drawn with a radius of ± 0.20 millivolt; these are believed to be the respective accuracies in the two determinations. The values of pK_{A1} and pK_{A2} obtained were, respectively, 2.50_1 (corresponding to $K_{A1} = 3.15_7 \times 10^{-3}$) and 4.87_4 (corresponding to $K_{A2} = 1.33_7 \times 10^{-5}$).

The following comparison of the values of the two ionization constants in water at 25°, as determined in this investigation, can be made with values already reported

	pK_{A1}	pK_{A2}	Method
This investigation	2.50_1	4.874	Galvanic cells without liquid junction
Klotz and Gruen (1945)[9]	2.504	...	Spectrophotometric
Albert and Goldacre (1942)[21]	2.49	4.83	Potentiometric titration
Kilpi and Harjanne (1948)[22]	2.38	4.89	Buffer capacity min. (liquid junction involved)
Johnston (1906)[23]	2.32	4.92	Catalytic method involving hydrolysis of methyl acetate
Winkelblech (1901)[24] and Walker (1904)[25]	2.32	4.92	Conductance

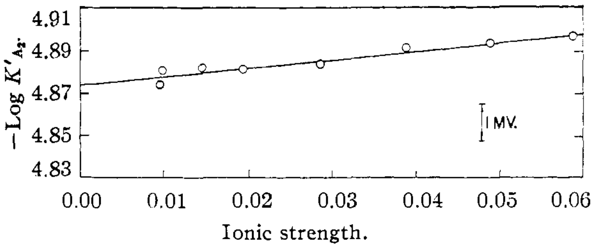

Fig. 2.—Determination of the second ionization constant of *p*-aminobenzoic acid in water at 25°.

The only previous completely thermodynamic method which has been applied to *p*-aminobenzoic acid is the spectrophotometric method, and excellent agreement was obtained between this investigation and the optical method for K_{A1}. The present investigation is apparently the only one in which corrections for the overlap of the dissociation reactions have been applied.

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AUSTIN, TEXAS

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[21] A. Albert and R. Goldacre, *Nature*, **149**, 245 (1942).

[22] S. Kilpi and P. Harjanne, *Suomen Kemistilehti*, **21B**, 14 (1948).

[23] J. Johnston, *Proc. Roy. Soc.* (