]
Amines	N—H···N	N—H	1.014[b]
NH_4X (X = F, Cl, Br)	N—H···X	N—H	1.025 ±.005[c]
$N_2H_4\cdot 2HF$	N—H···F	N—H in $N_2H_6^{++}$	1.075 ±.02[d]
NH_4BF_4	N—H···F	N—H	e
MBH_4	B—H···M^+	B—H	1.255 ±.02[f]
$Li_2SO_4\cdot H_2O$	O—H···O	H—H	~1.59[g]
$HClO_4\cdot H_2O$	O—H···O	H—H in H_3O^+	1.70 ±.02[h]
$HNO_3\cdot H_2O$	O—H···O	H—H in H_3O^+	1.72 ±.02[h]
$BF_3\cdot H_2O$	O—H···F	H—H	1.62[i]

[a] 1459; [b] 1153; [c] 849; [d] 512; [e] 1606; [f] 673; [g] 1466; [h] 1715; [i] 672.

ing the curve of Fig. 9-1 horizontally in accordance with the van der Waals radius correction and vertically in accordance with the covalent radius correction. Table 9-V suggests that these curves should permit reasonably accurate predictions of r, within about ±0.03 Å, if R(A····B) is known.

TABLE 9-V Predicted and Experimental Values of r(A—H)

$$R_{\mathrm{eq.}}(\mathrm{O}\cdots\cdots\mathrm{O}) = R_{\mathrm{expt.}}(\mathrm{A}\cdots\cdots\mathrm{B}) + 2r_v(\mathrm{O}) - r_v(\mathrm{A}) - r_v(\mathrm{B})$$

$$r_{\mathrm{calc.}}(\mathrm{A}—\mathrm{H}) = r_{\mathrm{eq.}}(\mathrm{O}—\mathrm{H}) + r_c(\mathrm{A}) - r_c(\mathrm{O})$$

r_v = van der Waals radius

r_c = covalent radius

COMPOUND	A····B	$r_{\mathrm{calc.}}$(A—H)	$r_{\mathrm{expt.}}$(A—H)	ERROR
$CuCl_2 \cdot 2H_2O$	O····Cl	0.986 Å	0.95[a] Å	+0.036 Å
NH_4Cl	N····Cl	1.020	1.03 ±.02[b]	−0.010
			0.98 ±.04	
ND_4Br	N····Br	1.01	1.03 ±.02[c]	−0.02
$N_2H_4 \cdot 2HF$	N····F	1.075	1.075 ±.02[d]	0.000
Formamide	N····O	1.026	1.036 ±.025[e]	−0.010
Oxamide	N····O	1.022	1.039 ±.013[e]	−0.017
Urea	N····O	1.014	1.077[f]	−0.063
			0.99	+0.024
KHF_2	F····F	1.095	1.13[g]	−0.035
		Standard deviation		±0.03

[a] 1618; [b] 1222, 1933, 850; [c] 1221, 1220; [d] 512; [e] 1459, 1153; [f] 2198; [g] 1621, 1645.

The reasonable agreement shown in the last column of Table 9-V encourages speculation about the significance of the method of calculation. It would seem that any shortening of the A—B distance below the van der Waals contact distance is accompanied by a lengthening of the A—H bond above its normal covalent length. Possibly the curve applicable to O····O bonds indicates the general behavior for a variety of systems.

9.3.3 Nonlinear Hydrogen Bonds. Experimental methods for determining hydrogen atom positions yield information concerning two other interesting structural parameters of the H bond. Aside from the A—H distance, the angular orientations are of importance. One of the most crucial questions is the evidence for the extent of deviation from linearity of the A—H···B bond. Of only slightly less interest and value is the angle between the H····B line and the bond made by B to its adjacent atom.

The hydrogen atom positions of the water molecule in $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ are specified as shown in Fig. 9-3. The O—H bond is only 3½° off the O····O line. Even more interesting, the HOH bond angle is less than the tetrahedral angle of 109°28′ even though this angle would make the H bonds more nearly linear. This implies that the rehybridization required to open the HOH angle a few degrees is energetically less favorable by an amount comparable to the energy required to bend the H bond a few degrees. Once the molecular positions are fixed, the protons of the water molecules select the HOH angle that represents the best compromise between the strain energy required to open the angle above the gas phase equilibrium value (105.5°) and the strain energy required to move the protons off the H bond line. This best compromise is reached here at 107°, 2½° below the tetrahedral angle. This result contradicts the assumption that H bonded water will involve a tetrahedral hybridization, a subject of debate, for example, in studies of the structure of ice (see 324a, Section 9.4.3).

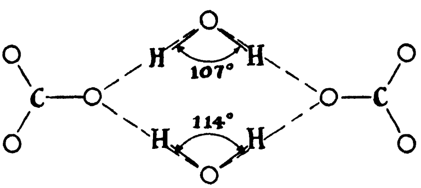

FIGURE 9-3 Hydrogen atom positions of water in sodium sesquicarbonate.

TABLE 9-VI Angle Between the A—H Bond and the A····B Line

COMPOUND	A····B	DEVIATIONS FROM LINEARITY	REFS.
$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	O—H···O	3.5°	95
α-Resorcinol	O—H···O	10°	94
$CuCl_2 \cdot 2H_2O$	O—H···Cl	15°37′	1618

The crystal structure of $CuCl_2 \cdot 2H_2O$ provides another example in which the protons apparently deviate from the linear H bond positions. This structure, in contrast to the sesquicarbonate, has protons placed *outside* the linear positions, in spite of the large HOH angle of 108°2′ (1618). The protons are 15°37′ off the O····Cl line. Although this geometry seems unlikely, the large HOH angle should possibly be explained in terms of a rehybridization around the oxygen atom to facilitate bonding to the Cu atom. (See also 1663.) The small number of compounds for which the protons are thought to be in nonlinear positions are listed in Table 9-VI. The deviation from linearity, ϕ, is the angle between the A—H bond and the A····B line. At least insofar as these few data support a generalization, they corroborate the generally accepted view that ϕ is not larger than ten or fifteen degrees. See also 883, 1019, 1153, 1459, Table 9-XVI.

9.4 Crystal Parameters: O—H ··· O Bonds

The variety of lattice arrangements of crystals involving H bonds is hardly surprising. While it is true that the arrangements bring the acidic and basic groups into proximity, the size and shape of the remainder of the molecules are also influential in the packing. Wells has discussed the geometrical basis of crystal chemistry in a general way in a series of papers, one of which gives special reference to H bonded structures (2152). Even more informative is the classification of H bonded crystals according to geometrical arrangements, given by Ubbelohde and Gallagher (2068). These discussions draw attention to the existence of one-dimensional chains linked by H bonds [e.g., CH_3OH (2006), formic acid (949)], two-dimensional planes linked by H bonds (e.g., γ-quinol, caprolactam, 4,4′-dihydroxydiphenyl), and many types of three-dimensional nets from the simple tetrahedral arrangements of the ammonium halides to such interesting structures as H bonded helices (e.g., urea) and H bonded clathrate structures (e.g., hydroquinone clathrates) (1567, 1568, 1664). We will discuss the different types, segregating them according to the nature of A and B. Only the simplest molecules will be considered in detail.

9.4.1 Carboxylic Acids. The crystal structures of formic acid and of acetic acid are well understood and are particularly interesting. These two crystals are discussed in detail, and then the parameters of other carboxylic acids are summarized in tabular form.

Both formic acid and acetic acid form lattices of almost coplanar molecules linked in H bonded chains, in contrast to the cyclic dimeric units characteristic of the gas phase. Even more surprising are the large differences in the bond lengths in the H bonded crystal compared to the gaseous state. The structural parameters for formic acid are shown in Table 9-VII. The carbonyl bond length and the O—C═O angle are almost unaffected by dimerization or crystallization. There are astonishing changes, however, in the C—O bond length and the R(O····O) distance. The very short H bond length of the crystal is

TABLE 9-VII Structural Parameters for Formic Acid

STRUCTURAL PARAMETERS	MONOMER[a] (gas)	DIMER[b, c] (gas)	CRYSTAL[d]
r(C—O) Å	1.312	1.36 ±.04 1.33	1.26 ±.03
r(C=O) Å	1.245	1.25 1.24	1.23 ±.03
r(O····O) Å	—	2.73 2.72	2.58 ±.03
∠O—C=O	124.3°	121° —	123 ±1°

[a] 1213; [b] 1081; [c] 147; [d] 949.

accompanied by a shortening of the single bond C—O length which can hardly be assigned to experimental uncertainty. This remarkable change was discussed by Davies and Thomas (504) who concluded that two possible causes must be considered:

"1) There are . . . appreciable structural differences between formic acid and other carboxylic acids, or

"2) marked changes (>0.05 Å) occur in the C—O bond length on condensation from the vapor to the solid."

The first alternative attributes the changes to the unique nature of formic acid, the only acid with H attached to the carbon of the carboxyl group. This rationalization, which has been preferred by many workers, can be positively discarded in view of the recent discovery of the same effect in acetic acid by Jones and Templeton (1053). The structural parameters of acetic acid in its various states are shown in Table 9-VIII. Figure 9-4 contrasts the angular parameters of the zig-

TABLE 9-VIII Structural Parameters for Acetic Acid

STRUCTURAL PARAMETERS	MONOMER[a] (gas)	DIMER[a] (gas)	CRYSTAL[b]
r(C—O) Å	1.43 ±.03	1.36 ±.04	1.29 ±.02
r(C=O) Å	1.24 ±.03	1.25 ±.03	1.24 ±.02
r(O····O) Å	—	2.76 ±.05	2.61 ±.02
∠O—C=O	130 ±8°	130 ±3°	122 ±2°

[a] 1081; [b] 1053.

zag chains found in the crystals of formic and acetic acids (from the scale drawing of 1053). The proton positions are unknown; the distances shown in Fig. 9-4 are those implied by the smooth curve of Fig. 9-1. Bonding among chains in either crystal is of a normal van der Waals type, as evidenced by "normal" intermolecular distances. The only significant difference between acetic acid and formic acid is revealed in Fig. 9-4. The angle between the carbonyl bond and the O····O bond is much larger in acetic acid than it is in formic acid. This is readily explained by the steric crowding by the methyl group, and the main interest lies not in the cause but in the nature of the change induced. Although there is a relatively slight change in the H bond length, the steric effect opens the angle by 22°. This suggests that the H bond interaction is relatively insensitive to the angle between the carbonyl and the O····O bonds.

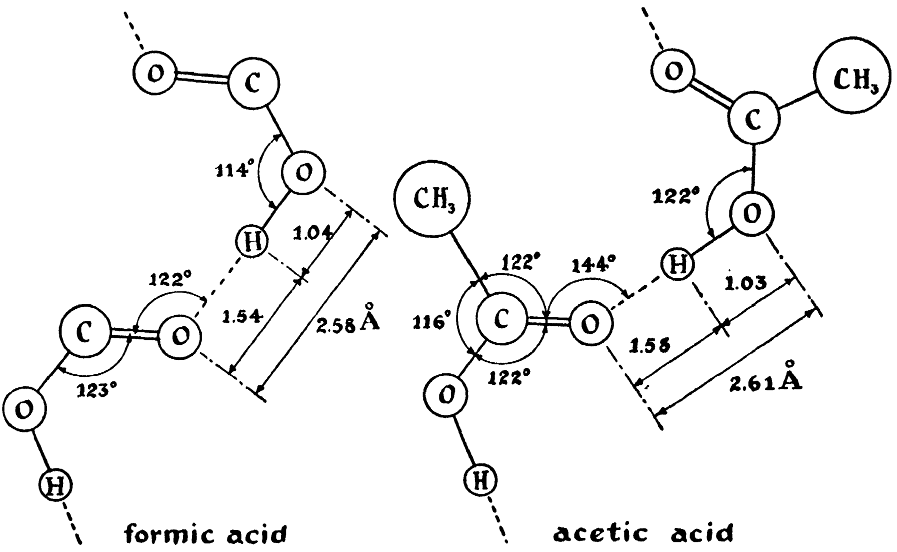

FIGURE 9-4 H bonded chains in the crystals of formic and acetic acids. [From Jones and Templeton, *Acta Cryst.* **11,** 487 (1958).]

Let us return to the significance of the large differences between the gaseous and crystalline H bonded aggregates of these two acids. The most conservative conclusion that can be drawn is that a given molecule can form H bonds of quite different H bond lengths (and, presumably, of quite different enthalpy of formation). The experimental evidence implies that a H bond length determined in one phase (e.g.,

TABLE 9-IX H Bond Lengths—Carboxylic Acids[a,b]: O—H···O Bonds

COMPOUND	R(O····O)	DESCRIPTION	REFS.
Feist's acid	2.4 Å 2.7		1251
Maleic acid	2.46 ±.02 2.75	*intra*molecular intermolecular chains	1834
KH dibenzoate	2.51	sym. H bond(?)	1890
KNa·*dl*-tartrate·$4H_2O$	2.52		1769
Oxalic acid·$2H_2O$	2.52 or 2.49 ±.01	COOH···OH_2	564, 7
2-Furoic acid	2.53		796
L-Glutamic acid	2.54	3-dimensional lattice	930
KH bisphenylacetate	2.55	acid-salt pairs	1927
Diacetylene dicarboxylic acid·$2H_2O$	2.55	COOH···OH_2	563
Lauric acid	2.56	cyclic dimers	2092
Acetylglycine	2.56		354
Acetylene dicarboxylic acid·$2H_2O$	2.56	COOH···OH_2	564
Formic acid	2.58	chains	949
Phenyl propiolic acid	2.60 ±.04	cyclic dimers	1744
Hydrate racemic acid	2.61 2.72	COOH···OH_2	1575
Acetic acid	2.61 ±.02	chains	1053
p-Cl benzoic acid	2.62	cyclic dimers	2029
Salicylic acid	2.63 ±.01	cyclic dimers	404
11-Amino undecanoic acid·HBr·½H_2O	2.64	cyclic dimers	1879
Benzoic acid	2.64	cyclic dimers	1880
β-Succinic acid	2.64 ±.04	chains of cyclic H bonds	1450
β-Nitropropionic acid	2.66	cyclic dimers	1976
L-Threonine	2.66		1861
Phthalic acid	2.67 ±.05		1805
Sebacic acid	2.68	chains of cyclic H bonds	1452
Adipic acid	2.68 ±.05	chains of cyclic H bonds	1451
β-Glutaric acid	2.69	chains of cyclic H bonds	1453
Malonic acid	2.695	chains	788
p-Aminosalicyclic acid	2.70	cyclic dimers	205
α-Oxalic acid	2.71	layers	452, 1845
β-Oxalic acid	2.71	chains of cyclic H bonds	905
NH_4H disalicylate·H_2O	2.76	COOH···OH_2	548
Tartaric acid	2.78 2.87		1956

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[a] In this table and in subsequent tables in this chapter and in Chapter 10 we have made no attempt to correct from *KX* units to Å units. This correction is +0.01 Å per 5 Å,

in the solid) cannot be assumed to apply to other phases of the same system. A more serious implication is that H bond lengths for a given acid-base pair of functional groups might vary widely even in the same phase. This conclusion casts doubt on the reliability of predictions of H bonded structures. It behooves us to give attention to the range of H bond lengths observed for different types of H bonds.

In Table 9-IX are compiled R(O····O) distances observed in crystals involving H bonded carboxylic acid groups. The values of R distribute fairly evenly between the two extremes of about 2.5 Å and 2.8 Å. This range, then, seems to define the uncertainty with which predictions of H bond lengths in carboxylic acids can be made. Undoubtedly the heats of formation of the H bonds are correspondingly variant. Insufficient data are available to check this proposal for solids (see Section 7.5.1). (See also 1361, 1583, 1890, 1845.)

9.4.2 Alcohols and Phenols. Again, the prototype alcohol, methanol, has been thoroughly studied, and it is discussed here in some detail. Following the discussion are compilations of data for other alcohols and phenols.

The crystal structure of methanol provides an interesting example. There is a λ point transition at 161.1°K from the low temperature phase, α, to the high temperature phase, β. The heat of transition is 170 cal/mole (2006). Tauer and Lipscomb find that both phases contain infinite zigzag chains of H bonds with the parameters shown in Table 9-X (2006). The last column of this table lists the parameters found by Dreyfus-Alain and Viallard (551). The following discussion is based on the work of Tauer and Lipscomb.

The zigzag chain molecular packing does not retain residual entropy at very low temperatures, a fact which settles a long-standing controversy. The nature of the λ transition is a puckering of the infinite chains into more compact packing. Most important, proposals involving rotation of the O—H group or of the entire molecule are disproved. Consequently, explanations which do not invoke rotation must be sought in discussing the high dielectric constant of the β phase.

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and hence would change the tabulated numbers at most by plus one unit in the second decimal place. This correction was not commonly inserted before about 1946.

[b] We have attempted to make this and subsequent compilations in this chapter as extensive as possible. Unfortunately, the large volume of x-ray crystal work in varying degrees of approach toward accurate location of the atom positions makes this a difficult task. Although these tables are undoubtedly the most complete collection of H bond distances presently available, we cannot claim comprehensive coverage.

TABLE 9-X Structural Parameters of Crystalline Methanol

STRUCTURAL PARAMETERS	α (below 161.1°K) (2006)	β (above 161.1°K) (2006)	β (165°K) (551)
R(O····O)	2.68 Å	2.66 ±.03 Å	2.65 Å
C—O····O angle	108°	118.9 ±2°	104°40′
C—O bond length	1.44 Å	1.42 ±.03 Å	1.42 Å

The dimensions of methanol are informative. The C—O bond length is quite normal (a normal C—O single bond is 1.43 Å), and is apparently unaffected by the participation of the oxygen atom in the H bond chain. The H bond length, 2.66 Å, is longer than that of crystalline formic acid (2.58 Å) but shorter than the 2.73 Å bond length of gaseous formic acid dimers. Furthermore, there are almost as many carboxylic acid H bonds that are longer than 2.66 Å as there are shorter ones (see Table 9-IX). This suggests that the acid strength is of less importance than the molecular packing in determining the values of the H bond parameters in crystals. Finally, the angle between the C—O bond and the O····O is surprising. As Tauer and Lipscomb commented, one might expect the angle to be less than the tetrahedral angle, 109.5°. This expectation is, of course, based on the assumption that the proton would lie on or close to the O····O line. Assuming a normal bending force constant, a strain energy of a few kilocalories per mole is introduced in opening the C—O—H angle 10–15°. On the other hand, if the proton is far from the O····O line, a large strain energy is expected for the bending of the H bond. Neither alternative is appealing in view of the low heat of transition to the low temperature phase which has a more normal C—O····O angle and approximately the same H bond length. Perhaps the smaller angle found by Dreyfus-Alain and Viallard is closer to the true angle (551).

The O····O bond lengths of other alcohols are shown in Table 9-XI, and those of phenols are given in Table 9-XII. Although many of these hydroxyl H bonds are within the range of lengths found for carboxyl H bonds, there are also a few that have longer and, presumably, weaker H bonds.

The fourth column of Table 9-XI gives the angle made by the H bond (the O····O line) and the base O—C (or O=C) bond. The variation of this angle is interesting in view of proposals that the angle is determined by the hybridization of the base (e.g., see 1812). For the carbonyl oxygen an angle of 120° is expected, whereas the entries of Table 9-XI indicate a range of 99–120°. In Fig. 9-4 the angle is shown for formic and acetic acids to be, respectively, 122° and 144°. Similarly, the angle varies over a wide range for the single bonded alcoholic oxygen (90–135°, see Table 9-XI) and for amides (95–164°, see Table 10-I). Apparently these angles cannot be predicted with confidence from a presumed hybridization. (The prediction of these angles is discussed in Section 8.2.1.)

TABLE 9-XI H Bond Lengths: Alcohols[a]

COMPOUND	A—H···B	R(O····O)	ANGLE, O····O╲C	REFS.
Pentaerythritol	O—H···O—H	2.55 Å	90°	1519
		2.69		1248
Diethyl silane diol	O—H···O—H	2.56		1080
Methanol (β)	O—H···O—H	2.65	104°40′	551
(β)		2.66	118.9°	2006
L-Threonine	O—H···O═C	2.66	120°	1861
dl-Serine	O—H···O═C	2.67	107°	537
	O—H···O—H	2.68	108°	
Dialuric acid·H_2O	O—H···O—H	2.68		21
KNa *dl*-tartrate·$4H_2O$	O—H···O—H	2.73		1769
Cytidine	O—H···O═C	2.74	117°	731
	O—H···O—H	2.83	135°	
Tartaric acid	O—H···O═C	2.74		1956
	O—H···O═C	2.87		
	O—H···O═C	2.92		
Hydrate racemic acid	O—H···O—H	2.75		1575
		2.83		
Alkali glutonate	O—H···O—H	2.71–2.80		1246
Hydroxy L-proline	O—H···O═C	2.80	99°	537
		2.82		2241
Glycol, glycerol	O—H···O—H	2.96		146

[a] See footnotes a and b, Table 9-IX.

9.4.3 Ice. The crystal structure of ice has been the subject of many studies and has excited much argument for three decades. Yet there remain unanswered questions which need further study. In 1951 Owston presented a detailed review of the structure, electrical properties, x-ray scattering, and theoretical models of ice (1561b). The following

TABLE 9-XII H Bond Lengths: Phenols[a]

COMPOUND	A—H···B	R(O····O)	REFS.
NH_4H disalicylate·H_2O	O—H···O=C	2.45 Å[b]	548
		2.63[b]	
1,4-Dihydroxy-5,8-naphthoquinone	O—H···O=C	2.50	1564
K *bis-p*-hydroxybenzoate	O—H···OH_2	2.58	1926
	O—H···O—H	2.69	1926
Salicylic acid	O—H···O=C	2.59[b]	404
Phenol	O—H···O—H	2.62	2145
p-Amino-salicylic acid	O—H···O=C	2.62[b]	205
Phenol-quinone	O—H···O=C	2.64	2135
			872
α-Resorcinol	O—H···O—H	2.66	1726
	O—H···O—H	2.75	1725
	O—H···O—H	2.69	94
	O—H···O—H	2.75	94
β-Resorcinol	O—H···O—H	2.70	537
	O—H···O—H	2.75	
Hydroquinone clathrates	O—H···O=C	2.7	1568
		2.75	1567

[a] See footnotes a and b, Table 9-IX.

[b] *Intra*molecular H bond.

year Bjerrum presented another survey article (224). Still more recently, two excellent summaries of our knowledge of the crystal parameters of ice have appeared, one by Lonsdale (1257a) and the other by Owston (1561c). Furthermore, Pauling has presented an authoritative discussion of the entropy of ice, a crucial datum (1585). In view of this detailed and authoritative coverage of the subject, a comprehensive treatment of the crystal properties of water is not needed here.

Ice at 0°C has a hexagonal structure. At temperatures below about −80°C a cubic, diamond-type structure can be obtained. Shallcross and Carpenter found that H_2O vapor condensed at very low temperatures sometimes forms amorphous solid and sometimes a mixture of the cubic and hexagonal forms (1835). Ice prepared or annealed above −80°C takes the hexagonal form and remains in this crystal form even though the solid is recooled to −196°C. There are other crystal structures which become stable at high pressures.

In the hexagonal form of ice, each oxygen atom occupies the center of a tetrahedron formed by its four nearest oxygen neighbors. This tetrahedron is emphasized in Fig. 9-5, both by the dark solid lines (which are not bonds) and by the shading of the oxygen atoms occupying the corner positions. Hydrogen atoms are presumed to lie on each of the lines connecting the central oxygen atom to its four nearest neighbors. Thus the tetrahedral arrangement provides the maximum possible number of H bonds. On the other hand, the spatial arrangement gives an open structure (relative to liquid water) with "channels" parallel to the *c* axis, as shown in Fig. 9-6 (the direction of the *c* axis in Fig. 9-5 is indicated by the dotted arrow). These voids offer a ready explanation for the observation that ice has lower density at 0°C than liquid water, despite the short interatomic distances caused by the H bonds (see Sections 2.4.7, 3.4.2).

Lonsdale (1257a) has analyzed carefully all of the data relative to the oxygen-oxygen distances in ice and heavy ice. In each case, two distances are found, the $O\cdots O'$ distances oriented along the *c* axis being about 0.01 Å shorter than the other $O\cdots O''$ distances. The data are interesting because they provide an accurate contrast of the H bond lengths in a H bonded crystal and its deuterated counterpart over a wide range of temperature. Table 9-XXVIII shows the values derived by Lonsdale from smoothed curves drawn through the data (1257a). Whereas the $O\cdots O$ distances decrease by about 1 percent on cooling from 0°C to −180°C, there is no significant difference in the H bond lengths in ice and in heavy ice.

From the standpoint of H bonding, the most interesting aspects of the structure relate to the locations of the H atoms. Models which have been discarded include the following proposals: the H atoms are centrally located between the two oxygen atoms (Barnes, 135); two H atoms are close to each oxygen with repeating orientations (Bernal and Fowler, 199); the H atoms rotate about the oxygen atoms as centers (2192). The model which has won general acceptance is attributed to Pauling (1587). The hydrogen atoms are presumed to occupy positions on the $O\cdots O$ lines with one hydrogen atom on each such line and four around each oxygen. Two hydrogen atoms are considered to be bonded more closely to each oxygen atom than are the other two. Thus the first feature of the model is that ice is a molecular crystal, in accord with the IR spectrum of ice. The several possible orientations of the two close hydrogen atoms, shown in Fig. 9-7, are considered to be equally likely, introducing randomness of arrangement. This randomness provides one of the principal advantages of this model—its intuitively satisfying explanation of the residual entropy of ice at low temperatures (see 1585). The structure received further support in the neutron diffraction studies of Wollan, Davidson, and Shull (2192) and, more recently, of Peterson and Levy (1620). Those experiments are completely consistent with the Pauling model, and indicate that the O—D distance of D_2O is 1.01 Å with a closely tetrahedral DOD angle (see also 951, 324a).

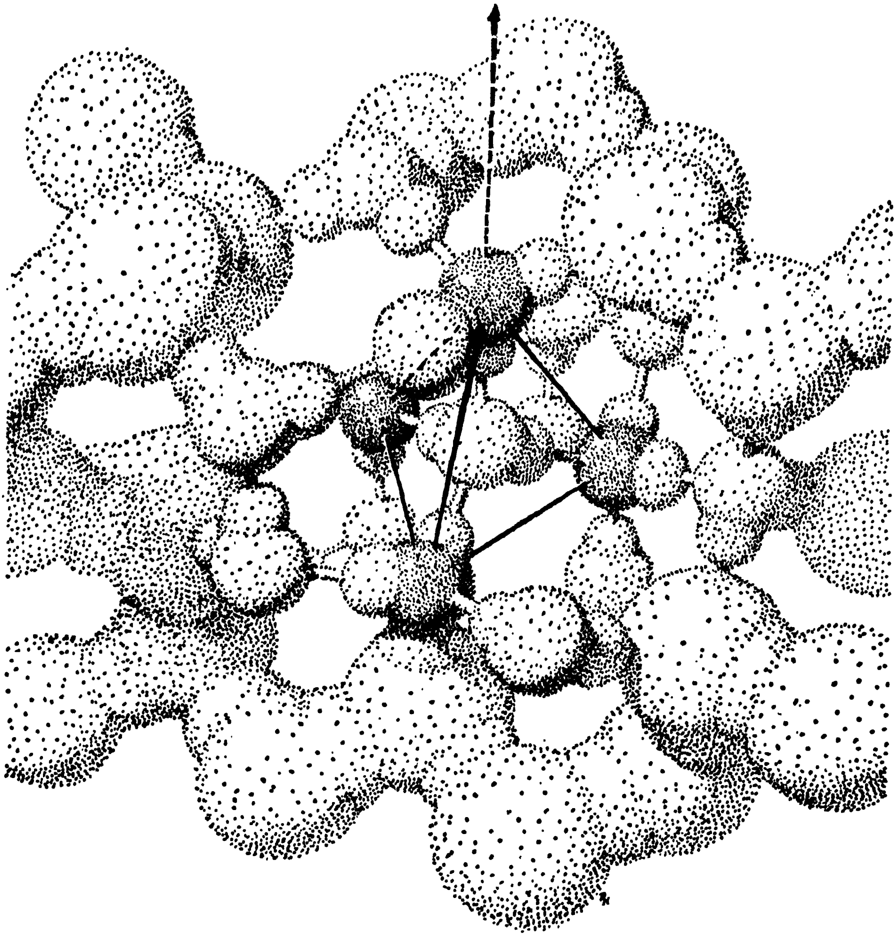


FIGURE 9-5 The crystal structure of ice: view emphasizing the tetrahedral arrangement of four oxygen atoms around each oxygen atom. (The *c*-axis of the crystal is indicated by the dashed arrow.)

Despite this success, certain questions are under further study (1644, 1761, 1561a, 223). Rundle (1761) has summarized evidence that seems to challenge the Pauling structure: the hexagonal structure of ice, certain electrical phenomena, and the disorder-streaking of x-ray diagrams. While Rundle concludes that the disordered nonpolar model remains the most probable, he indicates that there are still gaps in our understanding of the ice structure.

See also 1306, 989.

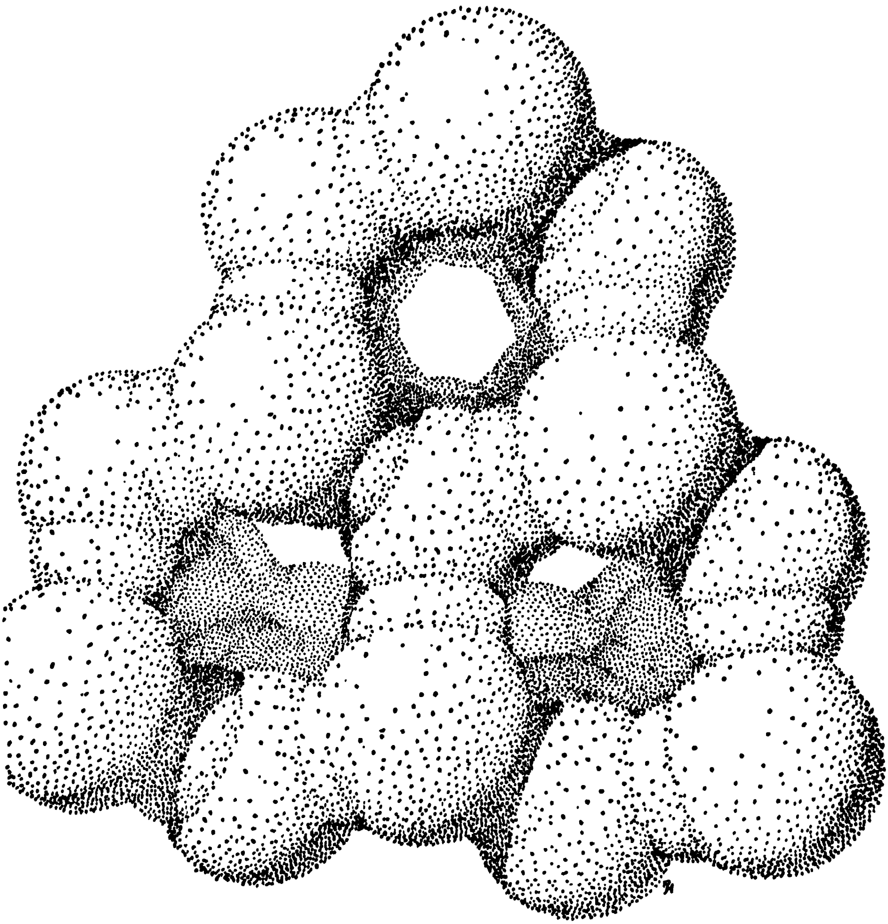


FIGURE 9-6 The crystal structure of ice, looking down the *c*-axis: view emphasizing the open structure of ice.

9.4.4 Hydrates. The compact size of a water molecule and its combination of both acid and base H bonding capacity no doubt account for the frequent occurrence and stability of hydrates. Of course, hydrates

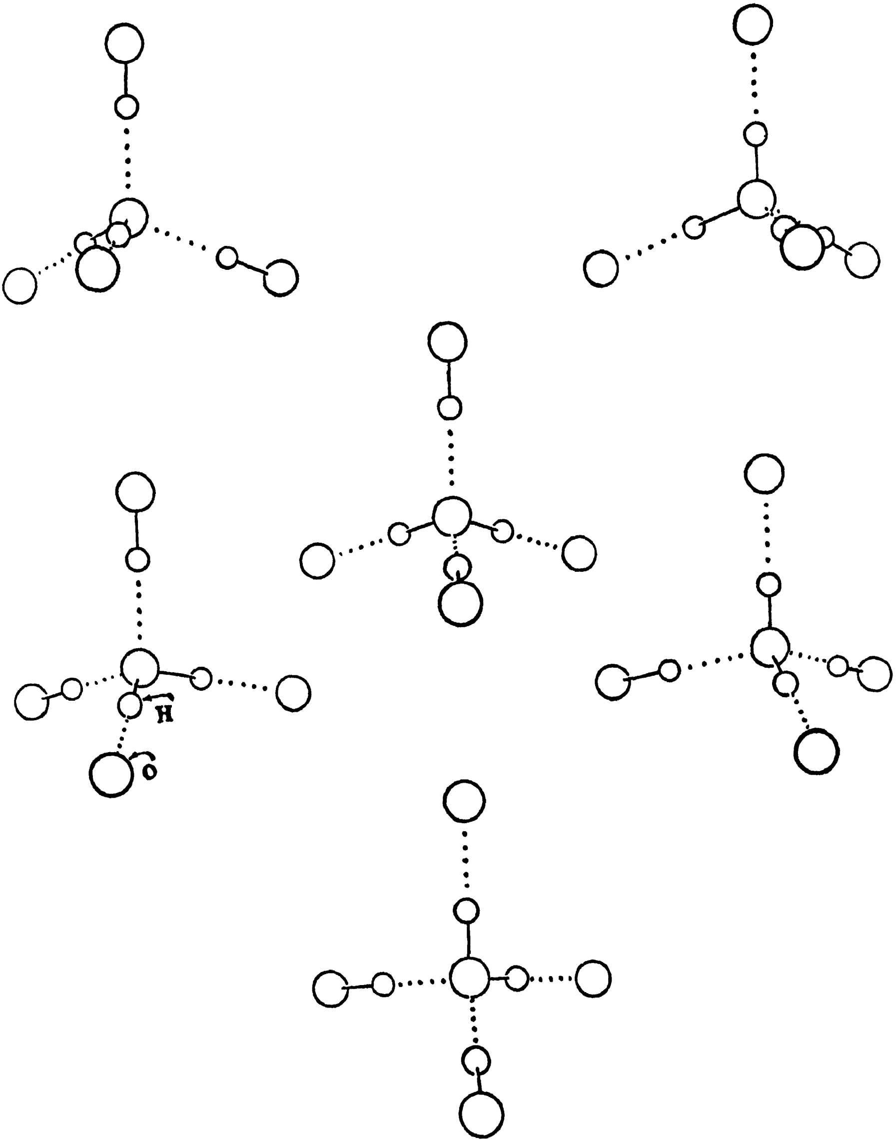
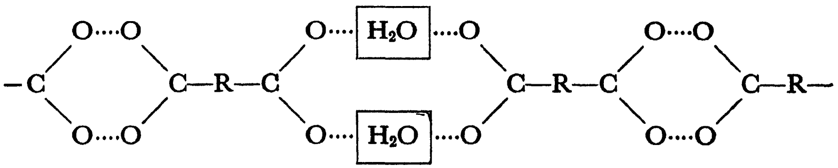


FIGURE 9-7 The six possible arrangements of the four H bonds connected to each oxygen atom.

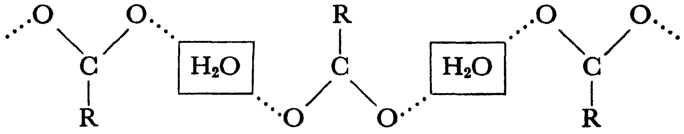
of organic substances are most commonly found for organic molecules containing functional groups with appreciable acidic or basic strength. Figure 9-8 reproduces some diagrammatic representations of the structures of hydrates, as given by Ubbelohde and Gallagher (2068). These

a. *Rings* alternating with hydrated rings



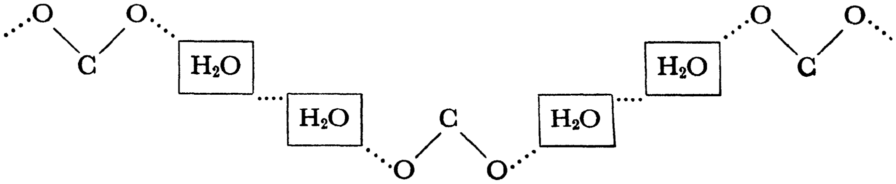
e.g., hydrate racemic acid

b. *Chains*, one molecule of water per carboxylic group



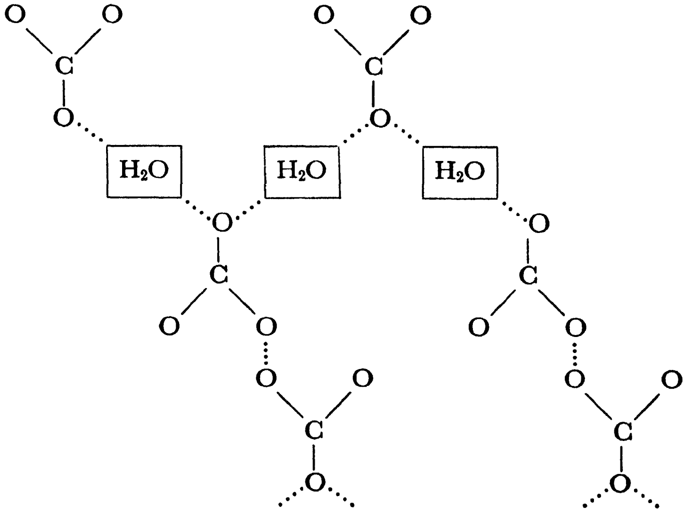
e.g., oxalic acid dihydrate, acetylene dicarboxylic acid dihydrate

c. *Chains*, two molecules of water per carboxylic group



e.g., Rochelle salt

d. *Sheets* bonded by hydrated chains



e.g., $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$

FIGURE 9-8 Structures of hydrates. [From Ubbelohde and Gallagher, *Acta Cryst.* **8,** 76 (1955).]

drawings show schematically how the water molecules serve as links binding the molecules together. It is to be emphasized that these hydrate molecules *rarely* occupy "cavities" within a lattice with rigidity independent of the presence of the water [dialuric acid monohydrate is apparently an exception (21)].

Hydrogen bond lengths involving water as a H bonding acid are listed in Tables 9-XIII, 9-XIV, and 9-XV. They are segregated in accord with the nature of the hydrated compounds. The molecules given in Table 9-XIV are salts of organic acids or bases. It seems that the entries of Tables 9-XIV and 9-XV range to shorter bond lengths than do those of Table 9-XIII. For a discussion of the binding of water in crystallized salt hydrates, see 783 and 2195.

TABLE 9-XIII H Bond Lengths—Water in Organic Crystals[a]: O—H···O Bonds

COMPOUND	B in O—H···B	R(O—H···O)	REFS.
NH_4H disalicylate·H_2O	···(OH)CO	2.65 Å	548
Dialuric acid·H_2O	···O—H	2.68	21
	···O—H	2.74	
Creatine·H_2O	···OCO^-	2.71 ±.01	1387
	···OH_2	2.87 ±.01	
4,6-Dimethyl-2-hydroxy-pyrimidine hydrate	···O—H	2.73	1642
		2.75	
		2.93	
Glycyl-L-tryptophan·$2H_2O$	···O=C	2.74	1581
	···O=C	2.77	
	···O=C	2.78	
	···O=C	2.99	
1,3,5-Trihydroxybenzene·$2H_2O$	···OH_2	2.76	44
1,3,5-Triaminocyclohexane·$2H_2O$	···O—H	2.76	44
Acetylene dicarboxylic acid·$2H_2O$	···O=C	2.82	564
	···O=C	2.89	
Diacetylene dicarboxylic acid·H_2O	···O=C	2.83	563
	···O=C	2.90	
Oxalic acid·$2H_2O$	···O=C	2.88	740 1673
Racemic acid·H_2O	···O=C	2.89	1575

[a] See footnotes a and b, Table 9-IX.

TABLE 9-XIV H Bond Lengths—Water in Inorganic-Organic Crystals[a]: O—H···O Bonds

COMPOUND	B in O—H···B	R(O—H···O)	REFS.
Zn acetate·$2H_2O$	···O═C	2.49 Å	2096
	···O═C	2.74	
KNa *dl*-tartrate·$4H_2O$	···O—H	2.52	1769
	···OCO^-	2.54	
	···OCO^-	2.56	
	···O—H	2.58	
	···OH_2	2.90	
	···OCO^-	2.92	
	···O—H	2.95	
Cu proline·$2H_2O$		2.52	1362
Rochelle salt, KNa *d*-tartrate·$4H_2O$	···OCO^-	2.56	186
	···OH_2	2.86	
	···O═C	3.07	
KH di-*p*-hydroxybenzoate·H_2O	···O—H	2.58	1926
Ni acetate·$4H_2O$	···O═C	2.59	2094
Co acetate·$4H_2O$	···O═C	2.64	2094
	···O═C	2.66	
Na $HOCH_2SO_2$·$2H_2O$		2.63	2038
Cu acetate·$2H_2O$	···O═C	2.82	2095
	···O═C	2.89	

[a] See footnotes a and b, Table 9-IX.

The hydrates provide an excellent opportunity to examine the constancy of angular orientation of H bonds. Water can act both as a base and as an acid, hence the angles may be indicative of the locale of the nonbonding electrons of the water molecule. Table 9-XVI lists some of the known angles $B_1\cdots O\cdots B_2$ where O is the oxygen atom of water. The range of angles, from 83° to 120°, is surprisingly large and suggests that nonlinear H bonds may be present in some of these cases (see Section 9.3.3). See also 2242, 1773, 841, 1837, 392, 281, 904, 923, 629, 324a.

9.4.5 Hydroxides. Glemser, Hartert, and Hofacker examined the properties of the crystalline metallic hydroxides (784, 882, 941, 783, 782). They have given particular attention to the systematic dependence of the O—H stretching frequency on the O····O distance. Their data, included in Table 9-XVII, have been incorporated into the plot

TABLE 9-XV H Bond Lengths—Water in Inorganic Crystals[a]: O—H···O Bonds

COMPOUND	B in O—H···B	R(O—H···O)	REFS.
$HNO_3\cdot 3H_2O$	···OH_2	2.49 Å	1293
	···OH_2	2.57	
	···O═N	2.62	
	···O═N	2.73	
	···O═N	2.79	
	···OH_2	2.81	
$HNO_3\cdot H_2O$	···O═N	2.54	1294
	···O═N	2.61	
$Cu(NH_3)_4SO_4\cdot H_2O$	···OSO_3^-	2.67	1367
$CaSO_4\cdot 2H_2O$	···OSO_3^-	2.70	2196
$Sr(OH)_2\cdot 8H_2O$	···OH^-	2.70 ±.03	1900
	···OH_2	2.82 ±.06	
	···OH_2	2.88 ±.02	
$Na_2CO_3\cdot NaHCO_3\cdot 2H_2O$	···OCO_2^-	2.72 ±.03	296
		2.77 ±.03	
Ice (273°K)	···OH_2	2.76	135
Ice (90°K)	···OH_2	2.73	1796
$LiOH\cdot H_2O$	···OH^-	2.99	1608
$BaS(S_2O_3)_2\cdot 2H_2O$	···$S_2O_3^-$	3.04	679
	···$S_2O_3^-$	3.15	

[a] See footnotes a and b, Table 9-IX.

of $\Delta\nu$ *vs.* R(O····O) in Fig. 3-10. See also 621, 1608, 620, 902, 1837, 901.

9.4.6 Oximes and Inorganic Acids. A number of bond lengths have been measured for inorganic acids or salts, and for oximes. These are tabulated in Table 9-XVIII, and are of the shortest H bond lengths known. See also 310, 1579, 106.

9.4.7 Range of O—H ··· O Bond Lengths in Crystals. A surprising feature of the bond length data in Tables 9-IX to 9-XVIII is the large range of distances observed for similar systems. This is emphasized by the histogram presentation of Fig. 9-9. For purposes of prediction, Table 9-XIX lists the averages for the various types of acids, the standard deviation, and the number of observed distances.

These average H bond lengths are informative. The increasing bond distance in the series inorganic acids, carboxylic acids, phenols, and

TABLE 9-XVI Bond Angles in H Bonded Water[a]: $\angle B_1 \cdots O \cdots B_2$

COMPOUND	B_1	B_2	ANGLE	REFS.
Glycyl-L-tryptophan·$2H_2O$	CO_2^-	CO_2^-	83° (also 103°)	1581
Oxalic acid·$2H_2O$	O═C	O═C	85°	564
Diacetylene dicarboxylic acid·$2H_2O$	O═C	O═C	87°	563
Acetylene dicarboxylic acid·$2H_2O$	O═C	O═C	89°	564
$MnCl_2 \cdot 2H_2O$	Cl^-	Cl^-	92°	2084
$COOH(CH_2)_{10}NH_3Br \cdot \frac{1}{2}H_2O$	Br^-	Br^-	93° (also 109°)	1879
Glycyl-L-tryptophan·$2H_2O$	CO_2^-	CO_2^-	103° (also 83°)	1581
Creatine·H_2O	···OH	···H—O—H	108° (also 120°)	1387
$BaS(S_2O_3)_2 \cdot 2H_2O$	$S_2O_3^=$	$S_2O_3^=$	108°	679
$COOH(CH_2)_{10}NH_3Br \cdot \frac{1}{2}H_2O$	N^+—H···	N^+—H···	109° (also 93°)	1879
$2NH_3 \cdot H_2O$	$H_3N\cdots$	$H_3N\cdots$	116°	1878
Creatine·H_2O	$H_2O\cdots$	$H_2O\cdots$	120° (also 108°)	1387

[a] See footnote b, Table 9-IX.

alcohols, is compatible with the decreasing acid strength. Of course the base strength is important also, perhaps accounting for the short bonds observed for oximes. Oximes display both weakly acidic and weakly basic chemical properties. Presumably the long H bonds formed by the hydroxides can be attributed to the relative absence of acidic properties. The more significant observation is, no doubt, that even the hydroxides crystallize to form H bonds.

The widespread occurrence of hydrates, even among organic molecules, is understandable in terms of the distances in Table 9-XIX. The distances show that the water molecules lodge in H bonding positions, thus contributing substantially to the stability of the crystal lattice.

Finally, we can compare the observed bond lengths to accepted covalent and van der Waals radii of the atoms involved. This topic is deferred to Section 9.6.2, where various types of H bonds are compared.

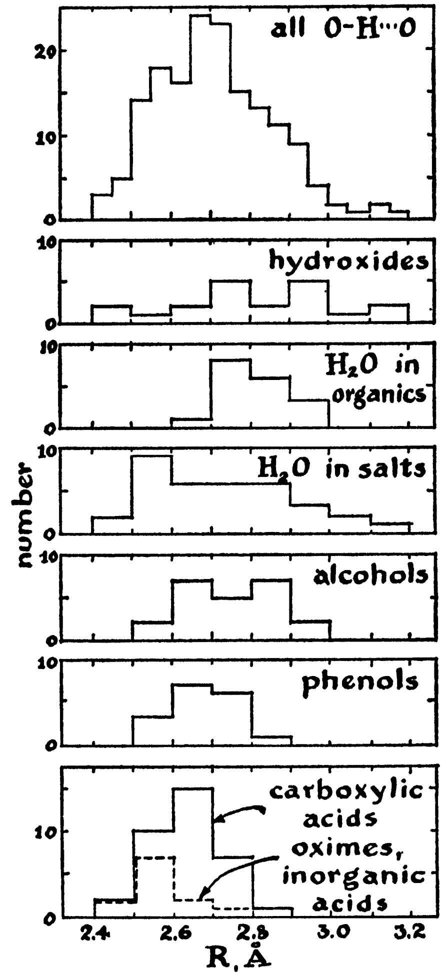


FIGURE 9-9 Distribution of O· · · ·O bond lengths.

9.5 Crystal Parameters: O—H · · · N, N—H · · · O, and N—H · · · N Bonds

9.5.1 Amides. Of the N—H acids which are known to participate in H bonding, the most thoroughly studied are, by far, the amides. The reason for this focus of attention is the importance of the H bonding of amides in fixing the molecular configurations of proteins. In recognition of the unique interest in this topic, an extended discussion of H bonds in amides and in proteins is presented in Chapter 10. Table 10-I compiles the structural parameters of H bonds in amides.

TABLE 9-XVII H Bond Length: Hydroxides[a]

COMPOUND	ν(O—H) (cm^{-1})	R(O—H···O)	REFS.
CoOOH		2.36 Å	1129
$Cu_4(NO_3)_2(OH)_6$		2.5–2.6	1527
α-AlOOH	2874	2.47 ±.07	1706
		2.66	b
α-FeOOH	3049	2.68	b
$B(OH)_3$	3096	2.72, 2.70	2228,[b,c]
γ-FeOOH	3125	2.70	b
γ-AlOOH		2.70	1407
γ-ScOOH		2.72	1407
γ-$Al(OH)_3$	3312	2.78	b
ϵ-$Zn(OH)_2$	3087	2.82	b
β-$Be(OH)_2$	3333	2.86	b
$Nd(OH)_3$	3473	2.90	b
$La(OH)_3$	3473	2.90	b
$Y(OH)_3$	3473	2.90	b
$Sr(OH)_2 \cdot 8H_2O$		2.90	1900
$Cd(OH)_2$	3521	2.98	b
NaOH	3571	3.02	1488
$Ni(OH)_2$	3585	3.10	b
$Mg(OH)_2$	3597	3.22	b
$Ca(OH)_2$	3597	3.36	b, d

[a] See footnotes a and b, Table 9-IX.

[b] From the summary of 782.

[c] See also 451.

[d] See also 1615.

9.5.2 Miscellaneous O—H ··· N, N—H ··· O, and N—H ··· N Bonds. Table 9-XX compiles the oxygen-nitrogen distances observed in crystals containing O—H···N bonds. Tables 9-XXI and 9-XXII refer to N—H···O bonds, the former table containing the data available for ammonium type bonds, N$^+$—H···O, and the latter for amine type bonds, N—H···O. Table 9-XXIII gives the distances for N—H···N bonds.

9.5.3 Range of Bond Lengths. Figure 9-10 presents in histogram form the distribution of bond lengths tabulated in Tables 9-XX, 9-XXI, 9-XXII, 9-XXIII, and 10-I. Table 9-XXIV gives the average bond lengths and the standard deviation as a measure of distribution.

TABLE 9-XVIII H Bond Lengths—Oximes and Inorganic Acids[a]: O—H···O Bonds

COMPOUND	A—H···B	R(O····O)	REFS.
Oximes: N—O—H···O			
Ni dimethylglyoxime	N—O—H···O	2.44 ±.02 Å	786, 787
Ni salicylaldoxime	N—O—H···O	2.52	1390, 1389
$HNO_3 \cdot H_2O$	N—O—H···OH_2	2.68	1294
$HNO_3 \cdot 3H_2O$	N—O—H···OH_2	2.75	1293
Misc. Acids			
KH_2PO_4	P—O—H···O	2.48 ±.005 (or 2.49)	97
$NH_4H_2PO_4$	O—H···O═P	2.49	2068
C_6H_5SeOOH	Se—O—H···O	2.52 ±.02	311
H_3PO_4	P—O—H···O═P	2.53	729
	P—O—H···O—H	2.84	730
KH_2AsO_4	As—O—H···O	2.52	740
		2.54	522[b]
KD_2AsO_4	As—O—D···O	2.52	740
		2.55	522
$CaH_2PO_4 \cdot 2H_2O$	—	2.55	923
$NaHCO_3$	C—O—H···O	2.55	2230
$BaHPO_4$	P—O—H···O	2.57	1443
$(NH_4)_2H_3IO_6$	O—H···O—I	2.60	1764
$KHCO_3$	C—O—H···O	2.61	1518[c]
$NH_4NO_3 \cdot 2HNO_3$	N—O—H···ONO_2^-	2.63	560
Urea·H_2O_2	O—H···O—H	2.63	1264
α-HIO_3	I—O—H···O	2.69 ±.01	740
H_2O_2	O—H···O	2.78	5

[a] See footnotes a and b, Table 9-IX.

[b] See also 2069.

[c] See also 913.

TABLE 9-XIX Distribution of Distances for O—H···O Bonds

ACID TYPE	AVERAGE R(O····O)	STD. DEV.	NO. DATA
Oximes, inorg. acids	2.58 Å	0.09 Å	19
Carboxylic acids	2.63	.10	36
Phenols	2.67	.08	11
H_2O in org.-inorg.	2.71	.17	19
Alcohols	2.74	.11	19
H_2O in inorg.	2.75	.16	20
H_2O in org.	2.80	.09	20
Hydroxides	2.82	.23	21

TABLE 9-XX H Bond Lengths: O—H···N Bonds[a]

COMPOUND	R(O—H···N)	A—H	B	REFS.
Guanine·HCl·H_2O	2.62 Å	O—H	N	287
	2.82	HOH	N	
Nicotinic acid	2.66	COOH	N	2200
4-*Iso*propylidene-aminophenol	2.66	ArOH	NR_2	948
Hydroxy-L-proline	2.70	COOH	NH	2241
	(or 2.67)			543
Hydroxylamine	2.74	NOH	NH_2	1396
	(or 3.07)			
Cyclohexanoxime	2.75	NOH	NOH	1488
Acetoxime	2.78 ±.03	NOH	NOH	215
Dialuric acid·H_2O	2.80	O—H	NH	21
p-Cl-benzaldoxime	2.82	NOH	NOH	1042
Dimethylglyoxime	2.83 ±.02	NOH	NOH	1391
p-Aminophenol	2.83	ArOH	NH_2	291
$2NH_3 \cdot H_2O$	2.84	HOH	NH_3	1878
	2.85			
Cytidine	2.87			731
Adenine·HCl·$\frac{1}{2}H_2O$	2.87	HOH	N	288
4,6-Dimethyl-2-hydroxypyrimidine	2.89	O—H	N	1642
Phloroglutinol diammoniate	2.91	O—H	NH_3	44
1,3,5-Triaminocyclohexane·$2H_2O$	2.93	HOH	NH_2	44

[a] See footnotes a and b, Table 9-IX.

9.6 Crystal Parameters: Miscellaneous A—H ··· B Bonds

9.6.1 A—H ··· B Bond Lengths. Table 9-XXV compiles the crystal data for a variety of A—H···B bonds, including O—H···Cl, O—H···Br, N—H···F, N—H···Cl, N—H···Br, F—H···F, C—H···N, and N—H···S.

9.6.2 Average Bond Lengths. From the tabulated data presented in this chapter can be drawn two inescapable conclusions. First, *H bonds between the same functional groups vary in length by several tenths of an Angstrom.* This range is, no doubt, due to the constraints of molecular packing; the molecules are not necessarily able to pack at the optimum distance. It is reasonable to assume that the packing will constrain the H bond at an A····B separation below the optimum as often as it will constrain it above the optimum. Hence, the average values probably represent reliable estimates of the optimum H bond lengths. Second, *the packing in almost all of the crystals listed in the tables is influenced*

TABLE 9-XXI H Bond Lengths—Ammonium Compounds[a]: N^+—H···O Bonds

COMPOUND	R(N^+····O)	B	REFS.
Glycyl-L-tryptophan·$2H_2O$	2.68 Å	OH_2	1581
	2.75	OH_2	
	2.86	O=C	
β-Glycylglycine	2.68	OCO^-	995
	2.81		
Hexamethylene diammonium adipate	2.72	OCO^-	931
	2.75		
Hydrazine·H_2SO_4	2.73	OSO_3^-	1514
	2.73		
	2.79		
	2.77–2.99 (bifurcated)		
dl-Norleucine	2.73	OCO^-	1360
	2.87		
	2.87		
Glycine	2.76	OCO^-	15
	2.88		
	2.93		
	3.05		
Creatine·H_2O	2.79 ±.01	OCO^-	1387
	2.85 ±.01		
	2.86 ±.01		
	2.94 ±.01		
dl-Serine	2.79	OH	537
	2.81	OCO^-	
	2.87	OCO^-	
dl-Alanine	2.80	OCO^-	538, 1219
	2.84		
	2.88		
NH_4H disalicylate·H_2O	2.84	(OH)CO	548
	2.87	O=C	
	2.91	OH_2	
	2.95	(OH)CO	
L-Glutamic acid	2.86	OCO^-	930
	2.92		
	2.94		
11-Amino-undecanoic acid·HBr·$\frac{1}{2}H_2O$	2.92	OH_2	1879
NH_4NO_3·$2HNO_3$	3.01	ONO_2^-	560
	3.10	ONO_2^-	
	3.13	ONO_2^-	
	3.14	ONO_2^-	
	3.17	ONO_2^-	
	3.24	ONO_2^-	

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[a] See footnotes a and b, Table 9-IX.

TABLE 9-XXII H Bond Lengths—Amine Compounds[a]: N—H···O Bonds

COMPOUND	R(N—H···O)	B	REFS.
Nitroguanidine	2.57 Å (*intra*)	ONO	309
	2.97 (inter)	ONO	
	3.03 (inter)	ONO	
	3.28 (inter)	ONO	
Urea-H_2O_2	2.63 (amide)	O=C	1264
	2.94	H_2O_2	
	3.04	H_2O_2	
Acetaldehyde·NH_3	2.71	O=C	1270
L-Threonine	2.80	O=C	1861
	2.90		
	3.10		
$NaHPO_3NH_2$	2.84 ±.02	O=P	937
Indigo	2.88 (*intra*)	O=C	824
	2.94 (inter)	O=C	
Cytidine	2.93	O=C	731
	3.00	OH	
Dodecanoic acid hydrazide	3.00	O=C	1039
Sulfamide	3.02	O=S	2037
N-acetylglycine	3.03	O=C	354
p-Nitroaniline	3.03	O=N	542
	3.08		
Nitramide	3.04	ONO	187
	3.12		
Hydroxylamine	3.07 (or 2.74)	OH	1396
β-Glycylglycine	3.07	OCO^-	995
sym-Trinitrobenzene-*p*-iodoaniline	3.10	ONO	1665
Ammonium oxide	3.13	OH_2	1878
	3.22		
	3.22		
p-Aminophenol	3.13	OH	291
	3.18		
2-Metanilylamino-5-Br-pyrimidine	3.15	OSO_2	1887
KNH_2SO_3	3.15	OSO_2	295
Hydroxy-L-proline	3.17 (or 2.70)	O=C	2241, 543

[a] See footnotes a and b, Table 9-IX.

or dominated by H bonding. This conclusion implies that the average bond lengths involve attractive H bond interactions and that the distances are *shorter* than the van der Waals contact distances. It is interesting, then, to examine the difference between R(A····B) and the quantity $R_v = [r_v(A) + r_v(B)]$, the sum of the van der Waals radii, r_v, of atoms

TABLE 9-XXIII H Bond Lengths: N—H···N Bonds[a]

COMPOUND	R(N—H···N)	REFS.
3-Hydrazino-5-thiol-1,2,4-triazole	2.88 Å	1830
$NH_4Cl \cdot 3NH_3$	2.89	1544
	2.93	
	2.98	
NH_4N_3	2.94	703
	2.97	
Dicyandiamide	2.94	993
	3.02	
	3.04	
	3.16	
Hydrazine·HCl	2.95	1778
5-Br-4,6-diaminopyrimidine	2.96	396
	3.07	
Isonicotinic acid hydrazide	2.97	1040
	3.04	
Adenine·HCl·$\frac{1}{2}H_2O$	2.99	288
Melamine	3.00	992
	3.02	
	3.05	
	3.10	
NH_4CN	3.02	1209
HNCO	3.07	2124
Guanine·HCl·H_2O	3.08	287
Nicotinamide	3.09	2199
4-Amino-2,6-diCl-pyrimidine	3.09	396
	3.28	
4,5-Diamino-2-Cl-pyrimidine	3.11	2169
	3.15	
	3.16	
Nitroguanidine	3.12	309
Formamidoxime	3.12	859
Dodecanoic acid hydrazide	3.17	1039
Methylamine	3.18	83
	3.27	
Hydrazine	3.19 (within chains)	420
	3.30 (within chains)	
	3.25 (between chains)	
	3.62 (between chains)	
	3.67 (between chains)	
Hexamethylenediamine	3.21	217
2-Amino-4,6-diCl-pyrimidine	3.21	397
	3.37	
Ammonia	3.38	1338, 1894
Sodium amide	3.81 (no bond)	2232

[a] See footnotes a and b, Table 9-IX.

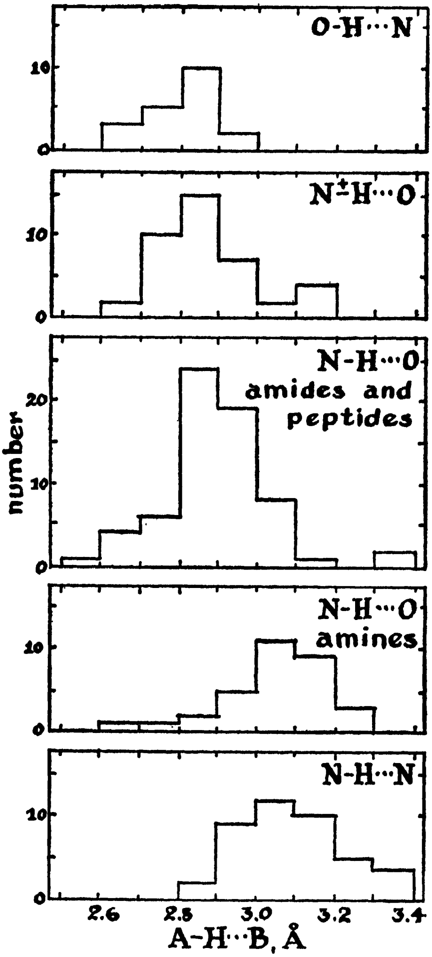

FIGURE 9-10 Distribution of A····B bond lengths: O—H···N, N—H···O, N—H···N.

TABLE 9-XXIV Distribution of Distances for O—H···N, N—H···O, and N—H···N Bonds

A—H···B	A—H TYPE	AVERAGE R(A—H···B)	STANDARD DEVIATION	NO. DATA
O—H···N	All O—H	2.80 Å	0.09 Å	21
N—H···O	Ammonium	2.88	0.13	41
N—H···O	Amides	2.93	0.10	35
N—H···O	Amines	3.04	0.13	30
N—H···N	All N—H	3.10	0.13	37

TABLE 9-XXV H Bond Lengths: Miscellaneous[a,b] A—H···B Bonds

COMPOUND	R(A—H···B)	A	B	REFS.
Tropolone hydrochloride	2.86 Å	O—H	Cl^-	1791
	2.97			
Hydroxylamine·HCl	2.99 ±.02	NOH	Cl^-	1043
	3.05	NOH	Cl^-	
Choline chloride	3.04	OH	Cl^-	1830
D(−)*iso*leucine·HCl·H_2O	3.07, 3.24	HOH	Cl^-	2035
Adenine·HCl·$\frac{1}{2}H_2O$	3.12	HOH	Cl^-	288
$MnCl_2 \cdot 2H_2O$	3.15	HOH	Cl^-	2084
$CoCl_2 \cdot 2H_2O$	3.19	HOH	Cl^-	2084
$CuCl_2 \cdot 2H_2O$	3.21	HOH	Cl^-	1618
D(−)*iso*leucine·HBr·H_2O	3.30, 3.35	HOH	Br^-	2035
11-Amino-undecanoic acid·HBr·$\frac{1}{2}H_2O$	3.38	HOH	Br^-	1879
Hydrazine·2HF	2.62 ±.02	N^+—H	F^-	1154
NH_4F	2.69	N^+—H	F^-	1649
NH_4HF_2	2.80 ±.03	N^+—H	F^-	1588
$NH_3 \cdot BF_3$	3.01 ±.03	N—H	F	935
trans-Dichlorodiethylenediamine·$CoCl_3$·HCl·$2H_2O$	2.91	N^+—H	Cl^-	1487
m-Toluidine·2HCl	3.10	N^+—H	Cl^-	680
	3.22			
	3.26			
Hydrazine·2HCl	3.10 ±.02	N^+—H	Cl^-	540
Hexamethylenediamine·2HCl	3.11 ±.04[c]	N^+—H	Cl^-	218
	3.24 ±.04			
Adenine·HCl·$\frac{1}{2}H_2O$	3.11	N—H	Cl^-	288
	3.21			
Hydrazine·HCl	3.12	N^+—H	Cl^-	1778
	3.12			
	3.41			
Hydroxylamine·HCl	3.16 ±.02	N^+—H	Cl^-	1043
	3.21			
	3.23			
	3.26			
Geranylamine·HCl	3.17	N^+—H	Cl^-	1036
	3.24			
Methylamine·HCl	3.18 ±.05	N^+—H	Cl^-	994
$NH_4Cl \cdot 3NH_3$	3.22	N^+—H	Cl^-	1544
NH_4Cl (NaCl lattice)	3.26	N^+—H	Cl^-	1544
NH_4Cl (CsCl lattice)	3.35	N^+—H	Cl^-	2110

TABLE 9-XXV (continued)

COMPOUND	R(A—H···B)	A	B	REFS.
4,5-Diamino-2-Cl-pyrimidine	3.51	N—H	Cl	2169
	3.52			
11-Amino-undecanoic	3.30	N^+—H	Br^-	1879
acid·HBr·½H_2O	3.44			
KHF_2	2.26 ±.01	$(F—H—F)^-$		900
NH_4HF_2	2.36	$(F—H—F)^-$		886
$TlHF_2$	2.4	$(F—H—F)^-$		1588
HF (solid)	2.49 ±.01	F	F	82
HF (gas, polymer)	2.55	F	F	173
$NaHF_2$	2.56	$(F—H—F)^-$		45
HCN	3.18	C—H	N≡C	562
Ethylenethiourea	3.44	N—H	S	2165
	3.48			
3-Hydrazino-5-thiol-1,2,4-triazole	3.44(?)	N—H	S	1830

[a] See footnotes a and b, Table 9-IX.

[b] For other compounds, see also 109, 1629, 678, 867, 2064.

[c] Donohue has recalculated these bond lengths from the data of Jerslev, obtaining 3.01 Å and 3.07 Å (537).

A and B. These differences are listed in Table 9-XXVI, using the van der Waals radii estimated by Pauling (1585).

Looking first at the O—H···O bonds, we see that they can be as much as a quarter of an Angstrom shorter than the van der Waals contact distance of the two oxygen atoms. The difference between R_v and $R_{av.}$ is near zero for the longest O—H···O bonds, those in hydroxides. Even this situation does not represent absence of H bonding, since the quantity R_v implies no contribution to the radius by the hydrogen interposed between the two oxygen atoms. Indeed, we see in Table 9-XVII that the IR frequency suggests there is a noticeable H bond interaction even at R(O····O) distances above 3.0 Å. In fact, we might use the extreme bond lengths of the hydroxides to define the R(O····O) at which the H bond interaction vanishes. In Table 9-XVII we find that the IR criterion suggests 3.2 Å for this limit. On this basis we calculate the last column of Table 9-XXVI, the estimated H bond contraction.

Turning to the examples involving nitrogen we find a contrast to the other A—H···B types. The values of $R_v - R_{av.}$ are uniformly

TABLE 9-XXVI Comparison of H Bond and van der Waals Distances

A—H···B	A—H TYPE	R_v[a, b] = $r_v(A) + r_v(B)$	$R_{av.}$	$R_v - R_{av.}$[b]	ESTIMATED H BOND CONTRACTION[c]
O—H···O	Inorg. acids	2.80 Å	2.55 Å	+0.25 Å	0.65 Å
	Oximes		2.58	+0.22	0.62
	COOH acids		2.63	+0.17	0.57
	Phenols		2.67	+0.13	0.53
	Alcohols		2.74	+0.06	0.46
	H_2O in salts		2.73	+0.07	0.47
	H_2O in organics		2.80	0.00	0.40
	Hydroxides		2.82	−0.02	0.38
O—H···N	All	2.90 (3.05)	2.80	+0.10 (+.25)	0.5
N—H···O	Ammonium salts	2.90 (3.05)	2.88	+0.02 (+.17)	0.5
	Amides		2.93	−0.03 (+.12)	0.4
	Amines		3.04	−0.14 (+.01)	0.3
N—H···N	All	3.00 (3.30)	3.10	−0.10 (+.20)	0.4
O—H···Cl	All	3.20	3.08	+0.12	—
N—H···F	All	2.85 (3.00)	2.78	+0.07 (+.22)	—
N—H···Cl	All	3.30 (3.45)	3.21	+0.09 (+.24)	—
F—H···F	All	2.70	2.44	+0.26	—

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[a] Van der Waals radii are from 1585.

[b] Parenthetical values are based upon $r_v(N) = 1.65$ Å; see text.

[c] These estimates are discussed in this section.

small, and actually negative in some cases. Despite the usually high base strength of nitrogen bases, the value of $R_v - R_{av.}$ is smaller for O—H···N bonds than it is for O—H···Cl bonds. The same unlikely difference is observed by comparing N—H···N bonds to N—H···O, N—H···F, and N—H···Cl bonds. The most likely explanation seems to be that the value used for the van der Waals radius for nitrogen, 1.5 Å, is too small. A van der Waals radius in the range 1.6–1.7 Å is probably a more useful value. This estimate may be compared to the interatomic distances found in solid nitrogen. In the low temperature cubic form, the closest approach of unbonded nitrogen atoms is 3.46 Å, giving a van der Waals radius of 1.73 Å. In the high temperature hexagonal form, the distance between molecular centers is 4.07 Å, implying a closest approach of unbonded atoms between 3.01 Å (for N_2 molecules freely rotating or oriented coaxially) and 3.58 Å (for N_2 molecules with axes perpendicular). This gives a range of 1.50–1.79 Å for the van der Waals radius. Thus, the solid nitrogen crystal data do not preclude a larger radius for nitrogen. The parenthetic values of $R_v - R_{av.}$ in Table 9-XXVI are based upon a value of 1.65 Å for the van der Waals radius of nitrogen.

The N····N distance for ammonia, 3.38 Å, probably yields an estimate of the limiting distance at which H bonding vanishes. Although there is some H bonding in solid ammonia, it is weak. Perhaps a distance of 3.5 Å gives a reasonable basis for calculating the H bond contraction for N—H···N H bonds.

The parenthetical estimates for the H bond contractions are based upon assumed values of the limiting H bond distances between the 3.2 Å for O—H···O bonds and the 3.5 Å value chosen for N—H···N bonds. The value used for O—H···N is 3.3 Å, and that for N—H···O is 3.4 Å.

9.7 Properties of Hydrogen Bonded Crystals

9.7.1 Deuterium Isotope Effect. Ubbelohde and co-workers have done much work on the effect of deuterium substitution on the structures of H bonded crystals (1729, 2067, 1728, 1727, 2071, 522, 739, 2068). The results are reviewed in the summary paper, 2068. In most crystals the D bond is slightly longer than the H bond. Furthermore, in those crystals which are ferroelectric, the deuterated crystal has a higher ferroelectric transition temperature (upper Curie temperature). Some of the results summarized by Ubbelohde and Gallagher are

TABLE 9-XXVII Isotope Effect in H Bonded Crystals[a]

CRYSTAL	R_H[b] (Å)	$R_D - R_H$ (Å·10^{-3})	$T_D - T_H$ (Curie temp.)[c]
KHF_2	2.26	Small contraction	—
$NH_4H_2PO_4$	2.49	+10.0	+82–94°K
Oxalic acid·$2H_2O$	2.49	+40.5	—
KH_2PO_4	2.52	+9.7	+91.0°
KH_2AsO_4	2.54	+8.0	+66.4°
Acetylene dicarboxylic acid·$2H_2O$	2.56	+34.0	—
Succinic acid	2.64	+18	—
β-Resorcinol	2.70	0	—
	2.75		
Ice	2.76	+1.5	—
Urea	2.99	Small contraction	—
$CuSO_4 \cdot 5H_2O$	—	Small contraction	—

[a] From 2068.

[b] $R_H = R(A—H \cdots B)$

$R_D = R(A—D \cdots B)$.

[c] T_H = Curie temperature of hydrogen compound; T_D = Curie temperature of deuterium compound.

listed in Table 9-XXVII, and more detailed results for ice (as summarized by Lonsdale, 1257a) are given in Table 9-XXVIII. The values of $R_D - R_H$ are calculated from the unit cell expansions and are based on the assumptions given in the various publications. The data show no systematic dependence of the isotopical expansion on the value of R.

The deuterium isotope effect is generally explained on the basis of

TABLE 9-XXVIII Oxygen-Oxygen Distances in Hexagonal Ice and Heavy Ice.[a]

t (°C)	H_2O O—H···O′ along c axis	H_2O O—H···O″	H_2O average O····O	D_2O O—H···O′ along c axis	D_2O O—H···O″	D_2O average O····O
0	2.760	2.770	2.765	2.761	2.772	2.766
−60	2.755	2.763	2.759	2.756	2.764	2.760
−120	2.748	2.755	2.752	2.751	2.755	2.753
−180	2.740	2.743	2.742	2.744	2.744	2.744

[a] 1257a.

the different H bond energy and amplitude of vibration implied by the different zero point energies of O—H and O—D bonds. This is presumed to result in greater "overlap" in the H bond (e.g., see 2068). More detailed but qualitatively similar interpretations have been offered by Nordman and Lipscomb (1522), and these were supported by Rundle (1763).

9.7.2 Thermal Expansion. See 1728, 1725, 2070, 1307, 1520, 2068, 738, 1641, 268.

9.7.3 Ferroelectric and Dielectric Behavior. See 1768, 1385, 2068, 1891a, 2070, 1094a.

9.7.4 Piezoelectric Behavior. See 1954, 1355, 1513, 2068.

9.7.5 Conductance. Two theories of conductance in H bonded systems have been discussed in Section 8.3.6, molecular rotation and proton migration ("jumping" or "tunneling"). Both models have been applied to H bonded solids. We shall not expand the argument concerning these two interpretations but will merely present in Table 9-XXIX some conductivity data collected by Pollock and Ubbelohde (1655). These authors calculated activation energies for proton migration, as shown in the last column of the table. See also 158, 223, 423, 1076, 1143, 1719.

TABLE 9-XXIX Conductivities and Activation Energies for Proton Migration in H Bonded Crystals[a]

SOLID	CONDUCTIVITY (50°C) (ohm^{-1}-cm^{-1})	ACTIVATION ENERGY (kcal/mole)
Acetylene dicarboxylic acid·$2H_2O$	$3.5 \cdot 10^{-6}$	6.5
Acetylene dicarboxylic acid	$7.1 \cdot 10^{-7}$	12.3
Oxalic acid·$2H_2O$	$2.2 \cdot 10^{-8}$	23.5
Oxalic acid	$1.1 \cdot 10^{-9}$	40.5
Benzoic acid	$1.8 \cdot 10^{-9}$	48.9

[a] 1655.

CHAPTER 10

Hydrogen Bonding in Proteins and Nucleic Acids

> *The problem that we have set ourselves is that of finding all hydrogen-bonded structures for a single polypeptide chain . . . [The] only configurations . . . compatible with our postulate of equivalence of the residues are helical configurations. We assume that . . . each residue is planar. It is further assumed that each nitrogen atom forms a hydrogen bond with an oxygen atom of another residue. . . .*[a]
>
> L. PAULING, R. B. COREY, and H. R. BRANSON
> *California Institute of Technology, 1951*

10.1 Introduction

The modern concepts of protein structure and of the H bond had their genesis about the same time, and have advanced together. Hydrogen bond theory began to flourish soon after Latimer and Rodebush presented their classical paper (1201), and x-ray diffraction methods were applied to proteins about the same time. Twenty years later, IR spectroscopy studies were begun. In this chapter we shall show the crucial role of the H bond in modern proposals for protein structures, but the treatment will be restricted to those phases of protein study which reveal this role. (Of course, such restriction dictates only passing mention of

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[a] From *Proc. Natl. Acad. Sci. U.S.* **37**, 205 (1951).

a number of major fields that are important to the over-all understanding of proteins.) For discussions of ways to determine molecular weight, particle dimensions, and amino acid sequence in a chain see the 1956–1958 issues of *Advances in Protein Chemistry*, Academic Press, Inc., New York, especially 1091b, and reference works on proteins. Further, we shall concern ourselves mainly with the H bond as a structural element—hence most of our data will be drawn from x-ray and IR spectral measurements since these are at present the most important experimental sources of the facts we need. Even within this confined area a comprehensive survey of every paper which mentions H bonds and proteins will not be attempted. Rather, we shall proceed, as the workers in this field have, from the simple "building blocks"—amino acids and amides—through the synthetic polypeptides of known, usually homogeneous, composition to the natural proteins.

10.2 Protein—A Definition

A protein molecule is a long chain (several hundred or thousand atoms) of condensed α-amino acid molecules (called residues) arranged in rather orderly fashion along the main chain but with various types of branch chains and, in some cases, crosslinking. The general representation of a residue is given in Fig. 10-1.

Here is a word picture that supplies a mental hook for remembering the *levo* configuration (for α-amino acids *only*). Visualize yourself on the N atom at the foot of an arch over C_α to C_β and passing between the other two bonds to C_α. As you walk over the arch, the C=O group is on your *left* (*levo*) side.

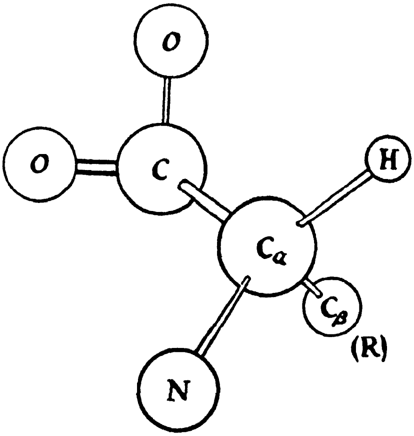


FIGURE 10-1 Schematic diagram of a *levo* α-amino acid residue.

In natural proteins the residues are from a group of about 20 acids—all in the L (*levo*) configuration, except glycine in which **R** = H. [Sanger and Smith list these acids and the abbreviations used (1785).] Apparently some D (*dextro*) acids occur in certain lower forms of life. They will be ignored here, although D acids are gaining importance, as revealed by optical rotation studies of synthetic polypeptides. In proteins usually three of four types of residues account for the bulk of the molecule, but minor amounts of fifteen or more other acids are present as well. The simplest protein, insulin, has 106 residues; hemoglobin has 580.

In Fig. 10-1, **R** (which includes C_β) represents the rest of the acid (or side chain) and can range from H (glycine) to a five-membered chain (lycine) and have single (phenylalanine) or multiple rings (tryptophan). **R** may contain OH (serine, tyrosine), COOH (glutamic acid), NH_2 (or $>$N—H) (arginine), —S— (methionine), or $CONH_2$ (glutamine) groups. Until fairly recently the exact order of the residues within the molecule was unknown (1784), and Sanger's epochal work on insulin is still almost the only completely solved case (51). That same volume (51) indicates in the preface that the order in ribonuclease is nearly solved, and C. H. Li's chapter describes the partially deciphered amino acid order in pituitary hormones. Bell described the order in ACTH (187a). Sanger reviewed the partial structures that were known in 1954 (1783). Obviously there will be many more advances in this area soon.

In spite of the complexity of the protein molecule, the structural principles are becoming clear, and the important role of the H bond in determining the structure is becoming increasingly evident.

10.3 Model Molecules

Several decisive groups of facts concerning protein structure have been derived from the monomeric amides. Basically, these facts deal with the size, shape, and electronic make-up of the model compounds, particularly the amide grouping. X-ray diffraction and IR spectroscopy have been the most important tools in obtaining this information.

10.3.1 X-ray Diffraction. X-ray diffraction data are a vital part of the foundation supporting the present knowledge of protein structures. Such determinations yield information on three major points: (1) the distances and angles between atoms, (2) their planarity, and (3) the *trans* configuration of the amide group. This section discusses these points, and Sections 10.4.2 and 10.4.3 present some of the uses of x-ray diffraction on synthetic and natural polypeptides.

Table 10-I lists the bond lengths and bond angles found by x-ray

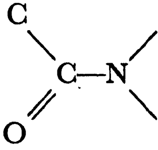
diffraction for about 30 amides and simple peptides. Most of this work is recent and of good accuracy; about half of the investigators used three-dimensional refinement of electron density to deduce crystal parameters. Generally the lengths are known within ±0.02 Å and the angles to ±2°.

From the data in Table 10-I the average values of the parameters have been found. Table 10-II compares these values with parameter sets used by various workers in proposing model structures.

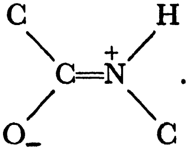
In general, the sets of parameters which were used are in good agreement with the average values established by Table 10-I, the only exception being those for the H bond length. Considering these sets in chronological order (i.e., from the bottom up in Table 10-II), Astbury's and Huggins' values were only estimates since just a few values of low accuracy were available when these sets were chosen. Pauling and co-workers had somewhat more x-ray data available for their first estimate of 2.72 Å, and for the 1953 value (2.79 ±0.12) they had still more. The last work, which may be considered as the definitive set of values from this school of workers, lists 23 values of N—H···O ranging from 2.67 Å to 3.17 Å and averaging 2.93 Å. However, four values over 3.00 Å were considered to be strained and hence exceptional. They were not included in the recommended value of 2.79 Å. The basis for this exclusion of the long H bonds is not well explained, and indeed the additional work collected in Table 10-I makes it seem somewhat arbitrary. The value selected by Bamford and co-workers, 2.94 Å, is based on essentially the same data as that presented in Table 10-I.

Most of the workers cited in Table 10-I comment directly on the planarity of the six atoms in the amide group or on the shortness of the C—N bond (average value, 1.32 Å; typical C—N single bond, 1.47 Å). In some cases (note *i*, Table 10-I) there is a slight divergence from strict planarity (up to a few degrees); but the effect is not large, and some of the examples may be nontypical (formamide is the first member of the series, and diketopiperazine has the amide group in the *cis* configuration).

The peptide group is planar as a result of the resonance between



and



. In addition to the generally observed planarity, experimental verification of the resonance effect comes from the lengths of the C—N and C=O bonds. Both of these

TABLE 10-I Some Crystal Structure Parameters of Amides and Peptides

COMPOUND	BOND LENGTH (Å)			BOND ANGLE (degrees)			N—H···O LENGTH (Å)	NOTES	REFS.
	C=O	C—N	C—C_α	O=C—N	C_α—C=O	N····O=C			
Containing Amido Groups									
Chloroacetamide (see below)	1.23	1.33	1.48	130	111	—	2.82		514
(β = 98.8°)							3.01		
Phthalylurea							2.82		822
Acetamide	1.28	1.38	1.51	122	129	—	2.83	i	1831
							2.89		
6-Amido-3-pyridazone[a]	1.25	1.33	1.46	123	119	—	2.84		466
							2.92		
Formamide[a]	1.26	1.30	—	122	—	120	2.88	i	1175
							2.94		
Urea, in complex with hydrocarbon							2.92		110
							3.03		
Tetradecanamide	1.26	1.26	1.49	116	130	—	2.93	c	2065
							2.99		
Succinamide	1.24	1.33	1.51	122	122	—	2.94	c	478
							2.94		
Oxamide[a]	1.24	1.31	1.54	126	120	117.3	2.94		90
						164.1	2.95		(cf. 1740)
Chloroacetamide (see below)	1.25	1.29	1.54	127	118	—	2.95	c	1607a
(β = 98.8°)							2.99		
Decanamide	1.28	1.31	1.47	107	125	—	2.99		267
							2.99		
Urea[a]	1.26	1.34	—	121	—	—	2.99	c	2107
							3.04		

Nicotinamide[a]	1.22	1.34	1.52	125	118	157	2.99		2199
Chloroacetamide[b]	1.25	1.40	1.51	116	124	—	3.05		1085
(unstable modification, $\beta = 102.5°$)							3.37		
							3.39		
							3.45		
Containing Imido Groups									
Uracil[a]	1.23	1.34	—	124	—	—	2.81	c	1574
							2.86		
N-Methylacetamide	1.23	1.29	1.55	123	120	—	2.83	c	1090
Diketopiperazine	1.25	1.33	1.47	120	120	—	2.85	i	442
	1.22	1.38	1.44	121	122	—	2.84		2081a
N,*N*′-Hexamethylenebisacetamide	1.22	1.35	1.52	124	120	—	2.88	c	108
N,*N*′-Hexamethylenebispropionamide	1.25	1.35	1.51	118	124	—	2.95	c	1041
Acetanilide[a]	1.23	1.33	1.48	121	120	141	2.97	j	293
Acetylglycine[a]	1.24	1.32	1.50	121	121	124	3.03	c	354
Containing Ammonium Groups									
Cysteylglycine · $\frac{1}{2}$NaI	1.21	1.32	1.54	*107*	*109*	—	2.55	i	569
							3.03		
α-Glycylglycine[a]	1.24	1.32	1.56	124	121	—	2.67		k
							2.67		
							2.75		
							2.77[f]		
β-Glycylglycine	1.23	1.29	1.50	125	121	—	2.68	c	995
							2.80		
							2.81		
							3.07[d]		
Glycyl-L-tryptophan · $2H_2O$[a]	1.23	1.32	1.54	125	121	—	2.68	c	1581
							2.75		
							2.86		
							2.89[d]		

TABLE 10-I (continued)

COMPOUND	BOND LENGTH (Å)			BOND ANGLE (degrees)					
	C═O	C—N	C—C$_\alpha$	$\overset{O}{\diagdown}$C—N	C$_\alpha$—C$\overset{O}{/\!/}$	N····O$\diagdown\!\diagdown$C	N—H···O LENGTH (Å)	NOTES	REFS.
Glycyl-L-asparagine[a]	1.23	1.32	1.50	124	120	—	2.75	c	1582
							2.86		
							3.03		
							2.88[d]		
							2.88[e]		
							2.93[e]		
N,*N*′-Diglycyl-L-cystine·$2H_2O$[a]	1.21	1.35	1.55	125	120	125.9	2.75	i	2211
						95.6	2.75		
						143.0	2.89		
L-Leucyl-L-prolyl-glycine[a]	1.27	1.34	1.50	122	119	—	2.83	c, g	1216a
	1.24	1.31	1.52	123	121	—	2.84	c, h	
							2.87		
							3.19[d]		
Glycyl-L-alanine·HCl	1.26	1.32	1.52	135	115	—	2.87	i	2031
Glycyl-L-tyrosine·HCl·H_2O[a]	1.16	1.35	1.53	132	117	—	2.91	j	1905

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[a] Structure determined by three dimensional refinement of electron density.

[b] Not included in averages of parameters.

[c] Amide group planar.

[d] H bond involves imido group.

[e] H bond involves amido group.

[f] Taken as imido group H bond; parallel to β-glycylglycine.

[g] This row of parameters for the amido group is common to prolyl and glycine residues.

[h] This row of parameters for the amido group is common to leucyl and prolyl residues.

[i] There is evidence for nonplanar amide group.

[j] Amido group approximately planar.

[k] Work by E. W. Hughes and A. B. Biswas quoted in our reference 122, p. 105–9.

TABLE 10-II Average Values of Some Crystal Parameters in Amides

BOND LENGTH (Å)			BOND ANGLES (degrees)		N—H···O (Å)		
C=O	C—N	$C—C_\alpha$	O=C—N	C_α—C=O		PARAMETERS GIVEN BY	TYPE OF GROUP
1.25	1.32	1.50	122	121	2.94 ±0.07[a]	Our Table 10-I	Amido
1.24	1.33	1.51	122	121	2.91 ±0.11[a]		Imido
1.23	1.32	1.53	124	118	2.84 ±0.12[a]		Ammonium
—	—	—	125	121	2.94	Bamford, Elliott, and Hanby (122)	All three
1.24	1.32	1.53	125	121	2.79 ±0.12[b]	Corey and Pauling (443)	Imido
1.23	1.32	1.53	122	121	~2.72	Pauling, Corey, and Branson (1601)	Imido
1.25	1.33	1.52	—	118	2.85	Huggins (987)	Imido
1.21	—	1.55	109	109	<3	Astbury (71)	—

[a] ± the standard deviation.

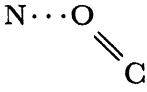
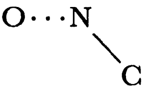
[b] Range of values.

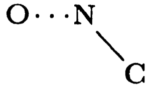
bonds are intermediate to normal single and double bonds. Consider the following bond lengths from 2107 and 443.

BOND	C—N	C=O
Normal single	1.48	1.42
Peptide	1.32	1.24
Normal double	1.24	1.20

Using these values and Pauling's method of calculation, Vaughn and Donohue (2107) find that the peptide C—N bond has 30–40 percent double bond character and the C=O bond has 70–60 percent double bond character.

With the x-ray data now available, there is little doubt that the amide group, alone or in dipeptides, is generally planar. Further, it typically has the average dimensions and angles shown at the top of Table 10-II. There is no reason to expect polypeptides to have different values, and the model structures for natural and synthetic polypeptides commonly use values derived in this fashion from simple molecules.

There is some discussion about the values to be expected for angles determined by the H bond. Table 10-I includes values for  $\mathrm{N}\cdots\mathrm{O}{=}\mathrm{C}$ that range from 95° to 165°. Apparently the sp^2 hybridization at the oxygen atom is not effective in restricting the H atoms along the p orbital direction (120°). Also,  $\mathrm{O}\cdots\mathrm{N}{-}\mathrm{C}$ varies from about 100° to 130° and is not fixed at the tetrahedral value of 109° 28′.

Sometimes the nonlinearity of H bonding is expressed by the difference of  $\mathrm{O}\cdots\mathrm{N}{-}\mathrm{C}$ from 110°. The procedure *assumes* that the N—H vector is actually along the tetrahedral direction, holding the H atom off the N····O line. Until recently this assumption could not be checked, but x-ray methods for locating H atoms are being improved and data may be available soon. (See Section 9.3.) Also, neutron diffraction work will give information on this point, and polarized IR studies may help (see Elliott 592, and the next section of this chapter). Finally, Robertson and Ambrose calculated some H—N···O angles from models (883). At present, Pauling's original criterion that the H atom may be as much as 30° off the linear position still expresses the known facts (1601). In view of the variation of environment around the amide group in different crystals, and the fact that other packing requirements of the molecule must be met, it is not likely that H bond linearity will always be preserved.

Before leaving the known crystal structures of amides, perhaps a comparison of the simplest amides and peptides will be helpful. Figures 10-2 and 10-3 show parts of the formamide and β-glycylglycine crystals.

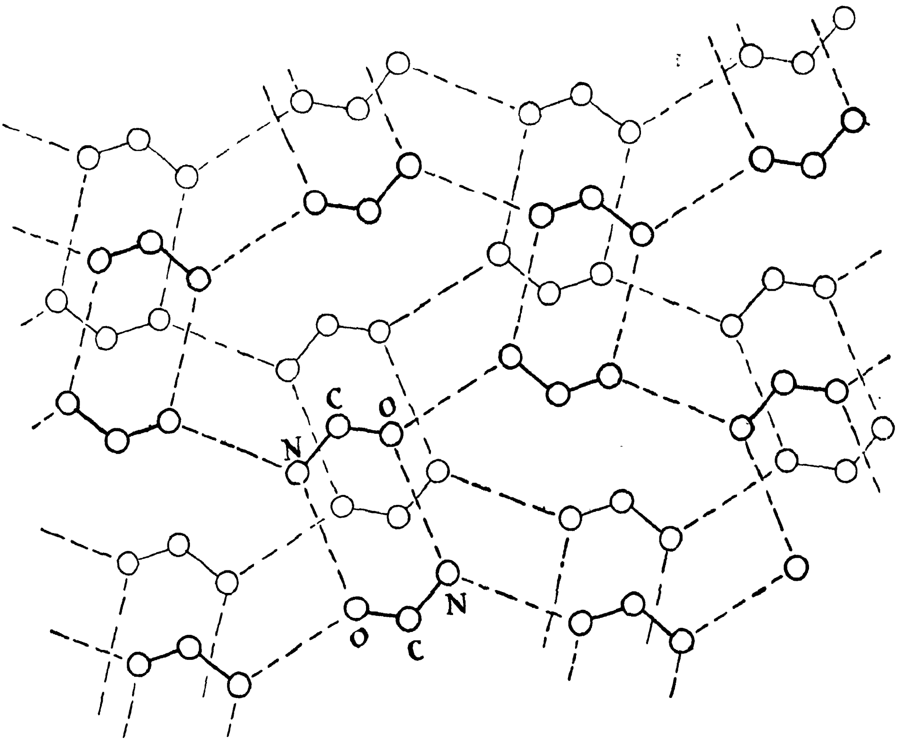


FIGURE 10-2 Formamide: view normal to 101 plane. [From Ladell and Post, *Acta Cryst.* 7, 559–64 (1954).]

The principal point to be noted is the relative simplicity of the H bond network in formamide. There are two H bond lengths, 2.88 Å and 2.94 Å, both between an amido N—H and a carbonyl oxygen. The molecules are linked in sheets but have only van der Waals interaction between sheets. This type of structure is the rule in the amides, although acetamide does not display such a simple arrangement. It has an interconnected, space-filling mesh of H bonds.

The peptide, in contrast, is held together by H bonds of four lengths from two kinds of N—H groups joining the molecules in a complex three-dimensional network. Other arrangements are found in peptides made up of more intricate residues. For example, a molecule of L-leucyl-L-prolyl-glycine is held to neighboring molecules at each end and at two places along the peptide chain.

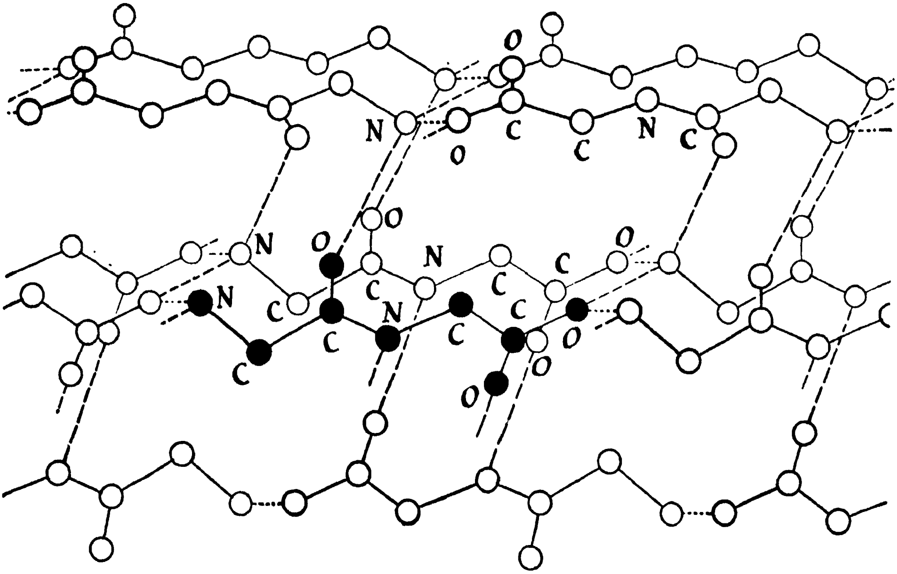


FIGURE 10-3 β-Glycylglycine: view 15° off b_0 axis. [From Hughes and Moore, *J. Am. Chem. Soc.* **71**, 2618–23 (1949).]

We conclude that: (1) molecular parameters determined from amides may be carried over to proteins with reasonable assurance of correspondence; (2) the H bond is an important ordering element in crystals of both small and large molecules; but, (3) there are many possible arrangements, so precise prediction of molecular arrangement is not to be expected. The average values of parameters are given in Table 10-II. The N—H···O bond varies in length from 2.67 Å to 3.07 Å, while the angles involving the H bond range from 95° to 165° (N····O=C) and 100° to 130° (O····N—C).

10.3.2 Infrared Spectroscopy. There are four principal contributions from IR measurements: (1) they show the presence of H bonded N—H groups; (2) they distinguish between *intra-* and intermolecular H bonds in solution; (3) they help establish the *trans* configuration of the substituted amide group[a] and, when polarized IR radiation is used; (4) they give information about the orientation of the bond moments.

There is ample evidence that when amides form H bonds the NH frequencies are shifted—in particular the stretching modes (3450–3500 cm^{-1}) move to lower frequencies (3200–3350 cm^{-1}). (See Fig. 3-3, and 492.) The same behavior has been found for peptides (1433, 1434, 1427) and proteins (330, 1852).

Mizushima gives clear evidence of the *intra*molecular character of the H bond in acetylpeptides, contrasting its low concentration dependence with that of *N*-methylacetamide which can form only intermolecular H bonds. Finally, the spectra show no indication of a H bonded OH vibration, so the amide group does not have a high percentage of enol form (1429).

The spectral evidence for the *trans* configuration in substituted amides is similar to that for internal bonding in peptides. Going to higher temperature or more dilute solution changes the N—H···O frequency in, for example, *N*-methylacetamide (1429). This is the result of changing the number of units in the H bonded chain. Some amides are confined to the *cis* form (diketopiperazine or δ-valerolactam), and dimerize in a ring. Such compounds do not exhibit the dilution shift. Davies discussed this point (503) and showed that some amides with rotational freedom (trichloroacetamide) form rings. The spectroscopic data reveal that this does not happen for peptides.

In addition to this evidence, both x-ray diffraction studies and dipole moment data (1139) confirm the predominance of the *trans* form in amides free to adopt this configuration. The crystal structure determinations discussed above are unanimous in showing the *heavy* atoms in positions corresponding to a *trans* form. In the few cases where hydrogen positions have been inferred from Fourier difference projections, they fit this picture. The dipole moment studies (1429, for example) show that continued dilution lowers the dipole moment. As discussed in Chapter 2, this is typical of the breakdown of chain association and is most easily explained if the amide group has the *trans* form.

Another way to obtain information about molecular structure is by means of polarized IR radiation (see Section 3.3.10). This method has the potential advantage of providing the direction of the vibrating dipole. There are also disadvantages: some kind of oriented sample is

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[a] The *trans* configuration is that with the N—H bond *trans* to the C═O bond [as used by Mizushima (1425) and others].

necessary, and such a sample is seldom easily obtained. Ambrose and Elliott discuss some of the problems (36) and their solution. Because of the relative newness of the method, many pertinent cases are still to be studied. Ambrose and Elliott are the leading exponents of this technique, but they have worked mostly with polypeptides and natural proteins (see later sections in this chapter). Kessler (1098), as well as Newman and Badger (1503), reports dichroic work on simple compounds. The latter study exemplifies the present state of accuracy in this area, and also serves to illustrate a controversial point—the linearity of the H bond. Newman and Badger conclude that the N—H bond (or more strictly the bond moment) in *N*-acetylglycine is essentially in the plane of the amide group but not pointing directly at the oxygen atom of the neighboring carbonyl. Although they specify that the C—N—H angle is 100° ±10°, it cannot coincide with the C—N···O angle, 132° (537). This is an important point in the current argument on the structure of proteins. It is clear that more research on substances of this type with known crystal structures is needed to establish whether or not this behavior is general.

10.4 Polypeptides, Polyamides, and Proteins

Proceeding to more complex compounds, let us consider the synthetic polymers. A fairly large number have been synthesized, and some of the amides are in commercial production in very large quantities. The most important examples of synthetic polyamides have a medium length carbon chain between the amide groups and differ in structure from the polypeptides. As a result, they are model compounds for proteins only in the β or stretched form (see Section 10.4.3 on structural models).

Although polypeptides were studied as early as 1934 (1393) the real impetus has come since Woodward and Schramm "rediscovered" the Leuchs polymerization reaction (2194). The English workers were most nimble in following this lead, and several groups attacked the structure problem through the polypeptides (see 76, 292, 36, 123). Bamford, Elliott, and Hanby, in their book (122, pp. 53–58), give a list of synthetic polypeptides and some of their properties.

In an over-all consideration, the following relatively few facts are well established. In general, polypeptides, like proteins, exist in two forms which Astbury termed α and β. Materials with the α form can be stretched by about 100 percent and have an x-ray pattern dominated by polar reflections at 5.1–5.3 Å and 1.5 Å, and a diffuse equatorial band around 10 Å. Polarized IR spectra of oriented samples show that the H bonds are more or less in line with the orientation—usually the fiber axis or rolling direction of a film. In the β form these materials are not stretchable, the H bonds are generally perpendicular to the orienting force, and the x-ray pattern has the main reflections at about 4.6 Å and 10 Å on the equator and near 7 Å polar. The exact x-ray patterns in either form vary somewhat, depending on the composition of the peptide and particularly on the crystallinity of the sample. Several recent reviews cover the subject well (2231, 1930, 122). Some help in understanding the x-ray diagrams may be found in Happey's chapter in *X-ray Diffraction of Polycrystalline Materials* (871).

The fibrous proteins from hair, quills, silk, feathers, etc., generally exist in one of these forms (α or β), and all have the same general properties. As might be expected, they show more variation, less crystallinity, and on the whole are more difficult to study, than the synthetic materials.

10.4.1 Structural Models—General. The development of today's models of protein structure had roughly four phases—the beginnings, the emphasis on H bonding, the assumption of the spiral form, and the deduction of nonintegral spirals. Each phase has made some use of H bonds, though H bonds were assigned roles of differing importance in the proposed models. Table 10-III summarizes some milestones in the development of α-keratin models, and Table 10-IV gives the criteria utilized by the principal investigators.

Criteria 1, 2, 3, and 6 of Table 10-IV as well as the use of *levo* configuration and parameters from simple compounds are now well substantiated. Criterion 5, as initially stated, probably went too far, though as yet there is not direct proof of the presence or lack of straight H bonds. The requirement may have to be restated in terms of the angles around the N and O atoms. Criterion 7 will then be decided also. Criterion 8 has a firm basis in Mizushima's work (see references 20 and 21 in our 883) but has not yet been fully demonstrated in actual proteins.

There are many other discussions of model structures. Pertinent reviews are those of Bragg, Kendrew, and Perutz (262), Robinson and Ambrose (1733), Donohue (536), and Pauling and Corey (1591a). Mizushima (1856) suggests a general mathematical approach to helical structures.

10.4.2 The α-Helix. The early proposals of protein structures served mainly as mental stimuli for later workers but individually failed under critical examination. We shall pass over these and describe the presently accepted model.

TABLE 10-III Principal Developments in α-Keratin Structural Models

YEAR	AUTHOR AND REFERENCE	BRAGG'S NOTATION[a]	GENERAL DESCRIPTION	REMARKS
1930	Astbury (73, 77, 78)	1–8–$\frac{1}{3}$	A chain—folded in two dimensions	First proposal of structure
1936	Mirsky and Pauling (1415)	—	—	First emphasis on H bond as a factor in protein structure
1937	Vasilu (2106 through *C.A.* 32, 8871^6; *C.A.* 34, 4397^3)		A spiral chain	First suggestion of spiral structure(?)
1943	Huggins (987, 988)	2–7–1	A zig-zag ribbon with **R**'s opposite; a two-residue spiral	First extensive search for structures based on average distances and angles from simple molecules. Some were discussed as early as 1937 (see his footnote 2). Apparently, first suggestion of nonintegral spirals (p. 211) —not emphasized or pursued.
1948	Simanouchi and Mizushima (1858)	2–7–1	A flat ribbon	Emphasized *trans* configuration of amide groups
1950–1951	Pauling, Corey, and Branson (1600, 1601)	3.6–13–1	3.6 residues/turn; N—H bonded to third successive residue, the α helix	Nonintegral spirals; 5.1 helix less favorable than 3.6 helix (1598)
		5.1–17–1	5.1 residues/turn; N—H bonded to fifth successive residue, γ helix	

[a] The three numbers represent, in order, the order of rotational symmetry, the number of atoms in the H bonded ring, and the fraction of H bondable groups actually bonded. Since the last number is 1 in all modern proposals, the symbols are often written without it; e.g., 2_7, 3.6_{13}, 5.1_{17}.

TABLE 10-IV Criteria Utilized by Principal Investigators of Protein Structure[a]

CRITERIA	Neurath (1498)	Huggins (982a, 987)	Mizushima (1425, 1858)	Bragg, Kendrew, and Perutz (262)	Pauling, Corey, and Branson (1601)	Robinson and Ambrose (883)
1. *Trans* amide group	Yes	Yes	Yes		Yes[b]	Yes
2. Planar amide group					Yes	Yes
3. Equivalent surroundings for like groups	Yes	Yes			Yes	Yes
4. Density of unit cell		As close-packed as possible				As close-packed as possible
5. Essentially linear H bonds formed		Yes(?)		Generally linear if possible	Up to 30° deviation[c]	Up to 30° deviation
6. All possible H bonds form				Favored structure with maximum H bonding but some had less than maximum	Yes	Yes
7. The O···H contact is on the ridge of electron density of the lone pair orbital						Yes
8. Rotation will produce a maximum number of staggered positions in covalent bonds						Yes

[a] All workers assumed *levo* configuration of the amide group and precise bond lengths and angles taken from simple molecules.

[b] Some structures for mixed *cis* and *trans* residues.

[c] See 444 for atomic models, with angle adjustable up to 20°. This same group described model atoms containing magnets to simulate the H bonding (356a).

In 1951, Pauling, Corey, and Branson (1601) made an outstanding advance which may be considered in two parts: the idea that α-proteins consist of nonintegral helical molecules, and a proposal for the specific structure of the helix. It is profitable to develop the two ideas separately, since they are not interdependent.

Using the amide group characteristics (Table 10-II), Pauling and co-workers presented detailed descriptions of two helices. One was subsequently discarded because it did not have close packing of the atoms and was judged unstable on theoretical grounds. In addition, no experimental evidence has been found for it. The other, 3.6_{13} or α-helix, is shown in Fig. 10-4. The left portion of the figure illustrates the generation of the helix and emphasizes the amide planarity. On the right is a drawing showing the H bonds to the third residue along the chain.

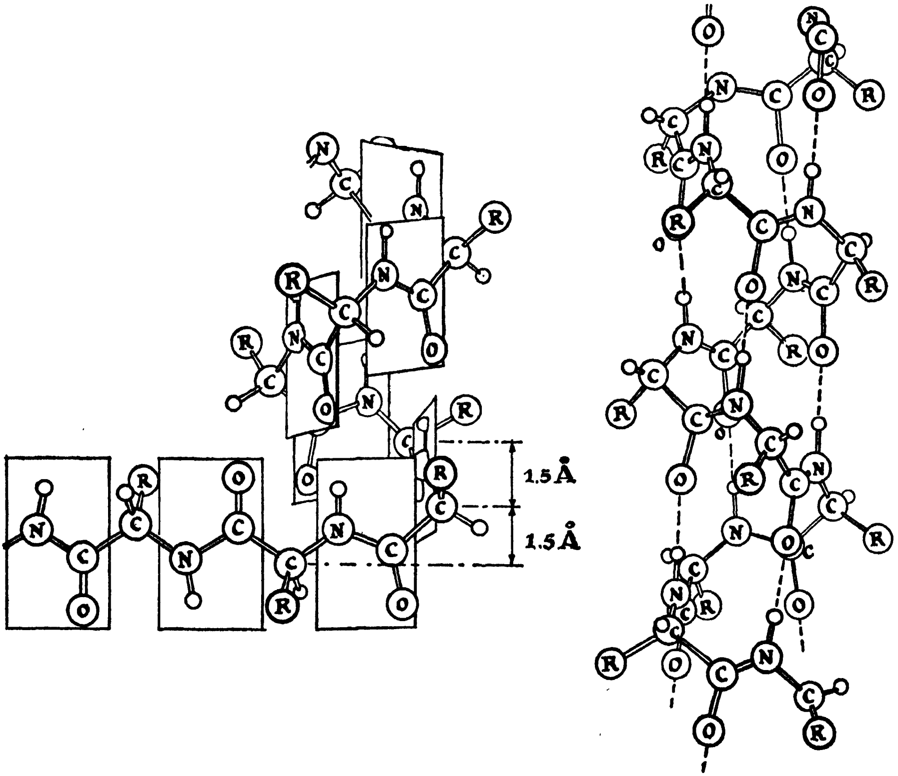

FIGURE 10-4 Two representations of the α-helix. Left, schematic view of formation emphasizing amide group planarity. Right, view showing H bonds. [From Corey and Pauling, *Proc. International Wool Textile Res. Conf. Australia*, **1955**, Vol B, 249–66.]

The two representations illustrate another point: the α-helix can be right- or left-handed, using *levo* residues. The spirals of opposite rotation are not mirror images.[a] Still another, somewhat idealized, representation of the α-helix can be used to show the important dimensional characteristics, as in Fig. 10-5.

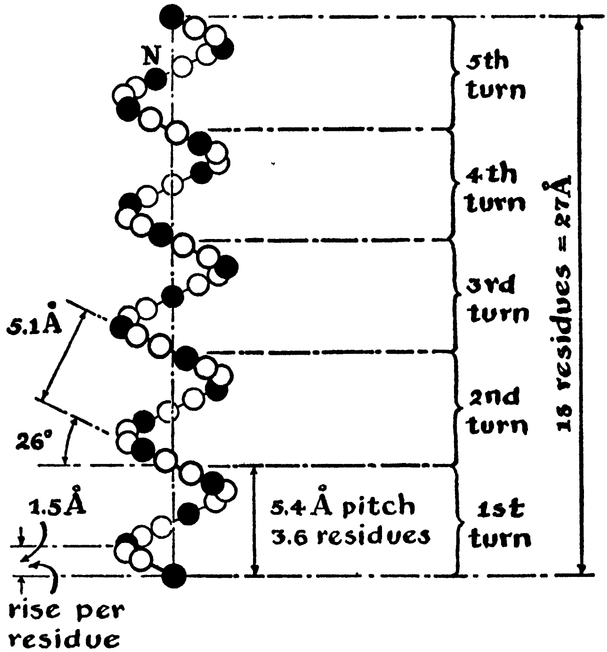

FIGURE 10-5 A schematic representation of the α-helix. The indicated dimensions are characteristic. [From Corey and Pauling, *Proc. International Wool Textile Res. Conf. Australia*, **1955**, Vol. B, 249–66.]

There were two specific triumphs of the nonintegral helical model. One was the correct prediction of a spacing (about 1.5 Å) in a region not normally observed. By tilting the fibers appropriately, Perutz found the 1.5 Å spacing (1613a), and it is now commonly reported. The other was to serve as a basis for the explanation of the x-ray diffraction pattern developed by Cochran, Crick, and Vand (405a). When the calculated values based on the α-helix were compared with Bamford's measured values for poly-α-methyl-L-glutamate, they agreed "in a striking manner."

One test that may be applied is matching this model against the prem-

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[a] Some of the early drawings of the α-helix show *dextro* residues. Neither the general representation nor the basic ideas are affected.

ises summarized in Tables 10-II and 10-IV. As can be seen in Table 10-II, the average values derived from the data in Table 10-I substantiate all the amide group parameters used by Pauling *et al.*, except the H bond length. The α-helix also meets a large fraction of the criteria in Table 10-IV.

The uncertainty in the H bond length (about 5 percent) would probably make an even smaller change in the helix parameters that provide the experimental check. Pauling computes 0.01 Å per residue change in helix length for 0.03 Å change in N—H···O. Thus, the question hinges on reliably distinguishing between 1.48 ±0.04 Å and 1.53 ±0.02 Å—not an easy matter with the techniques and samples available.

Nevertheless, the uncertainty directs attention to other proposals. These are of two kinds—the minor variations such as Pauling (1600) and Bamford *et al.* (121) found, and other, distinctly different helices. The first differ in having the number of residues per turn vary from 3.60 to 3.75. Such minor variations are not disturbing but probably reflect slight changes in the side groups, distortion of the helix, or disturbances caused by packing interferences from neighboring helices. Crick discussed these and other similar problems (461). However, Crick and others, such as Kendrew (1097a) and Edsall (579), give ample evidence of the general proof and acceptance of the α-helix, particularly for synthetic polypeptides.

The α-helix (3.6_{13}) is not the only nonintegral spiral model. At least five others have been proposed: 2.2_7, 3.6_{11}, 4.3_{14}, 4.4_{16} (π-helix), 5.1_{17} (γ-helix). Donohue (536) discusses all of these and ranks them in stability order 3.6_{13} (α), 4.4_{16} (π) and 2.2_7, 5.1_{17} (γ), 4.3_{14}, 3.6_{11}. The first three are very nearly equivalent in energy. Robinson and Ambrose (1733) carried out a somewhat different comparison, using integral spirals and the α-helix. They find the α-helix and a 2_7 model to be almost equivalent.

Something of the close relationship between various helices can be seen from Crick's description (461) of starting to build a model as a π-helix (1262) then, by omitting *one* H bond, changing to an α-helix. Crick suggests that this unmade bond may "move" up and down the chain in much the same manner as a "hole" moves in a crystal. In a polypeptide chain, presumably the most stable of all possible arrangements would eventually be achieved by such "movement." In a protein, the presence of cross-links and side chain interactions may cause more than one type of helix to be present and stabilized within a single molecule. Lindley (1236), using models and an *assumed* order of residues, showed how the α-helix could be folded 180°, modified to include proline, or have its spiral "handedness" changed in either direction. Some main H bonds were omitted, but the inclusion of side chain groups in the H bond network supposedly reestablished stability. These ideas, if proved and extended, will be useful in other structural models.

We may conclude that the α-helix is largely correct and that it is generally accepted. The remaining doubt about its uniqueness is not surprising in view of the molecular complexity involved, and there is no substantial body of evidence grossly contradicting the model. For natural proteins it describes only the main chain. Since it does not include the side chain interactions, some variations or minor discrepancies are to be expected.

10.4.3 α- and β-Keratin. The idea that natural keratin proteins have nonintegral helices, whether they are α-helices or some other, now has no opposition. The remaining problems, still far from insignificant, deal with the specific arrangement and interaction of the helices. It quickly became clear that the simple α-helix did not suffice. The 5.4 Å spacing of the α-helix is not found in keratin, but there is a strong 5.1 Å spacing. Crick (461a) pointed the way out of this impasse by suggesting

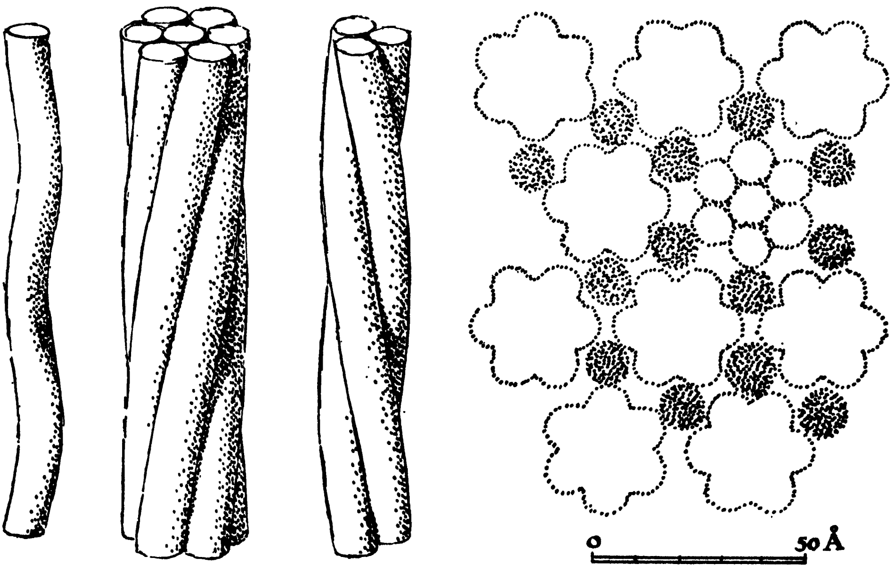


FIGURE 10-6 Schematic views of compound helices and their packing. Left, a coiled coil, seven-strand cable and three-strand rope; right, packing diagram for coils and cables in α-keratin. [From Corey and Pauling, *Proc. International Wool Textile Res. Conf. Australia*, **1955**, Vol. B, 249–66.]

that the α-helix itself takes a coiled form. Pauling and Corey (1595) extended this idea, visualizing a seven-strand cable and a three-strand rope. The pitch of the coiled α-helix was adjusted to explain the 5.1 Å reflection, and the x-ray pattern of α-keratin was then reasonably well duplicated by the model shown in Fig. 10-6.

The experimental data on α-keratin from various sources seems in general agreement with this model. Synthetic polypeptides fit fairly well, but confirmation is not as certain for natural products because they usually give poorer x-ray diagrams with fewer arcs or spots, and these are not as well defined.

The β form of keratin requires still additional models. And, continuing the order of decreasing certainty, these models are again less well corroborated by experimental observations than are the α-helix or α-keratin structures. Pauling and Corey (1598) presented the "pleated sheets" to explain β-keratins. These sheets are made up of extended peptide chains H bonded essentially side by side. Two are shown in Fig. 10-7.

In another paper, Pauling and Corey (1592) modified the two sheets slightly to achieve linear H bonds and give 7.0 Å (antiparallel sheet) and 6.5 Å (parallel sheet) as the repeat distances along the chains. The other major spacings of β-keratin are explained as the distance between chains (4.6 Å) and the distance between sheets (10 Å).

Fibroin from commercial (*Bombyx mori*) and wild (*tussah*) silk has been studied by x-rays (1341a,b), and both types have been shown to contain the antiparallel sheets. The two types are not exactly alike because the sheets are stacked differently—a result of the composition. *Bombyx mori* is almost one-half glycine residues, and its pleated sheet is composed of chains which alternate glycine with other residues (largely alanine and serine). As a consequence, the sheet has a "front" and a "back," with the methyl side groups on the back. The sheets stack in pairs front to front and back to back such that two spacings, 3.5 Å and 5.7 Å, are observed. Tussah silk, on the other hand, is only one-fourth glycine. There are too many side chains to be entirely accommodated on one side, so the sheet formed has groups on both sides. Hence, there is no front or back; and just one intersheet spacing, 5.3 Å, is observed. Pauling and Corey comment that the 5.3 Å spacing is not to be expected throughout the sheet because it will not provide room for the large groups (tyrosine, 4.9 percent). Therefore, the structures for both silks are pseudo-structures. This same feature will be present in other proteins and, depending on the type and percentage of the side groups, may make x-ray data difficult to reconcile with the basic models.

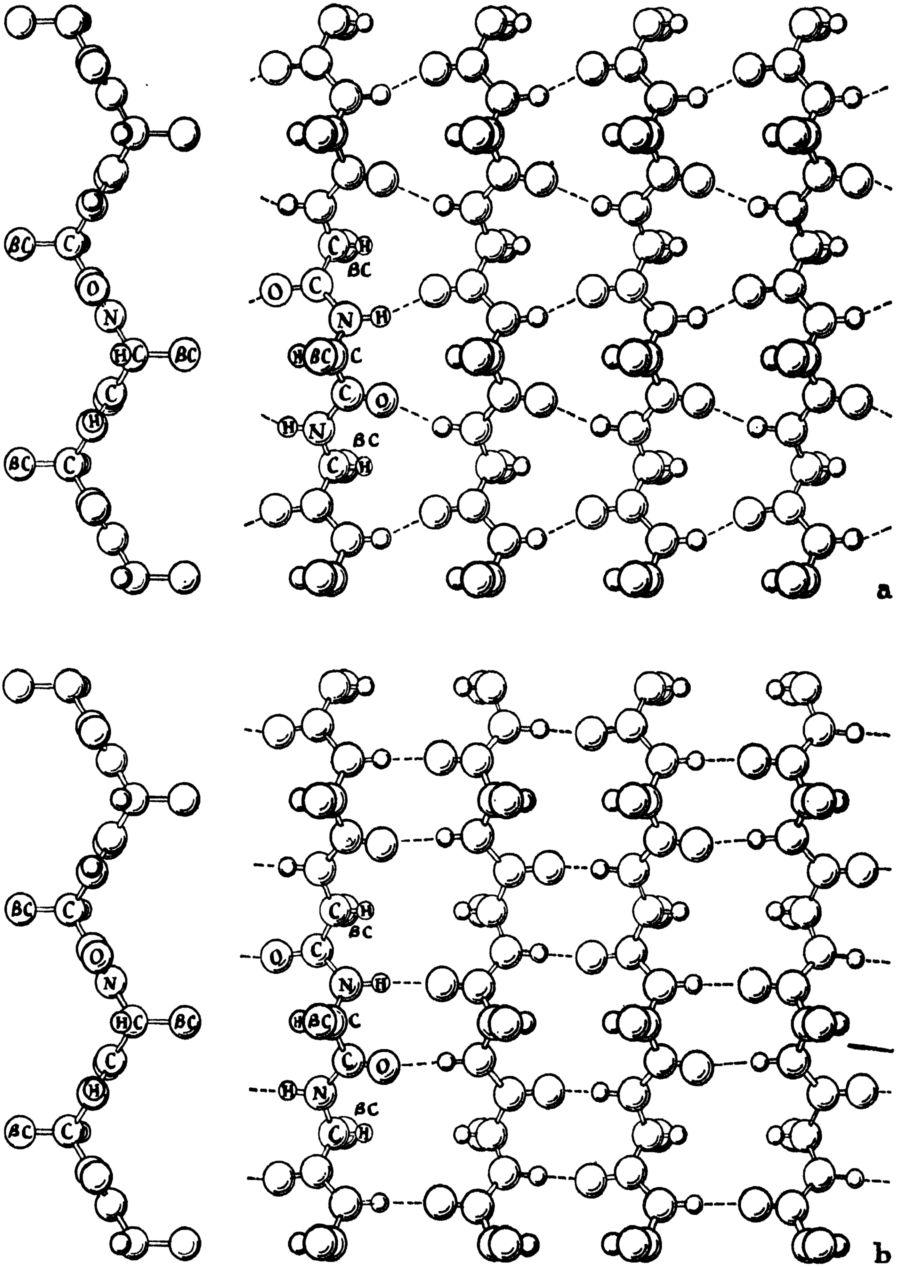


FIGURE 10-7 Pleated sheet structures proposed for β-keratin. (a) The parallel-chain pleated sheet. (b) The antiparallel-chain pleated sheet. [From Pauling and Corey, *Proc. Natl. Acad. Sci. U.S.* 37, 729–40 (1951).]

β-Poly-L-alanine (121) also has a pleated sheet structure. Pauling and Corey (1599) suggested a picture of the α- to β-keratin transformation in which each sheet forms a double row of α-helices. The model is not yet experimentally proven, but it gives the correct calculated extension.

10.4.4 Thermodynamics. There are some important lines of attack which have not been adequately applied to these models. One, the use of the thermodynamics of H bond formation, is generally hampered by lack of data. See, however, Speakman (1925), who gives 20 kcal as the energy of activation for $\alpha \longrightarrow \beta$ transition in the 15–20°C region, and Bamford, Elliott, and Hanby, *Polypeptides* (122, pp. 137–140).

Also, Schellman's work is pertinent (1809). From studies on heats of dilution of urea in water he concludes that the N—H···O=C bond has an enthalpy of 1.5 kcal/mole in aqueous solution, and he carries this value over to proteins and polypeptides. Among these complicated materials he is forced to approximate—but he deduces relations which show the stability of helices and sheets in terms of H bond enthalpy and configurational entropy. From this he draws the important conclusion that "H bonds, taken by themselves, give a marginal stability to ordered structures which may be enhanced or disrupted by the interactions of the side chains." Schellman ends his papers with a discussion of experimental tests needed to eliminate some of the assumptions in his theoretical analysis.

The change in H bond energy as a function of linearity has not received theoretical or empirical treatment. Since α-keratin may have variable arrangements of atoms or bond orientations, the linearity of H bonds will probably vary somewhat. The extent and importance of H bond linearity remains to be determined.

An interesting series on another aspect of protein H bonds is that by Laskowski and Scheraga (1196, 1969, 1195). They deal with H bonds in side chains and, in the first reference, present an orderly classification of H bonds based on type and number of interacting groups, including ionized groups as one possible partner in the H bond. Another unusual (though not unique) suggestion is the assumption of single H bonds between two carboxyl groups. Their equations show that a donor group cannot ionize as readily when H bonded as it can when free. This is the general behavior noted in Section 5.3.6. Corresponding, but opposite, behavior is found for acceptor groups.

Laskowski and Scheraga make another contribution in their consideration of several ways by which H bonding might affect ionization. These cases are too specific to discuss here, but they do provide steps leading toward the unraveling of equilibria in H bond networks. Their methods might be profitably tried on simpler ionizing systems.

All of this work on H bonds in *side chains* emphasizes the importance of this aspect of protein structure. In spite of the astounding progress in describing peptide helices, the biochemist often feels that the models too lightly dismiss the side chains. About half the atoms (other than hydrogen) are outside the helical "backbone" and have considerable influence on both physical and biological behavior. Laskowski and Scheraga refer to some of the previous work which is meager and not codified to the extent of the structural models.

10.4.5 Still More Complicated Structures. We will next mention a few of the postulated models for insulin and some of the other proteins, then discuss nucleic acids.

Insulin. As mentioned previously, insulin is one of the few biologically interesting compounds for which a full chemical structure is known. By using this knowledge, which is not available in other cases, Lindley and Rollett (1237) could build a more exact model which included H bonds in the side chains and which changed from right- to left-handed spirals in the main chains.

Other information on H bonding in insulin comes from D_2O exchange work. Linderstrøm-Lang has been the chief exponent of the exchange technique, and he has reviewed his findings recently (1235). Perhaps the most interesting result is the location of the exchangeable hydrogens in insulin. They are almost all "outside" the two cystine bridges—and these data support the idea that between the sulfur cross-links the two peptide chains are coiled more or less permanently. Without a "free end" to unravel, three H bonds must break simultaneously—at a high cost in energy.

Fibrous Proteins. Collagen is a fibrous structural protein found in tendons, skin, and bones. Gelatin is similar to collagen. In contrast to the proteins in the k-m-e-f group (keratin-myosin-epidermin-fibrogen), fibrous proteins have a high fraction ($\frac{1}{3}$) of proline or hydroxyproline residues. These cyclic residues introduce a special problem in structural models because (1) they have no hydrogen to H bond; (2) they introduce a stiffness to the spiral backbone; and (3) they cannot be accommodated in the α-helix. Astbury and Bell (75) offered a structure which fits the x-ray data, and they noted the presence of *cis* amide groups but did not discuss H bonding. Pauling and Corey (1599) put forward a three-chain helix which has successively two *cis* then one *trans* residue in each chain. The proline residues are to the outside of the cylinder formed by the chains. Finally, they suggested that the cylinders are arranged in hexagonal symmetry in an animal fiber.

Ambrose and Elliott (34) proposed a simpler spiral model that was similar to those suggested for keratin. Their model explained the IR dichroism (which Pauling and Corey's did not), but it had nonplanar amide groups. Randall, Fraser, and North (1686) reviewed these models briefly and added another which had some similarity to Ambrose and Elliott's. Huggins (984) suggested yet another arrangement—a single strand, low pitch helix of 30 residues in three turns. The matter is not settled, and various modifications are still appearing (1712, 449).

Globular Proteins. Despite their importance, globular proteins are not as thoroughly studied as fibrous ones. They include, for example, albumin and hemoglobin. There have been some suggestions which, with one exception, have involved H bonds. This exception, Wrinch's cyclol theory (see, for example, 2202–2204), is of only passing interest, but its lack of conformity with the observed H bonding (as indicated by IR spectra) was one factor in its rejection. See 1602 for a criticism of the cyclol theory.

Pauling and Corey (1599) made the point that under certain conditions globular proteins can be converted to forms similar to β-keratin, and on this basis they proposed the α-helix as a basic feature in the structure. Perutz's x-ray work (256, 1614) shows that parts of horse hemoglobin may have this structure. Ambrose and Elliott (35) present some IR work on globular proteins in a paper which particularly stresses the functions of H bonds.

10.5 Nucleic Acids

Nucleic acids constitute another vital class of compounds. They have received particular attention because of their presence in viruses and because of the part they play in reproduction, "gene carrying," and the growth process.

Pauling and Corey (1593) suggested the first really precise model—a helical one in which three chains, each composed of sugar, phosphate ion, and purine or pyrimidine groups, wind around the axis to produce a roughly cylindrical molecule. The phosphates form the core with H bonds and sugar (ribofuranose) rings connecting them. The purine or pyrimidine rings are attached at the outer part of the sugars. Watson and Crick (2144) proposed a different, H bonded, model for deoxyribose nucleic acid (DNA) which apparently fits the experimental facts a bit better. It is shown diagrammatically in Fig. 10-8.

In Fig. 10-8 the spiraling ribbons represent sugar-phosphate chains and the bars represent pairs of bases H bonding the chains together. Each base is a purine or pyrimidine analogue and contains H bonding acid and base groups such that the pair is held by two or more H bonds (see Fig. 10-9). There is, in effect, an "empty" spiral position. The chains are similar to those proposed earlier by Furberg (730a), but the base pairs joining the double spiral are unique. There are geometrical restrictions, due to the necessity to form H bonds; the result is an ordering of the succession of bases such that proper pairing results. Donohue has shown (535) that there are other possible combinations with less stringent requirements but still not allowing random order. All of the models, however, incorporate about the same H bonding structural parameters: the cyclic bases are essentially coplanar; the N—H···O and N—H···N distances are equal to 2.85 Å and 3.00 Å; and the H bonds are linear within 15°. For example, Pauling and Corey used 2.80 Å (N—H···O) and 3.00 Å (N—H···N) on the basis of the data then available (1591). They allowed some bond length adjustment in order that three H bonds could form, as seen in Fig. 10-9. The additional bond is thought to increase the specificity of pairing suggested by Watson and Crick.

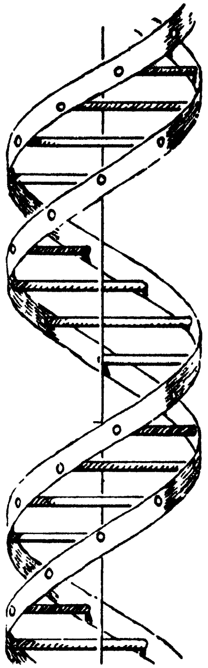


FIGURE 10-8 Diagrammatic structure of DNA according to Watson and Crick. [From *Nature* **171,** 737–8 (1953).]

We have collected in Table 10-V relevant data for crystals of pyrimidines and purines. The small number of values of the N—H···O distance average at 2.82 Å, in good agreement with the model estimates used. The average for the N—H···N bond length, 3.09 Å, is more reliably established and indicates that the model estimates are too small by about 0.10 Å. Nevertheless, the discrepancy is not large and, in total, the work cited tends to confirm Watson and Crick's proposal. Other confirmation comes from Alexander and Stacey's light scattering data (23) on ribonucleic acid (which are consistent with a two-strand model) and IR results on DNA when hydrated with regular or heavy water

(1212a). Rich and Davies (1713) suggested the double spiral structure for ribonucleic acid (RNA). None of these structures is proved yet.

Before leaving this class of compounds we might mention another paper by Watson and Crick (2143) and one by Overend and Peacocke (1560). These workers propose that H bonding plays a role in the genetic duplication of nucleic acids. The Watson and Crick model has some features difficult to reconcile with experiment or intuition, but it seems clear that H bonds and the processes by which they are formed are links in the character-determining chemicals of living matter.

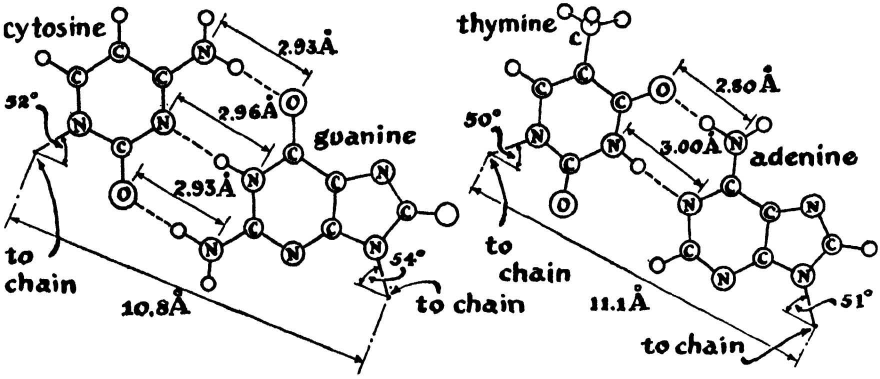


FIGURE 10-9 H bonding of purine and pyrimidine bases in nucleic acids. Left, cytosine and guanine. Right, thymine and adenine. [From Pauling and Corey, *Arch. Biochem. and Biophys.* **65**, 164–81 (1956).]

10.6 Denaturation and Other Topics

According to Webster, denaturation means the loss of original properties. This definition gives the word a large semantic burden. An interpretive rather than an operational approach is taken by Kauzmann (1091a) and by Wu as quoted there. *Denaturation* is the disorganization of the natural protein structure by rupture of the vital *intra*molecular bonds that stabilize it. This definition is in accord with the earlier interpretation of denaturation by Mirsky and Pauling (1415) in which they emphasized the key role of the H bond in protein reactions. They reviewed the behavior of native and denatured proteins and discussed proposed molecular changes responsible for it.

Denaturation may cause any of the following properties to change: solubility, biological activity, molecular size and shape, or susceptibility

TABLE 10-V H Bond Lengths in Pyrimidines, Purines, and Similar Compounds

	LENGTH OF H BOND (Å)		
COMPOUND	N—H···O	N—H···N	REFS.
5-Bromo-4,6-diaminopyrimidine		2.96 3.07	1591
2,5-Diamino-4-mercapto-6-methylpyrimidine		2.97	1353a
Adenine·HCl·½H_2O		2.99	1591
5-Aminotetrazole·N_2H_4 (bond between ring N atoms)		3.00	308
2-Methyl-5-aminotetrazole		3.04 3.08	308a
4-Amino-2,6-dichloropyrimidine		3.09 3.28	1591
4,5-Diamino-2-chloropyrimidine		3.11 3.16	2169
2-Amino-4,6-dichloropyrimidine		3.21 3.37	1591
Guanine·HCl·H_2O	2.62	3.08	287
Xanthazol·H_2O	2.74 2.82	2.90	1526
Theophylline	2.76		1975a
Uracil	2.81 2.86		1591
6-Amino-3-pyridazone	2.84 2.92		466
5′-Bromo-5′-deoxythymidine	2.8 (Form B) 2.9 (Form A)		975a
Cytidine	2.93		731
AVERAGE	2.82	3.09	

to enzymatic reactions. Clearly, there are various kinds and degrees of denaturation. Kauzmann's review gives extensive references (1091a).

It seems definite that denaturation of proteins and nucleic acids does depend on the *intra*molecular H bonds which are partly responsible for the structure. Apparently a critical number of H bonds must be broken before the irreversible denaturation occurs. Cox and Peacocke (455) present a simplified mathematical attack on denaturation which may have promise. They use a statistical method of finding the number of

H bonds (in sequence) which must be broken simultaneously for a DNA molecule to denature. Calculated values are small (10–50), compared to the total number of H bonds present per molecule (~20,000).

Kauzmann lists some $-\Delta H$ and $-\Delta S$ values for denaturation. Their range is 60–150 kcal/mole and 200–400 e.u. for several proteins. The entropy change is very large, hence denaturation involves a gross gain of entropy in a series of many small increments. In many instances the molecule cannot return to the previous orderly arrangement, and irreversible denaturation is observed.

Heat and titration with acid can accomplish the required H bond ruptures. Cavalieri and Rosenberg (358) have described this process, and they illustrate how it relates to the Watson and Crick structure for nucleic acids. They show further that the temperature required in an H bonding solvent is lower than in inert solvent, consequently these two factors can work in the same direction. Denaturation may also occur by ionization of amino groups (23), and the effect of radiation on DNA has been imputed to breaking of H bonds (454, 2147a). Mechanical stress may be able to break H bonds and denature proteins (1105).

Solubility, as well as the possibly related phenomenon of swelling, depends on the H bonding character of the solvent (or swelling agent). Indeed, the effect is not limited to proteins but also occurs for gelatin, cellulose, wood (1495), nylons, and probably for clays and other colloidal systems as well. Lloyd and co-workers discuss solubility and swelling of protein fibers (1250) (see, in fact, that entire discussion on swelling, 1252).

Brief mention should be made of some of the other biochemical areas in which H bonds are potentially important. Emphasizing the brevity of our list, we suggest: enzymes (1499); genetic duplication (2143, 1928); antibodies and their proposed "lock and key" structure (1584, 1511); surfaces, either within the cell or outside it (378); optical rotation of helical molecules (2216, 547); the steroid complexes recently proposed by Rich and Blow (1711b). See Chapter 11, where some of these topics are discussed.

10.7 Conclusion

The geometrical description of a peptide group, the basic structural element of proteins, is well defined (see Table 10-II). The length N—H···O is now well substantiated (2.94 Å), whereas the angles about O and N atoms are poorly characterized and the degree of linearity of the H bond is almost unknown. Bond lengths and angles found in the peptide group have been used in proposing helical structures which fit most of the properties of the backbone chain in crystalline proteins and DNA and establish the importance of H bonds. The side chains in these substances and globular proteins in general are represented by only speculative arrangements which contain H bonds as important features.

CHAPTER **11**

Practical Systems Involving Hydrogen Bonding

> *. . . the most fruitful applications of hydrogen-bridge theory will be to a better understanding of the nature and behavior of complicated organic substances such as gels, proteins, starch, cellulose, sugars . . . haemoglobin and related substances.*[a]
>
> M. L. HUGGINS *Kodak Research Laboratories, 1936*

11.1 Introduction

With the descriptive matter in the preceding chapters as a background, the perceptive reader will not be surprised to find that much of the chemistry in his everyday life depends on H bonding. After all, our bodies themselves, as well as plant cellulose and animal protein which form a major part of our food, clothing, fuel, and shelters, are H bonded in nontrivial ways. Huggins' remarks (990) have been prophetic, and entire industries have been founded on the connecting and disconnecting of H bonds.

In this chapter we present, in most cursory fashion, discussions of some of these important examples of H bonding. In some cases we can augment remarks which were initially made as asides in previous chapters; however, we have made no attempt to be exhaustive in this survey. In general, we discuss those regions of technology in which the theories and properties of H bonds have found explicit use. The order is more or less random, but some attempt has been made to present first those uses in which the effects of H bonds are most clearly established.

[a] Quoted from *J. Organic Chem.* 1, 405 (1936).

11.2 Analytical Methods

The variations in physical properties caused by H bonds provide the basis for both identification and quantitative analysis. We have already described the use of spectra (Chapters 3 and 4) in the latter. Two other methods—chromatography and polarography—deserve comment. The first, with its general dependence on some kind of partition, was mentioned in Section 2.4.5 but will be treated in more detail here. The second usually involves *intra*molecular H bonds—see Chapter 5.

11.2.1 Chromatography. The rate of passage of a compound through a chromatographic column is partly determined by interaction between the compound and the adsorbent. Hydrogen bonding is one form of this interaction. Strongly bound compounds move more slowly than similar species that do not interact with the adsorbent. Jennen (1038) and Le Rosen, *et al.* (1216), reviewed the influence of H bonds on solid-liquid chromatographic systems, and several recent books mention it (see, for example, 1205). Le Rosen developed a semiquantitative method for calculating the rate of movement in the column. He shows that consideration of only electron interaction and H bonding gives adequate treatment. Agreement is good, and the author recognizes the empirical nature of his development. In a later paper (1458) Le Rosen reviews other evidence of H bonds in chromatography.

Some typical trends can be illustrated with data from Schroeder (1816)—Table 11-I.

Similar trends for hydroxyacetophenones were reported by Hoyer (968–971).

Kay and Trueblood (1093) discuss the role of water in developing the column, and conclude that water is necessary in some cases to act as a H bonding link between the silicic acid and compounds such as alcohols and organic acids. The variation in different samples of silicic acid has been related to the amount of "bound" water present and its formation of H bondable sites (2036). See also 1032, 1215, 1545.

In some cases of gas-liquid partition chromatography, as well as in the solid-liquid type just discussed, H bonds have been proposed as an important factor in achieving some separations. James (1031) describes successive passage through columns having stationary phases of differing H bond properties to separate 15 aliphatic amines. James, Martin, and Smith (1033) also effected separation of some amines by changing the liquid composition. Bradford, Harvey, and Chalkley (257, 884) used a similar method to separate unsaturated hydrocarbons. In this case, the

TABLE 11-I Effect of H Bonding on Relative Adsorption Affinity for Silicic Acid

COMPOUND	RELATIVE ADSORPTION AFFINITY	REMARKS
Group A[a]		
Diphenylamine	1 (lowest affinity)	Not a strong proton donor
2-Nitrodiphenylamine	2	*Intra*molecular H bond keeps affinity for silicic acid low
4-Nitrodiphenylamine	10	Nitro group free to act as base for Si—O—H···O
Group B[a]		
N,*N*-Diphenylurethane	1	Increasingly more acidic hydrogens available and probably less steric hindrance
N,*N*-Diphenylformamide	5	
1,1-Diphenylurea	11	

[a] The affinity ratings apply only within the groups as shown.

stationary phase is a polar compound which H bonds to the double bond.

Similar considerations more than likely hold for other oxide surfaces or cellulose (paper chromatography) (6), but these systems have not been studied as exhaustively.

11.2.2 Polarography and Some Miscellaneous Tests. *Intra*molecular H bonding generally makes the reduction of a reactive group easier; consequently the internal bond will influence polarograms. Scaramelli has an early series on hydroxy aromatic aldehydes (1798–1800). Astle studied hydroxy nitro aromatics (81, 80), as did Seagers and Elving (1821). E. C. Wagner and collaborators studied amidines (1759) and nitroacetanilides (1760). Wagner's first paper is of more than routine interest since it reports a test of Hunter's conclusions based on his mesohydric tautomerism theory (see 1004, 1006, and our Chapters 2 and 8). According to Wagner, an *intra*molecular influence *may* cause a hydrogen atom or double bond to be less mobile in one tautomer and hence allow some detection. From the fact that *N*-phenyl-*N'*-*o*-nitrophenylacetamidine is reduced much easier than is the corresponding *meta* and *para* isomers, these authors conclude that a degree of stabilization occurred for the *ortho* compound. Catalytic hydrogenation confirmed the greater reducibility of the *intra*molecular H bonded *ortho* compound. Similar results were obtained for the nitroacetanilides. Astle (79) reviewed the role of H bonds in polarographic analysis. To date, polarography of compounds other than aromatics has, in general, been ignored.

A specific test for *intra*molecular H bonds in aromatics was proposed (1610), but it has not been followed up. Neither has the suggestion for an analytical D_2O/H_2O determination depending on the difference in upper and lower consolute temperatures caused by H bonds (46). Also among the unproved tests is a qualitative one for classifying organic substances by functional group (1922). This test depends on promotion or inhibition of the formation of an unknown complex in the system ferric chloride-propyl gallate-chloroaniline and its behavior with temperature. In that reference (1922) the possible function of H bonds is discussed. The classification according to this test agrees fairly well with grading by the system given in Table 2-IX. Generally, compounds of Class A promote complex formation, Class B materials inhibit it, and Class N compounds have no effect on it.

11.3 Fibers and Fiber Networks

11.3.1 Molecular Structure of the Fiber. The internal H bonded structures of several kinds of protein fibers were discussed in Chapter 10, and a few comments here on other substances will complete our treatment.

Another major type of natural fiber has cellulose as its main component. Cotton, flax, ramie, various hemps, and jute are the most common cellulosic materials used in making string, rope, or cloth of various weights. Wood and the many grasses are other important natural products with a high cellulose content. Any of the books on the subject will amplify the sources, preparation, and use of cellulose.

Cellulose is made up of saccharide units polymerized in chains containing many O—H groups and —O— links. X-ray diffraction and IR spectra show H bonds in these chains. Mark (1337) describes the evidence for H bonds in the *ab* plane of "native cellulose" ("Cellulose I"). The crystal modification called "regenerated or hydrated cellulose" ("Cellulose II") is shown to have a different arrangement of H bonds. The two forms may be interconverted. There are further modifications, some hydrated, which are less well studied but which apparently are minor variations of Celluloses I and II (961).

Ellis and Bath (603) offer confirming evidence in their IR spectra which show O—H lines shifted to lower frequencies—a distinct indication of H bonding. As do other H bonded substances, cellulose and its derivatives have solubility values that are determined by the H bonding ability of the solvent and which are perhaps modified or opposed by the interchain binding. Thus, water does not dissolve cellulose because cellulose is H bonded so completely in its prevalent crystalline regions. Rowen and Plyler (1750) offer IR evidence for their proposal that the crystalline regions contain four-membered "dimer" rings whereas the amorphous sections have single H bonds and some nonbonded hydrogen atoms—see Fig. 11-1.

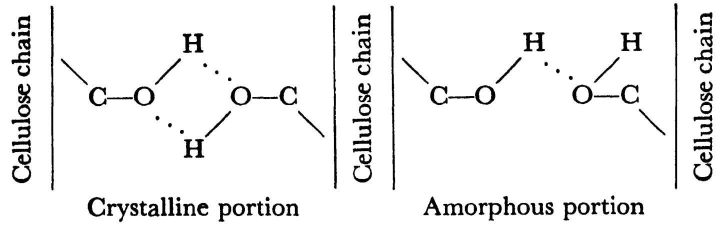


FIGURE 11-1 Proposed H bonding in cellulose. From Rowen and Plyler, *J. Research Natl. Bur. Standards.* **44,** 313–20 (1950).

Although he is less specific about the exact form of the H bonding, Mark agrees that it is a main feature of the crystalline regions.

This same four-membered ring has been proposed for simpler compounds. See, for example, the work on methanol (2098, 181), water (2097), and silanils (1079). The presence of this small ring, if it can be confirmed, will bear on the discussions of H bond linearity mentioned previously (Section 3.3.6).

A start has been made toward solving the structural problems of crystalline cellulose by the same method as that used for proteins. Jones (1046a) gave a set of criteria quite similar to that in Table 10-IV; namely, (a) the sugar residues have standard bond lengths and angles, (b) all the O—H groups are H bonded with C—O···O between 100° and 135°, and, (c) the residues are screw related. This paper also contains a helpful review of previous work on model cellulose structures.

The third principal type of fibrous materials comprises the synthetic polymers. Unlike natural fibers, which apparently are always H bonded, some synthetic fibers are not H bonded. The polyamides form the best example of man-made H bonded polymers. These include nylons or polyamides, polyamino acids, polythioamides, polyurethanes, and some less well known polymers of substituted urea, hydrazide, aminotriazole, sulfonamide, or others. Specialized reference books are available (954).

There are many articles treating the polyamides, but only a few need be mentioned. Brill (280) and Champetier (363) present reviews of some properties and their dependence on H bonding. (See our Section 2.3 for some rebuttal.) Bunn and co-workers (947), as well as Korshak and Frunze (1133), feel that the number of amide groups (per 100 carbons) and whether an odd or even number of —CH_2— intervene are the principal determinants of many properties. The melting point, elasticity, tensile strength, crystallinity, and solubility characteristics are some of the properties affected by H bonds. Mark and Tobolsky (1339) refer to some of the original work. Baker and Fuller (116) show the effect of changing the number, arrangement, and orientation of H bonding groups in 31 polyamides and copolymers. Loss of H bonds through mismatching gives lower melting points and lower elasticity (see also 362). Lewis and Reynolds (1226) review the evidence that similar changes in properties result from interfering with H bonds by substituting alkyl (or other) groups for the amino hydrogen (115, 216, 2188). See also 1132 and 1775 for a theoretical treatment.

In addition to the part it plays in the structure of the fibers themselves, H bonding has a role of varying magnitude in determining the physical properties of products made from the fibers. Among these products we will discuss only paper, cloth, and leather.

11.3.2 Paper. Paper is a matted, dried mass of cellulose fibers derived from wood, cotton linters or, more rarely, sugar cane bagasse or other plant stalks. Related products are cardboard and sound-proofing material.

Broughton and James (290, 289) give a good discussion of the commercial formation of paper in terms of H bonds (or polar bonds) as the important links between the fibers. According to their concept (which is based in part on other work which they cite), the individual cellulose fibers, which are suspended in water, are forced together by a combination of pressure and surface tension as the stock dries. Surface tension is the more important, though Ivanov (1020) finds paper strength increased by the application of pressures up to 3000 lb/sq in. As the fibers come together H bonds form, and they increase as the water is removed. The resultant irregular network of interfiber bonds is responsible for the flexibility and elasticity of paper.

By testing strips saturated with various liquids, Broughton and James showed that paper breaking strength is roughly proportional to the undisturbed H bond mesh. Table 11-II shows some of their data along with corresponding energy absorption capacities that may be considered as a measure of H bonding ability.

TABLE 11-II Breaking Strength of Paper Wet with Various Liquids

LIQUID	BREAKING STRENGTH[a] (lb/in.)	ENERGY ABSORPTION CAPACITY[a] (in.-lb)
Water	0.51	0.0063
Methanol	2.57	0.0200
Aniline	4.92	0.047
Dioxane	5.14	0.048
Diethyl ether	5.79	0.059
Acetone	6.36	0.061
Benzene	6.45	0.072
CCl_4	7.57	0.091
None	10.48	0.122

[a] Average of five specimens.

The correlation between breaking strength and energy absorption capacity is good. As a further test that no permanent disruption of fiber linking resulted from the liquids, some samples were soaked and redried. The average breaking strengths were within 10 percent of the original values for three liquids tested.

Corte and Schraschek (444a) used IR shifts on deuteration of cellulose to calculate binding energy in paper sheets. The values were of the proper order of magnitude but lower than experimental results. These authors also review the theories of paper strength and conclude that H bonds play a major part in it. Other workers (1788, 2225, 2224) have studied the same problem.

Kubát (1155) presented a review of agents used to soften paper, one class being those that operate by breaking interfiber H bonds. Hirst (933) mentioned the sizing of paper (and textiles) by various natural gums, and discussed briefly the mechanism of adhesion. Considering that the sources of many glues, gums, and mucilages are the same plant and animal parts that yield wood, paper, and cloth, it might be expected that H bonding occurs in glueing. Other workers (1309, 1310) showed that synthetic polymers adhere partly by H bonding. Again, it is well to remember that H bonding is probably only one part of the adhesion mechanism. Without giving specific references we suggest that paper dyeing, and perhaps colored printing, have certain facets in common with the dyeing of other forms of cellulose and that H bonds are probably involved.

11.3.3 Cloth. Cloth is a pliable fabric formed by weaving, knitting, or knotting threads of cellulose, protein, or synthetic polymers. It can range from the most delicate chiffon to heavy duty carpeting. In addition to the influence of H bonds in binding together the individual fibers, some of the treatments of cloth also depend on H bonds.

There is almost unanimous accord that H bonds help hold dye molecules and fiber molecules together. This is true particularly for the natural fibers in which there are more H bondable groups than are needed to hold the fiber together. The actual process of dyeing is a complex one involving H bonds in several of the steps. The dye must be dissolved or dispersed in a solvent which at least partly dissolves or "swells" the fibers (see 1931 for some aspects of H bonds in swelling cellulose) and carries the dye molecule in where it can cling to the substrate. Thus, there are probably at least three dynamic equilibria necessary between H bonds of various strengths. It is no wonder that heat of dyeing values do not represent directly H bond enthalpies, although these values are used as a rough guide (219, 2183). The practical aspects of dyeing are reviewed in Vickerstaff's book (2117) and by Happe (870, 869).

Some argument has revolved around the juxtapositioning of dye and fiber molecules, and for a time it was thought that the best structure of a dye would have a separation of H bonding units corresponding to that of cellulose (about 10.3 Å). Robinson (1732) used molecular models as evidence that this idea is not valid. Some of the diagrams of Robinson's paper are particularly instructive, and they illustrate clearly the rotational possibilities of molecules and the vast difference such rotation can make in H bonding. He also proposes that dyeing may be confined to the noncrystalline parts of a synthetic polypeptide where the less than perfect ordering of the backbone leaves more groups available to H bond (see also 1202 and our Fig. 11-1).

Perhaps the safest summary concerning dyeing is that H bonds are probably important, although the proof of this and the details of their operation remain largely undocumented.

Before leaving cloth we might mention some studies in which H bonds were postulated as affecting certain characteristics: texture (912, 1640, 2218, 427), elasticity and impact strength (785, 742, 2085), washing and washability (2020, 1810), oil repellency (598, 599).

11.3.4 Leather. Leather is animal skin that has been treated to produce pliancy and resistance to rotting. The tanning process by which leather is made is very old, but it is still not completely understood, mainly because the structure of animal skin is still unknown. In general, skin is polypeptide-containing collagen (see Section 10.4.5), but there are also present various amounts of keratin, reticulin, elastin, and water, plus other components such as carbohydrates, lipids, waxes, and triglycerides (1311).

Tanning, like dyeing, can be visualized as comprising several steps, some of which involve H bonds. Lollar and his colleagues (1244, 2058, 1245) have been active in gathering support for H bonds as a part of the tanning mechanism. In fact, they can relate the tanning achieved by a compound to its ability to form H bonds, provided the reacting molecule also has quinoid-like resonance. This latter factor explains why simple phenols and some other compounds (benzophenone) do not tan. Natural tannins have unknown structures but probably fit the requirements Lollar specifies. It is not surprising that leather dyeing may also depend on H bonding (1820).

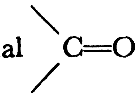
11.4 Industrial Processes and Products

A great many industrial products besides those mentioned in Sections 11.2 and 11.3 depend in some way on H bonds. For finished goods that require certain catalysts (hydrous metal oxides), color removal (by clay filtration), or flotation separation, adsorption influenced by H bonds is sometimes critical. Finally, some materials require H bonds to achieve or maintain their desired form or to carry out their functions; an example is the urea complexes used in separating paraffin hydrocarbons (110).

11.4.1 Adsorption. There is now ample evidence of H bonding in some adsorption systems, notably silica gels, mixed oxide gels (SiO_2-Al_2O_3, etc.), cellulose and protein solids, clays, and, strangely enough, perhaps carbon. Cassidy (2148) offers an excellent short discussion of this.

Silica gel surely presents a surface having many hydroxyl groups (1836 and references there; also 2017), as do other oxide gels if not treated too severely (Lindquist and Rea reported on Al_2O_3 at the September 1957 ACS meeting). However, only fairly recently has adsorption on these surfaces been interpreted in terms of H bonding. [But see Elder and Springer (585).] Most stimulation appears to be from IR measurements, which offer some promise of identifying the adsorbed species on SiO_2. The adsorbates studied include water (1300, 1507, 2217, 1634a, 89), alcohols [2226, 89, 1722 (area measurement, not IR)], amines (1816, 2220, 1506), and aromatic compounds (1300, 1112, 1730). In general, the IR bands behave as outlined in Chapter 3 for solutions; however, the spectra are modified in specific ways by each surface. There has been no definitive study as yet.

The adsorption of liquid ethyl alcohol on Al_2O_3 occurs by H bonding (1108), and without doubt other proton donors are similarly affected. Some part of adsorption from binary solutions (e.g. ethyl alcohol and benzene) is explained by the three-step process: alcohol H bonds to the surface, chemisorbs, and then the second component (and more alcohol) physically adsorb on this layer. (See Section 11.2.1 for a discussion of the similar action of water on silicic acid.) Such hydroxyl-covered surfaces are industrially important in cracking and other catalytic processes (2172, 956), and in drying. Plank and Drake (1646) discuss the influence of H bonds in the formation of such materials.

Most authorities feel that on carbon blacks, where the adsorption is largely physical, H bonds have the same importance they do in liquids. This approach to physical adsorption is the classical Brunauer-Emmett-Teller view of the adsorbed layer being essentially liquid (2123). Others suggest that H bonds to "surface oxides" or occasional  $>C{=}O$ groups are responsible (136, 557, and 556 which reviews some of the Russian work). The issue is not resolved, and perhaps both factors are present. Other materials which have been postulated as adsorbing on carbon blacks by H bonding are amines (516) and organic acids (225).

The effect of H bonded adsorbents on bentonite flocculation represents a less well studied case that has importance in flotation separation and oil well drilling (700).

Emerson published an interesting paper (608) on H bonds in organo-clay complexes. He defines two necessary conditions for H bonds: they must be linear, and they must be at the tetrahedral angle to the oxygen atom. Note that these conditions are the same as two of the criteria utilized for proteins (see Table 10-IV). If the surface oxygen is bonded nontetrahedrally to other atoms in the clay, H bonding is not favored. He gives calculated and experimental values as in Table 11-III. Superficially related to the expansion of clay in H bonding solvents are the changes in dimensions which occur when some ma-

TABLE 11-III The Influence of H Bonding on 001 Spacing in Organo-Clay Complexes

ORGANIC COMPOUND	CLAY	001 SPACING (Å)	
		EXPERIMENTAL	CALCULATED
Methanol	Montmorillonite	12.1[a]	12.7
Methanol	Halloysite	10.6	10.5
Propanol-heptanol	Montmorillonite	13.6	13.6
Methylamine	Montmorillonite	12.7	12.7

[a] Experimental data is questioned by Emerson.

terials adsorb on carbon black. Some of this effect is probably the result of H bonding (1178).

11.4.2 Coal, Lubricating Grease, and Other Products. Only in the most cursory fashion have H bonds been studied in many commercial fields. Without attempting a complete or exhaustive account, we will mention some of these fields.

In coal, and in the related lignites, H bonds between phenolic OH (and possibly COOH) groups are clearly indicated in IR spectra, and apparently they are a factor in determining coal structure (301, 300, 1572). This spectral band forms part of an analysis scheme suggested by Friedel and Queiser (719). Further, some improvement in compression strength of lignite briquettes can be achieved by forming them in H bonding liquids (1021).

A modern step in the formulation of some lubricating greases is the production of "complex" greases. Complex greases have an added nonsaponaceous component to provide greater gelling power or other desirable properties. The added materials are often H bondable—e.g., water, glycerol, acetate salts (41). Most greases are made from completely saponified materials, but aluminum based greases are an exception. The thickener is usually a mixture of mono-, di-, or trisoaps of Al. The first two compounds are H bonded (1840), and this may account for some of the problems that arise in making greases from them. Water can be determined in bentonite greases from the H bonded bands in the IR region (1403).

According to some workers, H bonds play a part in the formation of novolak resins (1929) and polyacrylic rubber (1829), and in the adhesion of rubber to rayon tire-cord (1125). Hydrogen bonds may be a factor in oil oxidation (149), which is of interest in the deterioration of motor oils, medicinal mineral oil, and painting quality linseed oil (915).

Purification of saline water by means of solvent extraction is being studied (951a). Amines especially tailored for the right H bonding properties are the most promising extraction solvents.

11.5 The Human Body

In Chapter 10 the molecular aspects of protein in several forms were discussed, and in Chapter 2 the interdependence of solubility, partition, adsorption, reaction rate and H bond formation in simple molecules was covered. Clearly, a large part of our body chemistry is a complex interplay of those factors intermingled with all the complicated chemical reactions that occur. Let us touch on some of these reactions briefly and refer to the extensive biological and physiological literature.

A key problem is the *in vivo* synthesis of chemicals such as proteins and nucleic acids with rigidly specific structures. Spiegelman (1928) gives a clear review. The "template" theory, which he favors, has ample opportunity for H bond participation. Enzyme action is also conceived as a template reaction (1584). In this case, somewhat less matching is needed, in comparison with the synthesis of genetic material. The enzyme and substrate need "fit" over only a fairly small percentage of their surface (50). Hydrogen bonds may help achieve this match and thus influence the specificity of the reaction.

Muscle action is a whole topic which we treat only by pointing out that the rapid, reversible contraction-relaxation reaction may depend on H bonding. The two proteins, actin and myosin, that combine in the presence of adenosine triphosphate to give the contraction are, of course, H bonded. Further, there is evidence for H bond formation and disruption during the muscle action (1806, 1013). Morales and Botts (1445) describe a possible "two-phase" model based on Hill's thermodynamic treatment. The two phases may be inter- and *intra*-chain H bonded forms of the myosin chains. See also Szent-Györgyi's outstanding work in this general field. Some interesting suggestions have been made that synthetic muscle systems involve H bonds (1675) as well as electrostatic interaction (1086).

In addition to the study of structural parts, there has been speculation about the role of H bonds in memory (982a), medicine (306, 819, 893, 1745, 1718), foods (464, 1561) and food production (1442, 1399, 1455).

This entire subject is a very difficult one because of the complex substances the human body contains. The peptides have been attacked via study of simple model compounds, and the techniques of polymer science are being used. The same approach may be useful for other types of compounds now that synthetic polyribonucleic acids and polyelectrolytes are being made. The latter include charged side chains and thus resemble biocolloidal molecules (1086).

In conclusion, it is a safe expectation that the H bond has a role of many aspects in the chemistry of living systems. This chemistry undoubtedly involves a most complex interweaving of strong and weak chemical bonds; surely the H bond will be found to be a prominent feature in that elegant pattern.

CHAPTER **12**

Looking Ahead

No single thing abides; but all things flow.
Fragment to fragment clings—the things thus grow
Until we know them and name them. By degrees
They melt, and are no more the things we know.

LUCRETIUS *De Rerum Natura*[a]

We shall conclude this book with a glance toward the future. This prophecy is guided by an examination of recent developments, as reported in the literature, in the light of the present status of our knowledge. We mention some experimental techniques which are particularly promising, and some new applications which are likely to become of increasing value. Finally, we speculate on the impact of the elucidation of the H bond interaction on current theories of the chemical bond.

12.1 Promising Experimental Techniques

12.1.1 Nuclear Magnetic Resonance. The NMR technique has demonstrated great sensitivity in studies of the H bond interaction. The potentiality of this method is emphasized by the large number of recent papers reporting NMR studies of H bonding. Although the significance of the direction and magnitude of the H bond chemical shift is not yet clear, certainly valuable information concerning the H bond electron distribution is contained in these data.

As a new tool, the NMR method opens another avenue of approach

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[a] From W. H. Mallock's translation, "Lucretius on Life and Death," 2nd ed., John Lane Co., 1910, New York.

to the study of H bond equilibria, the species present, and their thermodynamic properties. Because of the sensitivity of the technique it may be possible to extend this type of study to the weaker H bond systems. Possibly of unique value is the application of NMR methods to the determination of the rate of formation of H bonds. This should lead to a better understanding of the potential function for H bond formation. There is every reason to expect a growth in the use of NMR methods in H bond studies which will parallel that which we have seen for the IR method.

12.1.2 Location of Protons in Crystals. Both neutron diffraction and NMR band width measurements can give accurate information concerning the proton positions in crystals. There is prospect of the increased use of x-ray and electron diffraction methods for the same purpose, as refinements are developed (e.g., Fourier difference plots, thermal fluctuation analyses). Such data will indicate bond angles and distances between the atoms forming the H bond, and will aid in clarifying the role of the H bond as a factor determining crystal structure. They will also provide the basis for understanding the unusual dielectric properties of some crystals, such as the ferroelectric behavior of KH_2PO_4. Further, the results may influence present theories of hybridization and bond angles. When known, the positions of protons in H bonded crystals will present a most interesting aspect of crystal structures.

12.1.3 New Infrared Methods. Despite the volume of work to date, there are some areas of spectroscopic study which deserve mention here because of their promise. The determination of the low frequency modes of the H bond will yield direct information concerning the energy required to distort the H bond. Of course there could be no more useful data in predicting structures and thermodynamic properties of H bonded polymers. The current development of far-infrared instrumentation will accelerate study of these low frequency vibrations.

Equally promising, though more thoroughly explored, are the measurements of intensities and band shapes of IR bands. The unique spectral characteristics of H bonded substances bespeak interesting conclusions to come from such measurements. As in the NMR shifts, the intensities reveal details of electron distribution and mobility. Whether the band widths indicate anharmonicity of the low frequency modes is not yet clear, but low temperature studies will provide important clues to the proper interpretation. It is evident that the matrix isolation method has special possibilities and will be helpful.

Another type of IR measurement which should be mentioned is the study of IR dichroism. Such data are valuable in determining gross molecular conformation and, more important, they contain information about electron distributions and mobilities as interesting as that obtainable from intensities.

12.1.4 Raman Spectroscopy. The recent development of photoelectric recording Raman instruments should reawaken this type of study of the H bond. Of particular interest will be more complete examination of low frequency modes and the accumulation of information about Raman intensities of H bonded species.

12.1.5 Ultraviolet and Visible Spectroscopy. Spectroscopic examination of the electronic transitions of H bonded substances offers the novel prospect of revealing the H bonding properties of excited states. This is, in a sense, a means of determining chemical properties of excited molecules. Of course, UV and visible spectra have already shown usefulness in determining thermodynamics of H bond equilibria.

12.1.6 Dielectric Dispersion Measurements. Recent experimental and instrumental developments give promise of interesting results from measurements of dielectric dispersion. Examination of wider frequency ranges may elucidate the structures of H bonding liquids and solids, the electronic rearrangements in H bonds, and the activation energies for H bond formation and rupture.

12.2 Promising Applications

12.2.1 Kinetics. It seems likely that H bonding more commonly plays a role in fixing reaction mechanisms than is now realized. When H bonding groups are present in a reacting system the reaction may be affected by the formation of chelated configurations or by the intermolecular packing of H bonded aggregates of reactants or reactants and solvent. The evidence of Chapter 6 on the less well recognized H bond systems suggests that such effects may be more widespread than is realized. Whereas it may require an interaction energy of at least two or three kilocalories (at room temperature) to permit direct detection of H bonded species, still weaker interactions may influence the activated complex. For example, the C—H group in chloroform shows distinct H bonding properties, but apparently those in methyl chloroforms do not. However, there surely remains some tendency for H bonding in methyl chloroform, and it might be observed in kinetic processes because of the extreme sensitivity of the reaction rate to the activation energy. This same line of argument could be extended to C—H bonds in alkanes, aromatics, and olefins. Two of these, aromatics and olefins, also have the interesting possibility of acting as H bonding bases. Thus the orientation of approach of two reacting aromatics might be chiefly determined by the interaction of the weakly acidic C—H groups with the basic aromatic pi electrons. Indeed, the existence of such attractive orientations is already indicated by the packing in crystalline benzene and naphthalene. Instead of lying in a coplanar arrangement, as might be expected for flat molecules, each aromatic is tilted with reference to its neighbors such that the distance of closest approach is between C—H groups and the neighboring aromatic rings.

Of course the influence of the H bond on kinetic processes will be revealed most readily in cases of strong interaction involving the well recognized acid and base groups listed in Table 6-I (as already discussed in Section 5.3.8). For example, the sterols and alkaloids might be expected to demonstrate H bond reaction effects. These molecules have appropriate functional groups (e.g., carbonyls, hydroxyls, methoxyls, amine nitrogens) and also the skeletal flexibility to make possible *intra-* as well as intermolecular H bonded configurations.

12.2.2 Structures of Bio-organic Molecules. In view of the demonstrated importance of H bonds in fixing structures of proteins and nucleic acids, it is almost obvious that there will be an expanding recognition of H bonded molecular types in biologically important molecules. Surely it behooves every worker deducing structures of natural products to consider carefully the possibilities in which configuration is optimum for H bonding.

12.2.3 Chemical Processes in Living Systems. The importance of chelation in proteins almost implies that the H bond is important in the chemistry of formation of proteins. In a chemical process which brings together an amine and a carboxylic acid group it would be surprising if H bonding played no role. In fact, this interaction seems to be ideal for the types of chemical process which occur in nature. The H bond is strong enough relative to kT to hold a reacting molecule in a particular orientation while awaiting reaction with a suitably oriented counterpart. Then the energy of the new chemical bond is sufficiently large to displace the H bond. The orientational influence which the H bond might exert could be a major factor in the biosynthesis of the low entropy molecular species characteristic of living systems.

Additional clues to the possible importance of H bonding in chemical reactions in living systems lie in the rapid and reversible physical changes which occur. These changes bring to mind the rapid reversibility of H bond equilibria. For example, the contraction-relaxation cycle in muscle action might involve changes in molecular shape accompanying formation and rupture of H bonds. Perhaps the propagation of nerve impulses involves transfer of charge through H bond chains. It is even possible that memory action functions through information storage in H bonded configurations.

Whether or not these examples prove to be correct, we hope they are suggestive. It is certain that biological chemical processes are unique in at least two respects: many of the reactions are stereo-specific, and many of them are apparently rapidly reversible. Either of these features could well be realized through known properties of H bonded systems.

12.3 Possible Theoretical Developments

As we recognize additional chemical types which display the H bond interaction, we find that this interaction is important in an increasing segment of our chemical knowledge. With H bonding discernible for such weak acids as mercaptans, thiophenols, and halogen-substituted alkanes, and for such weak bases as aromatics, olefins, and thioethers, it becomes profitable to look for even weaker interactions which have properties in common with the H bond. Just such an example has already been mentioned in Section 12.2.1: the crystal structure of aromatics provides evidence of attractive interaction between the aromatic C—H protons and the pi electrons of adjacent molecules.

Of greater impact is evidence relating H bonds to chemical bonds now thought to be quite distinct in character. An example—the boranes—has been developed in some detail. Empirical evidence provides substantial basis for the conclusion that the borane bridge bond is a H bond insofar as operational criteria are concerned (see Section 6.5). This stimulates close scrutiny of the molecular orbital description of the H bond, a description which applies readily to the borane bridge bond (see Section 8.2.4). Even further, this description relates H bonds to interhalogen bonds, as was pointed out by Pimentel in his comparison of the molecular orbital descriptions of HF_2^- and I_3^- (1634). Person, Humphrey, and Popov (1613a) have since provided experimental evidence for just such a connection. They have related quantitatively the frequency shifts and intensity enhancements accompanying H bond formation to the exactly parallel behavior of halogen complexes with ICN. Thus we have a basis for favoring a theoretical framework which encompasses both orbital-deficient bonds (e.g., H bonds, polyhalogen bonds, Al_2Cl_6, halogen-ICN) and electron-deficient bonds (the boranes). Naturally, this enhances considerably the value of the molecular orbital description in the larger context of chemical bond theory.

Finally, a discussion of possible relationships between the H bond and other bond types must include a reference to the metal chelates. These compounds, treated in detail by Martell and Calvin (1342), involve metal atoms multiply bonded to electron donor atoms in *intra*molecular cyclic structures. The metal atom, functioning as an electron acceptor, can be compared to the hydrogen atom in the *intra*molecular H bond. The similarity of the metal and H bond chelates again directs attention to theoretical explanations which relate these bond types. In this instance the charge transfer theory of complex formation advanced by Mulliken (1465) may serve.

Whatever theoretical description of the H bond evolves, this discussion illustrates how the elucidation of the H bond will be reflected into the theory of the chemical bond. Knowledge of the H bond interaction will aid in closing the gap between the weak van der Waals interactions and normal chemical bonds. The possibility of such a fundamental gain adds to the appeal of an area which remains one of the most interesting frontiers of chemistry—the study of the H bond.

APPENDIXES

APPENDIX A

Symbols and Notation

Standard symbols are usually used, and ambiguities are avoided wherever possible by use of different type faces. Listed below are the symbols which occur throughout the book. Infrequently used symbols are defined at the point of use.

Abbreviations for experimental methods are listed at the beginning of Appendix B.

SYMBOL	DEFINITION
$\mathbf{A}$	Absorption coefficient
A	Class of compounds having proton donor groups
AB	Class of compounds having proton and electron donor groups
B	Class of compounds having electron donor groups
$\mathbf{B}$	Experimentally measured, integrated absorption
B	Second virial coefficient
C	Third virial coefficient
D	Fourth virial coefficient
D	Debye (unit of dipole moment equal to 10^{-18} e.s.u.-cm)
d	Density
ΔF	Free energy
ΔF^E	Excess free energy
ΔH	Enthalpy
ΔH_V	Heat of vaporization
ΔH_S	Heat of sublimation
ΔH^E	Excess enthalpy
K, K_{1n}	Equilibrium constant, equilibrium constant for formation of *n*-mer from monomer

SYMBOL	DEFINITION
$K_1, K_2, \cdots K_5$	Ionization constant for 1st, 2nd, $\cdots$ 5th hydrogens
K_A	Ionization constant for an acid
k	Partition coefficient
$\mathbf{k}$	Thermal conductivity
M	Molecular weight
M	Molarity, moles/liter of solution
MP	Melting point
m	Mass
N	Class of compounds having no donor properties
n	Refractive index
$\mathbf{n}$	Value of vibrational quantum number
$n \longrightarrow \pi^*$	An electronic transition from a nonbonding to an excited pi orbital
P	Pressure
q_1, q_2	Electrostatic charges (expressed in electron charges)
R	Gas constant
$[R]$	Molar refraction

SYMBOL	DEFINITION
$\mathbf{R}$	A portion of a molecule; in an amino acid, called a residue
R	$\mathrm{A}\cdots\cdot\mathrm{B}$ distance
$\mathrm{R}(\mathrm{A}\cdots\cdot\mathrm{B})$	”
$\mathrm{R}(\mathrm{A}—\mathrm{H}\cdots\mathrm{B})$	”
$\mathrm{R_v}$	Sum of van der Waals radii
r	A—H distance
$\mathrm{r_0}$	A—H distance in absence of H bond
r^*, $\mathrm{r_0}^*$	Same as r, $\mathrm{r_0}$, but for $\mathrm{H}\cdots\mathrm{B}$ bond
$\mathrm{r_v}$	van der Waals radius
$\mathrm{r_c}$	Covalent radius
ΔS	Entropy
ΔS^E	Excess entropy
T	Temperature, °K
t	Temperature, °C
$\mathrm{T_1}$	“Thermal” or “longitudinal” relaxation time
$\mathrm{T_2}$	“Transverse” relaxation time
u	Velocity of an acoustic wave
V	Volume
V_m	Molar volume
V	Potential
x	Mole fraction
X	An atom in a covalent bond
Y	An atom in a covalent bond
α	Fraction of monomeric form in a H bond equilibrium
δ	Solubility parameter; NMR chemical shift
δ_M, δ_D, δ_P	δ of monomer, dimer, polymer
$\delta(\mathrm{OH})$	H bond increment to heat of vaporization

SYMBOL	DEFINITION
Δ	A change in property; used with μ, ν, β, MP
ϵ	Dielectric constant
η	Viscosity
θ	The angle between A—H and $\mathrm{H}\cdots\mathrm{B}$
μ_0	Permanent dipole moment
μ	Dipole moment; micron, unit of wave length
ν	Vibration frequency
ν_s, ν_b, ν_t, ν_σ, ν_β	Frequency of stretching bending, torsion, $\mathrm{A}\cdots\cdot\mathrm{B}$ stretching, or $\mathrm{A}\cdots\cdot\mathrm{B}$ bending motion (See Fig. 3-1, Section 3.1.1.)
$\nu_{\frac{1}{2}}$	Band width at ½ maximum intensity
ν_a	Frequency of maximum absorption in an electronic transition
ν_o	Absorption frequency of an electron transition in the absence of H bond formation
π	A pi orbital, or the electrons in a pi orbital
π^*	An excited pi orbital (usually antibonding)
$\pi \longrightarrow \pi^*$	An electronic transition from a pi to an excited pi orbital
ρ	Distance between electron and nucleus
σ	Standard error of estimate
τ	Relaxation time
ϕ	The angle between A—H and $\mathrm{A}\cdots\cdot\mathrm{B}$
ψ, ψ_1	Wave function or component of an approximate wave function

APPENDIX B

Thermodynamic Properties of Hydrogen Bond Formation

Introduction to Table

The phase is shown in column 2; for pure materials the state is given; for solutions the solvent is named. In the first two and last two columns *only*, a blank space means the entry above is to be carried down. In the "Original K Units" column, units are given only for the first of a series of values from a single reference. Where the compound arrangement causes intervening entries from other studies, units are repeated with each reference.

In column 4 ($-\Delta H$) we use a symbol selected to show two aspects of the enthalpy: the original authors' *interpretation* of the number of H bonds, and the *measured* value of $-\Delta H$. For example, in the first entry, 2(7.25), 2 is the number of H bonds. The value in parentheses is $-\Delta H$ per H bond per mole. The product of the two numbers, 14.5 in this case, is the measured value. Where this style is not followed, we were unable to find the number of H bonds assumed; in such cases the figure given is the reported value.

Columns 5, 6, and 7 show, respectively, the units in which K is reported, the value of $-\Delta S$ for K in the original units, and the value of $-\Delta S$ for K in atm^{-1}. This conversion is required, since the magnitude of $-\Delta S$ depends on the units. In column 7 parentheses mean that we made the change in K units; values without parentheses are those reported by the original authors. For most of the latter cases the original units were atm^{-1}; we have given the resulting $-\Delta S$ only in column 7, though the same number might have been listed in column 6. To find $-\Delta S$ per H bond, use the number preceding the parentheses in column 4.

	CONCENTRATION UNITS			EXAMPLES		
Case	Original	Desired	Conversion Factor[a]	Solvent	Factor at 20°C	R ln (factor)
1	l/m	atm^{-1}	$\frac{(T)(22.4)}{273}$	—	24.0	+6.4
2	mf^{-1}	atm^{-1}	$\frac{(1000)(d)(22.4)(T)}{(M)(273)}$	Benzene	270	+11.2
				CCl_4	250	+11.0
				Acetone	256	+11.1
3	l/m	mf^{-1}	$\frac{M}{(1000)(d)}$	Benzene	0.089	−4.8
				CCl_4	0.096	−4.7
				Acetone	0.094	−4.7

[a] Divide K in original units by this factor to obtain K in desired units.

The conversions are made in the following manner. First, a correction factor is found that will convert concentration from one set of units to another; then this factor is allowed for in the entropy equation. The table above gives factors in general form, and lists some specific values used in this appendix.

There are some assumptions incorporated in these calculations—perfect gas behavior in cases 1 and 2, and (in cases 2 and 3) solutions so dilute that only the number of moles in the solvent need be considered in computing mole fraction.

The equation for ΔS is

$$+\Delta S = \frac{+\Delta H}{T} + R \ln K$$

but when K becomes K (factor), then

$$+\Delta S = \frac{+\Delta H}{T} + R \ln K - R \ln (\text{factor})$$

so the appropriate value from the last column above is added to the reported ΔS.

Column 8 indicates the experimental method used, by a code reference to the following list.

AA	Acoustic absorption	FP	Freezing point
ADS	Adsorption	HC	Heat conductivity
AL	Absorption of light	HM	Heat of mixing
BPE	Boiling point elevation	HSL	Heat of solution
BS	Band spectra	HV	Heat of vaporization
C	Cryoscopy	IR	Infrared spectra
CAL	Calorimetry	NMR	Nuclear magnetic resonance
CAP	Heat capacity	PVT	Pressure-volume-temperature
CC	Clausis-Clapeyron equation	R	Raman spectra
CN	Conduction of electricity	SH	Specific heat
D	Distribution or partition	UA	Ultrasonic absorption
DA	Dielectric absorption	UV	Ultraviolet spectra
DC	Dielectric constant	2VC	Second and higher virial coefficient
DEN	Density	VD	Vapor density
DM	Dipole moment	VP	Vapor pressure
EMF	Electromotive force		
F	Fluorescence		

All equilibria are for the formation of H bonds with K written in this form:

$$\text{AH} + \text{B} \longrightarrow \text{A—H}\cdots\text{B}$$

$$K \equiv K_{12} = \frac{[\text{A—H}\cdots\text{B}]}{[\text{AH}][\text{B}]}$$

K_{13}, K_{14}, etc. indicate equilibrium constants for trimer, tetramer, etc., formation from monomer.

All notes are listed at the end of the appendix.

Compound	State	t (°C)	$-\Delta H$ (kcal/mole)	Original K units	$-\Delta S$, e.u. based on		Method	Refs.
					K in original units	K in atm^{-1}		
Carboxylic acids—one component								
Formic	Gas	100	2(7.25)	—			2VC	689
		25	2(7.2)	atm^{-1}		36.7[a]	VD	857
		10–156	2(7.06)	atm^{-1}		36	VD	428
		25–84	2(7.05)	atm^{-1}		36	PVT	1685
		100	2(7.05)	atm^{-1}		36	PVT	2009
		50–150	2(6.2 ±0.3)				IR	908
	Gas and liquid		2(6.95)				IR	1866
Formic-*d*	Gas	50–150	2(6.4)				IR	908
Acetic	Gas	50–170	2(6.85)	atm^{-1}		33.2[a]	VD	1661
			3(7.6)	atm^{-2}		58.9[a]		
		25	2(7.97)	atm^{-1}		39.2[a]	VD	858
		~100	2(7.52 ±0.02)	atm^{-1}		36	CAP, IR	2155
		120–164	2(7.52 ±0.1)	atm^{-1}		35.95 ±0.5	PVT	1709 (cf. 1710)
		80–200	2(6.91 ±0.05)	atm^{-1}		33.1[a]	VD	1044
			3(7.57 ±0.1)	atm^{-2}		58.7[a]		
		75–185	2(6.9)				2VC	689
		50–170	2(7.25)	atm^{-1}		34.8[a]	VD	1721
			4(6.75)	atm^{-3}				
		110–435	2(6.89)	atm^{-1}		28.8[a]	VD	639
		350–435	2(6.75)	atm^{-1}		15.5[a]	PVT	1446
			3(6.83)	atm^{-2}		25.0[a]		
		100	2(7.6)	atm^{-1}		38.1[a]	PVT	2008
	Liquid	15–100	1(11.5)				R	2032

		20–50	2(3.10)				AA	699
Acetic through valeric	Gas and liquid		2(8–8.5)				IR	1866
Acetic-d_3, *d*	Gas	80–170	2(7.05)	atm^{-1}		34.0^a	VD	1661
			3(7.73)	atm^{-2}		60.3^a		
Acetic-*d*		24, 139	2(7.95 ±0.3)				IR	911
Trifluoroacetic		80–130	2(7.75)	atm^{-1}		36	VD	1271
		30–150	2(7.03)	atm^{-1}		36.6^a	PVT	2010
		20–100	2(6.85 ±0.2)				IR	1072
Trifluoroacetic-*d*		30–150	2(6.96)	atm^{-1}		36.3^a	PVT	2010
Trimethylacetic		133–200	2(7.01 ±0.1)	atm^{-1}		32.5^a	VD	1044
			3(7.73)	atm^{-2}		57.3^a		
Propionic		20–50	2(8.6)				AA	699
		50–150	2(7.58)	atm^{-1}		36.4	PVT	2009
		50–65	2(9 ±0.5)	atm^{-1}		46	VD	1304
			3(8)	atm^{-2}		59.3^a		
	Liquid	20–50	2(4.67)				AA	699
		8–50	1(3.9)	mf^{-1}	4.4	(16.0)	UA, AA	1180
Propionic-*d*	Gas	25–125	2(7.04 ±0.2)	atm^{-1}		33	IR	909
Butyric		140–200	2(6.95)	atm^{-1}		33	VD	1272
			3(7.66)					
Butyric-*d*		50–150	2(6.9)				IR	908
Heptanoic		185–230	2(7.05)				VD	639
		190–230	2(6.7)				VD	1272
			3(7.66)					
Stearic	Liquid	40–220	2(6.7 ±0.2)	mf^{-1}	23.6	(32.2)^b	IR	1789
Carboxylic acids—two components								
Acetic	CCl_4	20–60	2(5.38)^c				IR	1073
Bromoacetic		20–60	2(4.70)					
Chloroacetic		20–60	2(4.37)^c					
Trichloroacetic		20–60	2(5.17)^c					

Compound	State	*t* (°C)	$-\Delta H$ (kcal/mole)	Original *K* units	$-\Delta S$, e.u. based on		Method	Refs.
					K in original units	*K* in atm^{-1}		
Fluorodichloroacetic	CCl_4	20–60	2(5.03)				IR	1073
Difluorochloroacetic		20–60	2(4.75)					
Trifluoroacetic		20–60	2(4.42)					
Propionic	H_2O	15–45	2(5.1 ±0.1)				EMF	1491
Benzoic	Benzene	40–80	2(8.2)				VP	1116
		0–80	2(5.6)	100 g/g	21.0	(23.0)	C	528
	Benzene, naphthalene	80	2(5.25 ±0.5)				BPE	2190
	Benzene	30–55	2(4.2 ±0.2)	l/m	15.4^a	(21.8)	VP	2133 (cf. 2134)
		50–80	2(4.02 ±0.2)	mf^{-1}	9.6 ±1.5	(20.8)	BPE	26
	CCl_4	25	2(5.25)				UA	1320
		26–50	2(5.05)	l/m	16	(22.4)	IR	1232
	$CHCl_3$	40–80	2(6.35)				VP	1116
o-Toluic	Benzene	30–50	2(4.2 ±0.1)	l/m	16.3^a	(22.7)	VP	2133
m-Toluic		30–50	2(4.72 ±0.05)		18.6^a	(25.0)		
p-Toluic		50–80	2(4.52 ±0.2)	mf^{-1}	10.1 ±1.5	(21.3)	BPE	26
Anisic		50–80	2(4.37 ±0.2)		12.0 ±1.5	(23.2)		
m-Iodobenzoic		50–80	2(3.95 ±0.2)		9.7 ±1.5	(20.9)		
o-Chlorobenzoic		50–80	2(4.3 ±0.2)		13.0 ±1.5	(24.2)		
Phenylpropiolic		50–80	2(4.55 ±0.2)		16.8 ±1.5	(28.0)		
o-Methoxybenzoic	CCl_4	23–72	1(3.3 ±0.5)^d	l/m	6.8^d	(13.2)^d	IR	483 (cf. 494)
p-Methoxybenzoic	Benzene	23–73	2(5.0)		21.1	(27.5)		
Diphenyl phosphinodithioic	CCl_4	25–60	2(0.5)				IR	27

"Carboxylic"	CCl_4	20–75	2(3–5)				IR	500
	Benzene, cyclohexane	80	2(5.2)				BPE	2190
Carboxylic acids—three components								
Acetic	Benzene-H_2O	25–60	2(4.85)	l/m	22.32	(28.7)	D	1438
		6–45	2(0) in H_2O	l/m	6.55	(13.0)	D	495
		6–45	2(4.45 ±0.1) in benzene		19.82 ±0.04	(26.2)		
	Benzene-H_2O	25–45	2(4.09–4.40)	l/m	17.79	(24.2)	D	499
	Hexane-H_2O	25–45	2(4.49 ±0.27)		16.70	(23.1)		
	CCl_4-H_2O	25–45	2(3.78 ±0.37)		13.07	(19.4)		
	CS_2-H_2O	25–45	2(3.52 ±0.21)		11.20	(17.6)		
	Chlorobenzene-H_2O	25–45	2(2.51 ±0.17)		7.00	(13.4)		
	Nitrobenzene-H_2O	25–45	2(2.62 ±0.21)		7.20	(13.6)		
Propionic	Lt. petroleum-H_2O	20–50	2(4.68 ±0.03)		17.62	(24.0)		
	Benzene-H_2O	20–50	2(3.87 ±0.28)		16.25	(22.6)		
	CCl_4-H_2O	20–50	2(3.71 ±0.12)		12.06	(18.5)		
	$CHCl_3$-H_2O	20–50	2(3.33 ±0.06)		15.72	(22.1)		
	Chlorobenzene-H_2O	20–50	2(3.19 ±0.11)		11.19	(17.6)		
	Nitrobenzene-H_2O	25–75	2(2.93 ±0.28)		15.92	(22.3)		
Propionic -naphthylamine	Toluene-H_2O	e	1(7.6 ±0.8)					487
Benzoic	Benzene-H_2O	e	2(4.35)					906[a]
	Dioxane-CCl_4	26–50	1(6.2)	l/m	13	(19.4)	IR	1232
	$CHCl_3$-H_2O	e	2(4.2)				D	906[a]
	$CHCl_3$-H_2O	15–45	2(4.1 ±0.1)	l/m	18.8 ± 0.7	(25.2)		494

Compound	State	t (°C)	$-\Delta H$ (kcal/mole)	Original K units	$-\Delta S$, e.u. based on		Method	Refs.
					K in original units	K in atm^{-1}		
Benzoic-benzyl alcohol	Benzene	20.5	1(11.8)				D	489[b]
o-Hydroxybenzoic	Benzene-H_2O	e	2(2.8)					906[a]
	$CHCl_3$-H_2O	e	2(3.85)					
	$CHCl_3$-H_2O	15–40	2(3.9 ±0.1)	l/m	20.6 ±0.7	(27.0)		494
	CCl_4-H_2O	40–70	2(6.1 ±0.2)		28 ±1.2	(34.4)		
o-Methoxybenzoic	Benzene-H_2O	40–70	1(3.4 ±0.2)[d]		9.3 ±0.8[d]	(15.7)[d]		
p-Methoxybenzoic		40–70	2(5.0 ±0.1)		21.2 ±0.9	(27.6)		
Alcohols—one component								
Methanol	Gas	120–164	1(6 ±0.7)	atm^{-1}		27.25 ±2	PVT	1709
		100	1(4.66)				2VC	1753
		40–120	1(4.0)				2VC	1149
			4(5.52)					
		40–130	1(3.2–7.3)				2VC	1183
		170–250	1(3.2)	atm^{-1}		16.5	CAP, 2VC	2156
			4(6.05)	atm^{-3}		81.3		
Ethanol	Gas	40–120	1(4.0)	atm^{-1}		20.1	2VC	1149
			4(5.02)					
		50–110	1(3.4)	atm^{-1}		16.57	2VC	140a
			4(6.2)	atm^{-3}		81.4		
	Liquid	−25 to 60	1(∼4)				DC	1555
Propanol	Liquid (and dissolved in CCl_4)	18–104	6.0				IR	1218
iso-Propanol	Gas	40–120	1(4.0)	atm^{-1}		22.6	2VC	1149

			4(5.65)					
n-Butanol	Liquid (and dissolved in CCl_4)	18–104	6.0				IR	1218
n-, *iso*-, and *sec*-Butanol	Solid	−25 to 80	1(6–8)	l/m	15–25	(21–31)	DC	471
3-Ketobutanol-2	Liquid	293–340	1(2.02)^{d}				IR	559
Ethylene chlorohydrin	Gas	150–250	1(2.0)^{d,f}				IR	2240
Alcohols, C_1, C_3, *iso*-C_3, C_4	Gas	75–130	~6				2VC	688
-normal	Liquid-gas	80–160	1(5.0 ±0.3)				HV	2021
-branched		25–140	1(3.8)					
Alcohols	Liquid-gas	at b.p.	1(7.5)				HV^{g}	101
Alcohols—two components								
Methanol	CCl_4	25–65	13.0				BS	1328
		20	1(5.15)				HSL	1377
		10–20	1(4.59)				IR	1379
		20–30	1(4.72)					
		30–40	1(4.82)					
		10–40	1(4.72)				IR	1375
		−15 to 60	2(4.6 ±1.2)	mf^{-1}	28	(39)	IR	1228
	Hexane, heptane	10–45	2(5.8)				HM	2124a
	Benzene	20	1(4.25)				HSL	1377
		20	1(3.67)				IR	1375, 942
		20	1(0.3)				IR	1670
	1-Propanol	−110 to −70	1(3.8)				DC	517
Ethanol	Methylcyclohexane	35–55	1(5.4 ±1)				VP	1148
	CCl_4	−15 to 60	2(3.6 ±0.8)	mf^{-1}	20	(31)	IR	1228

Compound	State	t (°C)	$-\Delta H$ (kcal/mole)	Original K units	$-\Delta S$, e.u. based on		Method	Refs.
					K in original units	K in atm^{-1}		
n-Propanol	Hexane, heptane	10–45	2(5.8)				HM	2124a
t-Butanol	CCl_4	20–40	1(5.3 ±0.5)				IR	942
		−15 to 60	2(2.4 ±0.6)	mf^{-1}	11	(22)	IR	1228
	Heptane	10–45	2(5.8)				HM	2124a
	Cyclohexane	27	4(3.85)				UA	1476a
Benzyl alcohol	CCl_4	20	1(4.60)				IR	1375
	Benzene	20	1(4.38)					
Hydroquinone	Acetone	24	2(4.82)				HSL	1978
Chloral hydrate	CCl_4	50–60	2(5 ±1.5)	1/m	20	(26.4)	IR	2051
Alcohols—three components								
Methanol								
-pyridine	CCl_4	30–60	1(3)	1/m			IR	2048
-dioxane		30–60	1(<3)					
-anisole		30–60	1(<3)					
-pyridine oxide		14–38	1(5.0)	1/m	13	(19.4)	UV	1159
-quinoline oxide		11, 21	1(5.3)		14	(20.4)		
2-Methoxy ethanol-dioxane		25–50	1(2.0)	1/m	5.9	(12.3)	IR	1232
Benzyl alcohol-dioxane		25–50	1(2.1)		5.4	(11.8)		
Benzylhydrol (diphenyl methanol)-dioxane		25–50	1(2.6)		6.7	(13.1)		
Benzyl alcohol -azobenzene		25–60	1(3.7(±0.1)^h)	mf^{-1}	9(±4)^h	(20 ±4)		669

-dimethylformamide		25–60	1(4.5(±0.5)[h])		7(±2)[h]	(18 ±2)		
Phenols—one component							
o-Chlorophenol	Gas	180	1(3.9 ±0.7)[d, f]	e	2.4[d]			2240
Phenols—two components							
Phenol	CCl_4	10–60	4.3 ±0.2				DC	1381
			4.35				IR, UV	
		20	1(4.35)	mf^{-1}	13.1[a]	(24.1)	IR	1375 (cf. 1376)
		15–60	3(2.2) cyclic	(l/m)^2	18	(30.8)		1698
	Benzene	20	1(3.55)					1375 (cf. 1376)
		25–50	1(2.4 ±0.3)	l/m	19.1[a]	(25.5)	VP	1199
	Chlorobenzene	20	1(3.48)	mf^{-1}			IR	1375 (cf. 1376)
p-Chlorophenol	CCl_4	20	1(3.72)					
o-Cresol		20	1(3.80)					
p-Cresol		20	1(4.4)					
Phenols—three components							
Phenol								
-dioxane	CCl_4	22–60	1(5.5(±0.5)[h])	mf^{-1}	11 (±1)[h]	(22)	IR	669
		10–50	1(4.7)	l/m	11.5	(17.9)	UV	1480
		25–50	1(4.0)	l/m	9.2	(15.6)	IR	1232
		10	1(3.8)	l/m	18[a]	(24.4)	DM, UV	1481
		30–60	1(3.5)				IR	2048
	Pet. benzene	10–50	1(5.4)	l/m	13.1	(19.5)		1480
-methylacetate	*n*-Heptane	5–35	1(5.3 ±0.1)	l/m	12.8 ±0.2	(19.2)	UV	1479

Compound	State	*t* (°C)	$-\Delta H$ (kcal/mole)	Original *K* units	$-\Delta S$, e.u. based on		Method	Refs.
					K in original units	*K* in atm^{-1}		
Phenol								
-methyl monochloro-acetate	Pet. benzene	0–50	1(5.0 ±0.4)	l/m	13.7 ±1.2	(20.1)	IR	1478
-ethylacetate		0–50	1(5.7 ±0.2)		13.7 ±0.6	(20.1)		
	CCl_4	0–50	1(4.8 ±0.1)		11.9 ±0.3	(18.3)		
-benzylacetate		25–60	1(3.3(±0.6)^{h})	mf^{-1}	4 (±2)^{h}	(15)		669
-pyridine		30–60	1(5)	l/m			IR	2048
-trimethylamine	Cyclohexane	25–45	1(5.8)	l/m	10	(16.4)	D	518
		25	1(5.7 ±0.2)				CAL	
-hexamethylene tetramine	CCl_4	27–50	1(6.9)	l/m	13.6	(21.0)	IR	2054
-dimethylformamide		25–60	1(6.4(±1.0)^{h})	mf^{-1}	9 (±3)^{h}	(20)	IR	669
-*N,N*-dimethyl-acetamide	*iso*-Octane	9–40	1(7.7)	l/m	14.8	(21.2)	UV, IR	1436
-anisole	CCl_4	30–60	1(<3.5)				IR	2048
-diethyl ether		30–60	1(3.7)	l/m	7.6	(14.0)	IR	2047
-quinoline oxide		10–35	1(5.10 ±0.2)	l/m	7.10 ±0.5	(13.5)	UV	1158
		12–35	1(6)	l/m	9	(15.4)	UV	1159
-acetonitrile		25–60	1(4.2 (±0.8)^{h})	mf^{-1}	7 (±3)^{h}	(18)	IR	669
-Al_2O_3 [$Al(OH)_3$]	H_2O	40–60	1(4–4.5)				CC	763
o-Chlorophenol								
-methylacetate	*n*-Heptane	5–35	1(1.4 ±0.3)^{d}	l/m	3.5 ±1.0^{d}	(9.9)^{d}	UV	1479, 907
-pyridine	Benzene	0–50	1(6.8)	mf^{-1}	12.8^{a}	(24.0)	C	776
-quinoline oxide	CCl_4	10–35	1(2.56 ±0.2)	l/m	1.31 ±0.7	(7.7)	UV	1158
m-Chlorophenol								
-methylacetate	*n*-Heptane	5–35	1(6.5 ±0.3)	l/m	15.2 ±1.0	(21.6)	UV	1479, 907

-quinoline oxide	CCl_4	10–35	1(5.89 ±0.2)	l/m	7.05 ±0.3	(13.4)	UV	1158
p-Chlorophenol								
-methylacetate	*n*-Heptane	5–35	1(6.7 ±0.1)	l/m	16.9 ±0.4	(23.3)		1479 (cf. 907)
-quinoline oxide	CCl_4	10–35	1(7.22 ±0.4)	l/m	12.2 ±1.1	(18.6)		1158
-trimethylamine	Cyclohexane	25–45	1(7.0)	l/m	13	(19.4)	D	518
		25	1(8.0 ±0.6)				CAL	
o-Cresol								
-methylacetate	*n*-Heptane	5–35	1(5.3)	l/m	13.7	(21.1)	UV	1479 (cf. 907)
-dioxane		5–35	1(5.4)		13.4	(19.8)		
-quinoline oxide	CCl_4	10–35	1(4.90 ±0.4)	l/m	7.07 ±1.0	(13.5)		1158
m-Cresol								
-methylacetate	*n*-Heptane	5–35	1(5.7)	l/m	14.7	(21.1)		1479 (cf. 907)
-dioxane		5–35	1(5.7)		14.1	(20.5)		
-quinoline oxide	CCl_4	10–35	1(6.39 ±0.2)	l/m	11.7 ±0.7	(18.1)		1158
p-Cresol								
-methylacetate	*n*-Heptane	5–35	1(5.5)	l/m	13.9	(20.3)		1479 (cf. 907)
-dioxane		5–35	1(5.3)		13.0	(19.4)		
-quinoline oxide	CCl_4	10–35	1(5.48 ±0.3)	l/m	8.54 ±0.8	(14.9)		1158
-trimethylamine	Cyclohexane	25–45	1(3.8)	l/m	5	(11.4)	D	518
Guaiacol								
-quinoline oxide	CCl_4	10–35	1(2.06 ±0.4)	l/m	4.74 ±1.0	(11.1)	UV	1158
-dioxane		25–50	1(3.1)	l/m	10.8	(17.2)	IR	1232
			1(0.9)[d]					
Catechol-dioxane		25–50	1(6.8)		17.5?	(23.9?)		
Vanillin-dioxane		25–50	1(3.6)		11.8	(18.2)		
Acetoguaiacone-dioxane		25–50	1(3.8)		12.4	(18.8)		

Compound	State	t (°C)	$-\Delta H$ (kcal/mole)	Original K units	$-\Delta S$, e.u. based on		Method	Refs.
					K in original units	K in atm^{-1}		
2,6-Dimethoxyphenol-dioxane		25–50	1(0.3) prob- 1(1.6) ably *intra*-molecular		2.2	(8.6)		
Dehydrodiisoeugenol-dioxane		25–50	1(2.6)		10.0	(16.4)		
Phenylazo-1-naphthol-$Al(OH)_3$	Benzene	40–60	1(4.5–5)				CC	763
2,4-Dinitrophenol-$Al(OH)_3$	H_2O	50–60	1(4.5–5)					
Amines—one component								
Ammonia	Gas	20–130	1(4.4)	atm^{-1}		26.8	2VC	1183 (cf. 1185)
		100	1(3.7)	atm^{-1}		26.8		1753
Methylamine		40–120	1(3.4)	atm^{-1}		22.0		1183 (cf. 1185)
Ethylamine		40–120	1(3.6)			22.0		
Dimethylamine		40–120	1(3.1)			21.5		
Diethylamine		40–120	1(3.3)			20.3		
Acetaldoxime		120–164	2(5.05 ±0.2)	atm^{-1}		31.96 ±1.3	PVT	1709 (cf. 1710)
NH_2OH	Solid	−78	~13				IR	1505
ND_2OD		−78	~8					

Amines—two components								
Aniline	Benzene, naphthalene	0–100	2(4.5)				C	1808
Pyrrole	Pyridine	30	1(3.8)				HM	2120
Phenylazo-1-naphthylamine	CCl_4	40–60	1(21.5–22.5)				ADS, CC	763
Phenylazo-2-naphthylamine		40–60	1(10–10.5)					
Diethylamine-$CHCl_3$	Gas	50–100	1(4.19)			19.4	2VC	1182a
Triethylamine	$CHCl_3$	−23, 28	1(4.0)				NMR	982
Amines—three components								
Aniline	H_2O-CCl_4	e	1(1.93)				D	487
Diphenylamine								
-dioxane	CCl_4	25–60	1(2.3(±0.4)[h])	mf^{-1}	5 (±2)[h]	(16)	IR	669
-dimethylformamide		25–60	1(3.6(±0.7)[h])		5 (±2)[h]	(16)		
p-Benzotoluide								
-dioxane		25–60	2.3		4	(15)		
-dimethylformamide		25–60	3.8		3	(14)		
Aniline-benzophenone	H_2O-CCl_4	e	1(2.0)				D	487
Amides—two components								
Propionamide	CCl_4	25–60	2(3.9 ±0.1)	1/m	18.6	(25.0)	IR	104
N-Methylformamide	Benzene	25–50	1(3.5 ±0.2)	mf^{-1}	1.3 ±0.5	(12.5)	VP	503
N-Methylacetamide		25–50	1(3.6 ±0.2)		3.7 ±0.7	(14.9)		
Trichloroacetamide		25–50	2(3.55 ±0.2)		15.8 ±0.4	(27.0)		
N-Methyltrichloroacetamide		25–50	2(3.55 ±0.1)		19.6 ±1	(30.8)		
N-Methylbenzamide		25–50	1(3.6 ±0.2)		8.8 ±0.6	(20.0)		

Compound	State	*t* (°C)	$-\Delta H$ (kcal/mole)	Original *K* units	$-\Delta S$, e.u. based on *K* in original units	$-\Delta S$, e.u. based on *K* in atm^{-1}	Method	Refs.
Acetanilide	Benzene	25–50	1(3.2 ±0.2)				VP	503
δ-Valerolactam	CCl_4	30–60	2(5.15)	l/m	16.1[a]	(22.5)	IR	2049
Acetyl-DL-norleucine-*N*-methylamide		30–60	1(1.6)[d]	l/m	5.4[d]	(11.8)[d]	IR	2044
			1(3.9)					
	$CHCl_3$	30–60	1(1.4)[d]					
			1(1.7)					
Benzenesulfanilide	Benzene	5–80	1(6.5)	l/m	17.2[a]	(23.6)	C, BPE	1808
p-Toluenesulfanilide		5–80	1(6.5)		17.2[a]	(23.6)		
Benzenesulf-*p*-toluide		5–80	1(6.5)		17.2[a]	(23.6)		
α-Naphthalenesulf-α-naphthylanilide		5–80	1(4.7)		13.5[a]	(19.9)	D	
Formanilide		5–80	1(3.8)		10.6	(17.0)		
Benzamide		5–80	9.0		23.0	(29.4)		
"Amides"		30	2(~1.8)				DC	938
Amides—three components								
Acetamide	$CHCl_3$-H_2O	6–45	3(1.1)				D	497
Various oxygen containing compounds								
$CHCl_3$-ether	Gas	50–120	1(6.02)	atm^{-1}		26.0	2VC	1182
$CHCl_3$	Ether	20	1(6–7)				DC, HM	572
$CHCl_3$	Acetone	−23 to 28	1(2.5)	mf^{-1}	7.1[a]	(18.2)	NMR	982
$CHCl_3$-methylacetate	Gas	50–100	1(1.98)	atm^{-1}		12.9	2VC	1182a

-ethylacetate		50–100	1(3.87)			18.4		
-methylformate		50–100	1(5.05)			23.7		
-*n*-propylformate		50–100	1(5.62)			24.1		
Styrene-methacrylic acid copolymer	Solid	100–160	2(4–5)	mf^{-1}	13.0[a]		IR	1255a
Inorganic compounds								
Ammonia (see amines)								
Water	Gas	100	1(5.0)	atm^{-1}		25.8	2VC	1753 (cf. 1182)
	Liquid	7.5	2(3.4)				VP	836, 1801
	Solid	−35 to 0	2(5.75 ±0.1)				CN	1469
H_2O, D_2O		−65 to 0	13.3[i]				DA	86
HF	Gas (high pressure)	160–300	*n*(7.0 ±0.5)	atm^{-1}		25 ±1	PVT	1924a
				l/m	18.6	(25.0)		
					9.2[j]	(15.8)		
	Gas	0–40	6(6.80)	atm^{-1}		20.6[a]	PVT	1253
		−5 to 220	6(6.8)				HC	694
		−70 to 73	6(6.7)				IR	1897a
			4(6.3)					
		−45 to 15	6(6.67)				VD	1882
		0–105	6(6.65)	atm^{-1}		18.2[a]	PVT	1034
DF		0–40	6(6.85)	atm^{-1}		19.8[a]	PVT	1253
HCN		0–200	1(3.28)	atm^{-1}		16.5	PVT	749
		0–100	2(4.36)	atm^{-2}		38		
	Liquid	−13 to 26	1(4.6)				DC	415
HN_3	Solid	−193	1(∼5)				IR	549

[a] $-\Delta S$ calculated by present authors.

[b] Original authors calculate 34.6 by a procedure we believe to be in error since it uses the correction factor for benzene instead of that for stearic acid.

[c] Corrected for temperature dependence of extinction coefficient by original author.

[d] *Intra*molecular H bond.

[e] Not given by original authors.

[f] *cis-trans* change, i.e., *intra*molecular H bond.

[g] Extrapolated to zero carbon atoms.

[h] Limits quoted by Davies (480).

[i] Reported value per H_2O molecule. Original authors suggested three H bonds. See discussion following Table 7-III.

[j] $-\Delta S$ for closing six-membered ring.

APPENDIX C

Equilibrium Constants for Hydrogen Bond Formation

Introduction to Table

The arrangement of this table has much in common with that of Appendix **B**. See the description there for the reaction considered, and a list of the symbols used to indicate the experimental method. In the second column, gas, liquid, and solid have their usual meaning. Solutions are indicated by the name of the solvent appearing in the second column. As in Appendix B, in the first three and last three columns *only*, a blank space means the entry above is to be carried down. In the other columns a blank space means the information is not known to us.

All notes are listed at the end of the appendix.

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Carboxylic acids—one component							
Formic	Gas	120 mm	25	345	atm^{-1}	PVT	1685
			40	100			
			60	29			
		1130 mm	10–156	$\log K = -10.13 + 3075/T$	mm^{-1}	VD	428
			10–156	$\log K = -24.6070 + 3754.9/T + 4.7034 \log T$	mm^{-1}	VD	857, 428
		0.1 atm	50–150	$\log K = -10.743 + 3083/T$	mm^{-1}	PVT	2009
		560 mm	160	0.18	atm^{-1}	VD	1271
Acetic		500 mm	110	117.00	l/m	VD	639
			132	44.16			
			155	16.86			
			184	6.296			
		20 mm	25–40	$\log K = -11.789 + 3590/T$	mm^{-1}	PVT	1305
		500 mm		$\log K = -25.732 + 4120/T + 4.910 \log T$	mm^{-1}	VD	858
		800 mm	50–170	$\ln K = -11.997 + 3645/T$	mm^{-1}	VD	1721
				$\ln K_{14} = -13.52 + 3390/T$	mm^{-3}		
		1150 mm	80–200	$\log K = -10.108 + 3018/T$	mm^{-1}	VD	1044
				$\log K_{13} = -18.59 + 4960/T$	mm^{-2}		
		60 mm	50–150	$\log K = -10.931 + 3347/T$	mm^{-1}	PVT	787
		560 mm	160	0.56	atm^{-1}	VD	1271
			350	$K_{12} = 3 \cdot 10^{-2}$ $K_{13} = 9 \cdot 10^{-5}$	mm^{-1} K_{12}		1446
			371	$= 1 \cdot 10^{-2}$ $= 1 \cdot 10^{-5}$	mm^{-2} K_{13}		
			401	$= 0.25 \cdot 10^{-2}$ $= 0.2 \cdot 10^{-5}$			
			433	$= 0.07 \cdot 10^{-2}$ $= 0.03 \cdot 10^{-5}$			
		800 mm	80–170	$\log K = -10.149 + 3000/T$	mm^{-1}	VD	1661
				$\log K_{13} = -18.591 + 4970/T$	mm^{-2}		
		1 atm	100–260	$\log K = -11.53093 + 3513.10/T + 1.11716 \log T + 3.582 \cdot 10^{-4}\, T - 6.75 \cdot 10^{-8}\, T^2$	atm^{-1}	CAP	2155

	Liquid	Heading not applicable	20	62.0	mf^{-1}	UA	699
			30	43.6			
			40	31.3			
			50	23.0			
			60	17.2			
Acetic-d_3 acid-*d*	Gas	800 mm	80–170	$\log K = -10.322 + 3083/T$	mm^{-1}	VD	1661
				$\log K_{13} = -18.984 + 5080/T$	mm^{-2}		
Trifluoroacetic		150 mm	30–150	$\log K = -10.869 + 3071/T$	mm^{-1}	PVT	2010
		560 mm	160	0.14	atm^{-1}	VD	1271
Trifluoroacetic-*d*		150 mm	30–150	$\log K = -10.815 + 3042/T$	mm^{-1}	PVT	2010
Trimethylacetic		1150 mm	80–200	$\log K = -9.978 + 3063/T$	mm^{-1}	VD	1697
				$\log K_{13} = -18.29 + 5070/T$	mm^{-2}		
		560 mm	160	0.91	atm^{-1}	VD	1271
Propionic		20 mm	50	$K_{12} = 0.35$	mm^{-1}	VD	1304
			55	$= 0.22$			
			60	$= 0.14$			
			65	$= 0.10$			
			50	$K_{13} = 3.3\cdot10^{-3}$	mm^{-2}		
			55	$= 1.8\cdot10^{-3}$			
			60	$= 1.0\cdot10^{-3}$			
			65	$= 0.6\cdot10^{-3}$			
		0.1 atm	50–150	$\log K = -10.834 + 3316/T$	mm^{-1}	PVT	2009
	Liquid	Heading not applicable	8	3040	mf^{-1}	UA	699
			21	1450			
			31	868			
			41	526			
			51	332			
Propionic-*d*	Gas	18 mm	30–150	$\log K = -10.13 + 3075/T$	mm^{-1}	IR	909
Butyric		560 mm	160	0.61	atm^{-1}	VD	1271
Heptanoic		500 mm	186	20.17	l/m	VD	639
			206	17.06			
			213	14.93			
			227	11.59			
		560 mm	160	0.61	atm^{-1}	VD	1271

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Stearic	Liquid	Heading not applicable	71	1400	mf^{-1}	IR	1789
			92	400			
			123	115			
			142	49			
			160	26			
			182	15			
			220	4.7			
Carboxylic acids—two components							
Formic	Heptane	0.015 mf	30	$1.9 \cdot 10^4$	l/m	DC	1652
	Benzene	0.01 mf	30	126	l/m	DC	1352, 1652
		0.6 molal	5	256	Not given in *C.A.*	C	1023
	H_2O	0.1 m/l	25	$8.3 \cdot 10^{-3}$	l/m	CN	355
Acetic	Benzene	Extrapolated to zero conc.	0	760		DC	1438, 1908
			10	406			
			20	226			
			30	131			
			40	78			
			50	48			
			60	31			
			70	20			
		0.01 mf	30	370		DC	1352, 1652
	Heptane	0.015 mf	30	$3.7 \cdot 10^4$		DC	1652
	CCl_4	0.05 m/l	a	1000–2650		IR	141
	$CHCl_3$	0.35 m/l		100–420			
				0.2 Acid-$CHCl_3$ interaction			
	CCl_4	0.02 m/l	25	4000		IR	880
	H_2O		20	90		DEN	1109
				100 Acid-H_2O interaction			

		0.1 m/l	25	0.053		CN	355
			25	0.036		D	
			25	0.036		C	
			25	0.050		VP	
	CCl_4	0.2 m/l	24	2370		IR	2157
	Benzene	0.8 molal	5	400	Not given in *C.A.*	C	1023
Acetic-*d*		0.01 mf	30	296	l/m	DC	1652
Chloroacetic		0.01 mf	30	102		DC	1352, 1652
		0.8 molal	5	192	Not given in *C.A.*	C	1023
	CCl_4	0.02 m/l	25	1610	l/m	IR	880
Dichloroacetic	CCl_4	0.02 m/l	25	1080		IR	880
Trichloroacetic	Benzene	0.30 wt. f.	25	24		DC	1208
		0.8 molal	5	14	Not given in *C.A.*	C	1023
	CCl_4	0.02 m/l	25	530	l/m	IR	880
Trimethylacetic	Benzene	0.01 mf	30	690		DC	1352, 1652
			25	416		IR	1255a
	CCl_4	0.02 m/l	29.6	1730			365a
	$C_2H_2Cl_4$	0.03 m/l	29.6	77			
Phenylacetic	Benzene	0.01 mf	30	342		DC	1352, 1652
		0.1 m/l	80	34.5		BPE	2190
	CCl_4	0.2 m/l	24	1940		IR	2157
o-Hydroxyphenylacetic	Benzene	0.1 m/l	80	35.7		BPE	2190
Propionic		0.01 mf	30	390		DC	1352, 1652
	H_2O	0.1 m/l	25	0.050		CN	355
	CCl_4	0.2 m/l	24	2480		IR	2157
Butyric	Benzene	0.01 mf	30	428		DC	1352, 1652
		a	5.5	450 ±50		C	493

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Butyric	H_2O	0.1 m/l	25	0.091	l/m	CN	355
			0	0.091		C	
Valeric	CCl_4	0.2 m/l	24	2720		IR	2157
Caproic			24	1860			
1,3-Hexadienoic (sorbic)			24	5100			
Octanoic	Heptane	0.01 m/l	23	5800		D	795a
Decanoic			23	6900			
Lauric			23	7000			
	CCl_4		24	1960		IR	2157
	Benzene	0.1 m/l	80	37.0		BPE	2190
Myristic	Heptane	0.01 m/l	23	9300		D	795a
Palmitic	Benzene	0.1 m/l	80	50.0		BPE	2190
	Cyclohexane		80	244			
Stearic	Benzene	0.01 mf	30	530		DC	1352, 1652
		0.1 m/l	80	45.5		BPE	2190
	Cyclohexane		80	286			
	Paraffin wax	1 mf	70–220	$\log K = -5.16 + 2930/T$	mf^{-1}	IR	1789
β-Phenylpropionic	Benzene	0.01 mf	30	340	l/m	DC	1352, 1652
Phenylpropiolic		0.1 molal	5.4	370	$molality^{-1}$	C	1135
		0.01 mf	50–80	$\log K = -3.680 + 1992/T$	mf^{-1}	BPE	26
Crotonic (*trans*)		0.01 mf	30	390	l/m	DC	1352, 1652
Benzoic		0.1 m/l	80	103		BPE	2190
		0.015 mf	30	190		DC	1652
		3 g/l	32–56	$\log K = -3.790 + 1977/T$		VP	2134
		25 g/l	32–57	$\log K = -3.383 + 1841/T$		VP	2133
	Cyclohexane	0.1 m/l	80	222		BPE	2190
	Benzene	0.1 molal	5.4	1560	$molality^{-1}$	C	1135
		0.01 mf	50–80	$\log K = -2.090 + 1757/T$	mf^{-1}	BPE	26

	CCl_4	0.02 m/l	25	14,286	l/m	IR	880
	Benzene	0.8 molal	5	1610	Not given in *C.A.*	C	1023
	CCl_4	0.2 m/l	24	4420	l/m	IR	2157
		1 m/l	26	8247		IR	1232
			50	2310			
o-Toluic	Benzene	25 g/l	32–57	$\log K = -3.533 + 1836/T$		VP	2133
		0.01 mf	30	37		DC	1352
	CCl_4	0.2 m/l	24	2760		IR	2157
m-Toluic	Benzene	25 g/l	32–57	$\log K = -4.056 + 2063/T$		VP	2133
		0.01 mf	30	50		DC	1352
p-Toluic		0.01 mf	50–80	$\log K = -2.202 + 1977/T$	mf^{-1}	BPE	26
o-Hydroxybenzoic		0.1 m/l	80	18	l/m	BPE	2190
Anisic		0.01 mf	50–80	$\log K = -2.633 + 1916/T$	mf^{-1}	BPE	26
m-Iodobenzoic			50–80	$\log K = -2.113 + 1722/T$			
o-Chlorobenzoic			50–80	$\log K = -2.827 + 1879/T$			
		0.1 m/l	80	35.7	l/m	BPE	2190
o-Bromobenzoic		0.1 molal	5.4	830	$molality^{-1}$	C	1135
o-Fluorobenzoic		0.01 mf	30	190	l/m	DC	1353
m-Fluorobenzoic			30	1800			
p-Fluorobenzoic			30	1250			
Cinnamic (*trans*)		0.01 mf	30	600		DC	1352, 1652
		0.1 molal	5.4	4550	$molality^{-1}$	C	1135
β-Methyladipic		0.1 m/l	80	250	l/m	BPE	2190
Sebacic (decandioic)			80	167			
Dodecandioic			80	167			
Tetradecandioic			80	120			
Hexadecandioic			80	109			
Octadecandioic			80	91			
Carboxylic acids—three components							
Acetic	Benzene-H_2O	1 m/l	17	250		D	1438
			24.09	179			

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Acetic	Benzene-H_2O	1 m/l					
			25	167	l/m	D	1438
			34.66	102			
			45	62			
			62	28			
			25	500			297
			25	130			499
			35	81			
			45	55			
		1.5 m/l	6.27	374			495
		(benzene)	25.00	134			
			45.08	52			
			6.27	K_{13} = 425	$(l/m)^2$		
		6 m/l	6.27	0.037	l/m		
		(H_2O)	25.00	0.036			
			45.08	0.039			
	$CHCl_3$-H_2O	1 m/l	25	11			297
		a	25	7.0			1438
	CCl_4-H_2O		25	164			499
		1 m/l	25	483			
			35	322			
			45	217			
	CS_2-H_2O		25	725			
			35	495			
			45	327			
		a	25	426			1438
	Hexane-H_2O	1 m/l	25	854			499
			35	519			
			45	328			
	Diisopropyl-ether-H_2O		25	0.67			297
	Diethylether-						

	H_2O		25	0.36			
	Chlorobenzene-H_2O		25	141			499
			35	106			
			45	83			
	Nitrobenzene-H_2O		25	7.35			
			35	5.50			
			45	4.22			
-diethylamine	CCl_4	0.01 m/l	25–30	2800		IR	2222
	$CHCl_3$		25–30	3000			
-pyridine	CCl_4	0.5 m/l	Rm. temp.	220			
	$CHCl_3$		Rm. temp.	70			
Chloroacetic	$CHCl_3$-H_2O	1 m/l	25	1250		D	297
	Diethylether-H_2O		25	45			
	Toluene-H_2O		25	500			
	Nitrobenzene-H_2O		25	1.8			
	Ethylbromide-H_2O		25	3.4			
	Methyliodide-H_2O		25	16			
Dichloroacetic	Diethylether-H_2O		25	3.1			
	Toluene-H_2O		25	270			
	Nitrobenzene-H_2O		25	53			
	o-Nitrotoluene-H_2O		25	24			
Trichloroacetic	$CHCl_3$-H_2O		25	830			
	Toluene-H_2O		25	555			
	Cumene-H_2O		25	5.3			
	Nitrobenzene-H_2O		25	830			
	o-Nitrotoluene-H_2O		25	5000			

Compound	State	Upper conc. limit	*t* (°C)	Association constant (*K*)	Units of *K*	Method	Refs.
Trichloroacetic							
	Ethylbromide-H_2O	1 m/l	25	71	l/m	D	297
	Methyliodide-H_2O		25	67			
	n-Pentanol-H_2O		25	7.7			
	Benzyl alcohol-H_2O		25	28			
Propionic	Light petroleum-H_2O		20	135			499
			30	80			
			40	49			
			50	30			
	CCl_4-H_2O		20	800			
			30	518			
			40	356			
	Benzene-H_2O		20	162			
			30	108			
			40	73			
			50	48			
	$CHCl_3$-H_2O		20	34			
			30	23			
			40	16			
			50	12			
	Chlorobenzene-H_2O		20	173			
			30	117			
			40	88			
			50	64			
	Nitrobenzene-H_2O		25	6.7			
			50	3.2			
			72	1.5			
Butyric	Benzene-H_2O	2 molal-H_2O	0	0.095	molality^{-1}		493
		4 molal-C_6H_6	6.32	542			

Benzoic		0.1 m/l	25	0.1	l/m	D	355
		1 m/l	25	176		D	1438
	$CHCl_3$-H_2O		15	119		D	494
			45	31			
	iso-Pentyl ether-H_2O		25	1.7			
			40	1.6			
			55	1.5			
	Ethyl benzoate-H_2O		35	0.35			
-dioxane	CCl_4		26	40.2		IR	1232
			50	18.5			
o-Hydroxybenzoic	CCl_4-H_2O		40	210		D	494
			55	91			
			70	38			
	$CHCl_3$-H_2O		15	26			
			35	11			
p-Hydroxybenzoic	Ethyl benzoate-H_2O		15	2.3			
o-Methoxybenzoic	Benzene-H_2O		40	2.3			
			50	2.0			
			60	1.7			
			70	1.4			
p-Methoxybenzoic			40	214			
			50	132			
			60	85			
			70	53			
Alcohols and thiols—one component							
Methanol	Gas	1 atm	40–120	$K = \frac{100}{RT} + \frac{2.148}{RT} \exp(1986/T)^b$	atm^{-1}	PVT	1149
Ethanol			40–120	$K = \frac{290}{RT} + \frac{0.284}{RT} \exp(2730/T)^b$			
iso-Propanol			40–120	$K = \frac{300}{RT} + \frac{0.755}{RT} \exp(2483/T)^b$			

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Alcohols and thiols—two components							
Ethanol	CCl_4	1 m/l	25	0.64	l/m	IR	839
n-Propanol		0.7 m/l	Rm. temp.	$K_{12} = 0.89$ K all steps after first $= 0.33$			411
n-Butanol		0.8 m/l	Rm. temp.	$K_{12} = 0.78$ K all steps after first $= 0.33$			
t-Butanol			Rm. temp.	$K_{12} = 0.58$ K all steps after first $= 0.40$			
	Cyclohexane	0.02 mf	27	$K_{14} = 2.49 \cdot 10^4$	mf^{-3}	UA	1476a
n-Octanol	CCl_4	0.6 m/l	Rm. temp.	$K_{12} = 0.77$ K all steps after first $= 0.35$	l/m	IR	411
2,4-Dimethyl-3-ethyl-pentanol		1 m/l	25	0.68			839
Octadecanol	Cyclohexane	0.1 m/l	80	0.5		BPE	2190
Benzyl alcohol	CCl_4	0.7 m/l	Rm. temp.	$K_{12} = 0.80$ $K = 0.33$ for all polymers beyond dimers		IR	411
Triphenyl methanol	Benzene	0.1 m/l	80	0.22		BPE	2190
β-Naphthol			80	0.33			
Ethanethiol	CCl_4	7.5 m/l	24	0.021		IR	1930a
Propanethiol-1			24	0.052			
Propanethiol-2			24	0.018			
Butanethiol-1			24	0.016			
2-Methylpropanethiol-2			24	0.016			
Alcohols and thiols—three components							
Methanol -pyridine oxide		0.2 m/l	14	8.87^a		UV	1159
			22	6.20			
			29	5.37			

			38	4.11			
-quinoline oxide			11	8.8			
			21.4	6.3			
Ethanol							
-acetic anhydride		1 m/l	25	2.0		IR	839
-ethylacetate			25	1.7			
-triethylamine		0.02 m/l	a	2.9		IR	142
t-Butanol	Dioxane-CCl_4	0.5 m/l	25	1.32		IR	1232
2-Methoxyethanol		1 m/l	25	1.41			
			50	1.09			
Benzyl alcohol			25	2.46			
			50	1.86			
Benzhydrol(diphenyl			25	2.74			
methanol)			50	1.95			
Phenols—two components							
Phenol	CCl_4	1 m/l	21.5	2.26		IR	1095a
		0.9 m/l	Rm. temp.	0.72		IR	411
		0.5 m/l	15	K_{13} = 16.6	$(l/m)^2$	IR	1698
			20	13.6			
			30	8.9			
			40	7.7			
			50	4.23			
			60	3.36			
	Benzene	1.4 m/l	25	0.570	l/m	VP	1199
			50	0.416			
		0.8 molal	5	61	Not given in *C.A.*	C	1023
			25	0.57	l/m	IR	839
		6 m/l	Rm. temp.	2.32		IR	1199
		0.14 m/l	25	0.575		D	1628a
	Toluene	0.1 m/l	25	0.843			
	Chlorobenzene	0.13 m/l	25	0.648			
	Nitrobenzene	0.28 m/l	25	0.196			

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Thiophenol	CCl_4	7.5 m/l	24	0.019	l/m	IR	1105
o-Cresol	Benzene	0.06 m/l	5	1.1, 0.28^{d}		C	507
p-Cresol			5	1.1, 0.42^{d}			
m-Nitrophenol			5	2.3			
p-Nitrophenol			5	5.2			
		0.1 m/l	80	1.13		BPE	2190
p-tert-Butylphenol	CCl_4	0.9 m/l	Rm. temp.	0.58		IR	411
2-Naphthol	Dioxane	1 m/l	10	19		F	1356
	Methylacetate		10	140			
	Ethylacetate		25	127			
	Butylacetate		10	145			
	Ethylchloro-acetate		25	123			
Phenols—three components							
Phenol							
-dioxane	CCl_4	0.5 m/l	25	24.6		AL	1272a
				8.7		IR	1480, 2048
			24	4.1			669
			25	8.24		IR	1232
			50	4.89			
	Xylene	0.5 m/l	25	12.3		AL	1272a
	Toluene		25	17.3			
	Benzene		25	15.2			
	CS_2		25	39.2			
-acetone	CCl_4	0.5 m/l	25	8.5		IR	1272a
		0.1 m/l	30	8.35		IR, UV	1436
		0.6 m/l	24.6	8.47		IR	2174
	iso-Octane	0.1 m/l	11	15.2		IR, UV	1436
-methylethylketone	CCl_4	0.6 m/l	24.6	8.00		IR	2174
-diethylketone			24.6	7.35			

-4-heptanone			24.6	7.19			
-acetophenone			24.6	6.85			
-diethyl ether	*n*-Heptane	5 m/l	30	9.6		IR	2054
		0.5 m/l	25	10.8		UV	1484
	CCl_4	0.05 m/l	30	10.0		IR	2047
			45	7.4			
			60	5.75			
-methylacetate	*n*-Heptane	0.3 m/l	15	15.7		UV	1478
			25	11.5			
			35	8.6			
-methylmonochloro- acetate	Naphtha	0.6 m/l	15	6.3			
			25	4.7			
			35	3.8			
			45	2.7			
-methyltrichloro- acetate		0.2 m/l	20	2.9			
-ethylacetate		0.4 m/l	2	34			
			6	30.2			
			20.5	18.5			
			30	12.6			
			40	10.1			
	CCl_4	0.2 m/l	20	9.2			
			30	7.1			
			40	4.7			
	n-Heptane	1 m/l	30	17.5		IR	2054
-ethyltrichloroacetate	Naphtha	0.2 m/l	2	3.4		UV	1478
-benzylacetate	Xylene	0.5 m/l	25	23.5		AL	1272a
	Toluene		25	19.3			
	Benzene		25	28.0			
	CCl_4		25	57.6			
			21	4.8		IR	669
-acetonitrile	*n*-Heptane	0.2 m/l	30	9.3		IR	2054
	CCl_4		22.5	2.7			669
-triethylamine	*n*-Heptane	0.25 m/l	25	83.8		UV	1484

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Phenol							
-hexamethylene tetramine	CCl_4	0.04 m/l	27	113	l/m	IR	2054
			40	69[e]			
			50	51[e]			
		0.03 m/l	30	40		IR	2047
-dimethylformamide	Xylene	0.5 m/l	25	290		AL	1272a
	Toluene		25	352			
	Benzene		25	442			
	CS_2		25	920			
	CCl_4		25	532			
			24	43		IR	669
-dimethylacetamide	*iso*-Octane	0.1 m/l	9	530		IR; UV	1436
			20	310			
			31	213			
			39	138			
	Cyclohexane		19	276			
			50	70			
	CCl_4		20	270			
			30	136			
-pyridine			18–20	55 ±10		IR	735a
-chlorobenzene		2 m/l	18–20	0.30 ±0.04			
-benzene		2 m/l	18–20	0.37 ±0.05			
-mesitylene		1 m/l	18–20	0.58 ±0.06			
-hexamethylbenzene		0.8 m/l	18–20	0.85 ±0.09			
-quinoline-1-oxide		0.02 m/l	12	226 247[f]		UV	1158
			21.5	166 198[f]			
			26.7	146 158[f]			
			35.0	115 124[f]			
o-Chlorophenol-methyl-acetate	*n*-Heptane	0.6 m/l	5	2.0			1478
			15	1.8			
			25	1.6			

			35	1.6			
-pyridine	Benzene	0.04 m/l	5	353, 216[g]	mf^{-1}	C	776
-quinoline-1-oxide	CCl$_4$		12.1	46.8	l/m	UV	1158
			19.4	42.3			
			27.1	37.2			
			34.9	33.7			
m-Chlorophenol	*n*-Heptane	0.15 m/l	5	40.5			1478
-methylacetate			15	25.8			
			25	17.6			
			35	12.3			
-quinoline-1-oxide	CCl$_4$	0.02 m/l	11.2	968			1158
			19.4	736			
			27.2	557			
			35.8	425			
p-Chlorophenol	*n*-Heptane	0.3 m/l	15	36.5			1478
-methylacetate			25	24.3			
			35	17.6			
-quinoline-1-oxide	CCl$_4$	0.02 m/l	11.3	776			1158
			19.5	533			
			27.2	407			
			35.0	286			
o-Cresol-quinoline-1-oxide			11.9	162			
			19.4	128			
			27.2	106			
			35.5	83			
m-Cresol-quinoline-1-oxide			11.8	215			
			19.6	161			
			27.3	122			
			35.1	91			
p-Cresol-quinoline-1-oxide			12.1	220			
			19.5	169			
			27.1	132			
			34.9	109			

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
Guaiacol-quinoline-1-oxide	CCl_4	0.5 m/l	7.95	3.76	l/m	UV	1158
			15.8	3.32			
			23.7	3.01			
			32.4	2.80			
Guaiacol-dioxane		1 m/l	25	0.82		IR	1232
			50	0.55			
Catechol-dioxane			25	10.06			
			50	4.14			
Vanillin-dioxane			25	1.15			
			50	0.72			
Acetoguaiacone-dioxane			25	1.29			
			50	0.78			
2,6-Dimethoxyphenol-dioxane			27	0.56			
			50	0.54			
Dehydrodiisoeugenol-dioxane			25	0.54			
			50	0.38			
α-Naphthol							
-triethylamine	*n*-Heptane	0.1 m/l	25	121		UV	1484
-ether		0.5 m/l	25	15.7			
-nitromethane		0.2 m/l	25	3.3			
β-Naphthol							
-triethylamine		0.1 m/l	25	103			
-ether		0.5 m/l	25	14.5			
-nitromethane		0.2 m/l	25	2.6			
Special group[h]							
Phenol-trimethylamine	Cyclohexane	1 wt. frac.	25	86		D	518
p-Chlorophenol-trimethylamine			25	200			
o-Cresol-trimethylamine			25	70			
m-Cresol-trimethylamine			25	70			
p-Cresol-trimethylamine			25	65			

α-Naphthol-trimethylamine			25	110			
β-Naphthol-trimethylamine			25	230			
Triphenylmethanol-trimethylamine			25	12			
n-Heptanol-trimethylamine			25	3.5			
2,5-Dimethylpyrrole-trimethylamine			25	3.5			
Indole-trimethylamine			25	9			
Amides							
Acetamide	Benzene	0.005 mf	30	40 ±10	mf^{-1}	DC	938
	H_2O-$CHCl_3$	0.12 m/l	25	$K_{13} = 35$	l/m	D	497
	Acetone	1.5 m/l	56	0.49 ±0.04		BPE	
Trichloroacetamide	Benzene	0.02 mf	24.7	93	mf^{-1}	VP	503
			35.07	64			
			48.90	43.5			
Propionamide		0.005 mf	30	27 ±5		DC	938
	CCl_4	0.01 formal	25	45 ±6	l/m	IR	104
n-Butyramide	Benzene	0.005 mf	35	62 ±5	mf^{-1}	DC	938
i-Butyramide			35	92 ±6			
Benzamide			35	40 ±6			
		0.1 m/l	80	6.66	l/m	BPE	2190
		0.11 m/l	45	14^{i}		FP, BP	1808
			80	3.4^{i}			
m-Chlorobenzamide		0.005 mf	30	290 ±70	mf^{-1}	DC	938
p-Chlorobenzamide			30	160 ±20			
m-Bromobenzamide			30	220 ±40			
p-Bromobenzamide			30	60			
N-Methylformamide		0.02 mf	24.7	213 ±5		VP	503
			35.07	175 ±3			
N-Methylacetamide			24.7	69 ±3			
			35.07	56 ±2			
			48.90	43 ±2			

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
N-Methylbenzamide	Benzene	0.02 mf	24.7	5.2 ±0.1	mf^{-1}	VP	503
			35.07	4.3 ±0.1			
			48.90	3.3 ±0.05			
N-Propylacetamide			21.8	50			
N-Methyltrichloroacetamide			24.7	8.5 ±0.2			
			35.07	5.6 ±0.1			
			48.90	3.4 ±0.05			
Formanilide			5	5.0^{i}			
			80	1.1^{i}			
Benzenesulfanilide and p-toluenesulfanilide		0.11 m/l	5	22	l/m	FP, BP	1808
			45	4.3			
			80	2.2			
Benzenesulf-p-toluidide			5	22			
			45	4.3			
			80	2.0			
α-Naphthalenesulf-α-naphthylamide			5	5.6			
			80	0.91			
Methanesulfonanilide	$CHCl_3$	0.16 m/l	a	5.24		IR	1862
	CCl_4			218			
N-Ethyltoluene-p-sulfonamide		0.014 m/l	—	121			
p-Toluenesulfonmethylamide	$CHCl_3$	0.5 m/l	—	1.32		DM	
δ-Valerolactam	CCl_4	0.03 m/l	30.1	206		IR	2049
			45.3	90			
			60.7	45			
Miscellaneous compounds							
Diethyl ether	$CDCl_3$	0.25 mf	Rm. temp.	0.80 ±0.15	l/m	IR	1259
Dioxane	$CHCl_3$	1.0 mf	50	1.11 1:1 complex	mf^{-1}	VP, HM	1306a
			50	1.24 1:2 complex	mf^{-2}		
Acetone	$CHCl_3$	1.0 mf	−23	4.0	mf^{-1}	NMR	982

-methylformate	Gas	1 mf	28	1.8	atm^{-1}	2VC	1182a
			50	0.017			
			77	0.0096			
			95	0.0065			
-methylacetate			50	0.0281			
			65	0.0247			
			80	0.0211			
			95	0.0192			
-ethylacetate			50	0.0422			
			65	0.0284			
			80	0.0223			
			95	0.0200			
$CHCl_3$							
n-propylformate			95	0.0200			
n-diethylamine			50	0.0390			
			64	0.0297			
Triethylamine	$CHCl_3$		−23	12.0	mf^{-1}	NMR	982
			28	3.0			
Triethylamine-$CDCl_3$	CCl_4	2 m/l	a	0.36	l/m	IR	142
Pyrrole-pyridine		0.3 m/l	30	5–9^j		SH	2120
		0.02 m/l		1.2		IR	
		0.3 m/l	18–20	2.7 ±0.3		IR	735a
-chlorobenzene		2.0 m/l	18–20	0.23 ±0.03			
-benzene		2.0 m/l	18–20	0.30 ±0.03			
-mesitylene		1.0 m/l	18–20	0.40 ±0.04			
-hexamethylbenzene		0.8 m/l	18–20	0.72 ±0.07			
β-Naphthylamine	Benzene	0.1 m/l	80	0.21		BPE	2190
Inorganic compounds							
H_2O	Gas		40–400	$\log K = -5.650 + 1250/T$	atm^{-1}	2VC	1753
HF	Gas	1 atm	0–40	$\log K = -43.65 + 8910/T$	mm^{-6}	PVT	1253
		0.86 atm	−45	18	atm^{-n}	VD	770
			0	3	$n = 4–2.4$		
			16	0.3			
		10 atm	0–105	$\log K = -42.38 + 8660/T$	mm^{-6}	PVT	1034
			180	$\log K = -3.85 + 1530/T$	l/m	DEN, SH	1924a

Compound	State	Upper conc. limit	t (°C)	Association constant (K)	Units of K	Method	Refs.
DF	Gas	1 atm	0–40	$\log K = -43.65 + 8970/T$	mm^{-5}	PVT	1253
HCN			0–190	$\log K = -3.616 + 717/T$	atm^{-1}	PVT	749
				$\log K_{13} = -8.320 + 1905/T$	atm^{-2}		
NH_3			−30 to 250	$\log K = -5.869 + 967/T$	atm^{-1}	2VC	1758
HNO_3	H_2O	16 m/l	Not given	0.045	l/m	NMR	953
$HClO_4$		18 m/l		0.026			

Notes

[a] Not given by original authors.

[b] R in 1 atm deg^{-1} mole^{-1}.

[c] Listed values are the mean values found from K at three frequencies.

[d] Calculated from data in *J. Chem. Soc.* **1934**, 688.

[e] Calculated from value at 27°C with assumed constant absorption coefficient.

[f] Value by same author in earlier paper.

[g] Using activity instead of concentration.

[h] Original authors state that these eleven K's vary with concentration and are to be compared only one another.

[i] Values for $K_{(n-1)n}$, e.g., for addition of nth monomer unit to chain.

[j] Depending on concentration.

BIBLIOGRAPHY

Introduction

In this bibliography we have assembled the references dealing specifically with H bonds. We have not tried to include every casual mention of this t[illegible]c. *Chemical Abstracts*, plus cross checking of review article reference lists, wer[illegible]e main sources, and reasonable completeness is claimed through the year 1956. During 1957 and 1958 some additional entries were inserted but without comprehensive search.

The arrangement is alphabetical according to first author. Abbreviations of journal titles follow *Chemical Abstracts* as given in their 1956 "List of Periodicals Abstracted."

To shorten the annotations we have used symbols (see Appendix A) and abbreviations for experimental methods (see Appendix B). To this same end we have adopted a telegraphic style.

The bibliography is indexed both by authors and subject. The subject index is included in that for the text and is explained on p. 461.

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AUTHOR INDEX

The entries in this index refer only to the bibliography (not to the text), and are listed by bibliography reference number. Names of the first author of each paper are not included here. A complete collection of articles by a given author can be obtained from the entries in this index plus those in the alphabetical listing by first authors in the bibliography.

SUBJECT INDEX

This index refers both to the text and to the bibliography. Text page numbers are given in roman type, and bibliography reference numbers in italics. Italicized table numbers and italicized page numbers indicate the locations of reference lists given in text.

Compounds are usually indexed under generic names (such as acids, alcohols, hydrates) except for compounds of particular importance (such as acetic acid, formic acid, methanol, ethanol, water, ice). In this index only, the entry "acids" refers to "carboxylic acids." Inorganic acids and inorganic acid salts are identified separately. Except for D_2O (which is alphabetized as "water–d_2"), a deuterated compound is included with the corresponding nondeuterated compound.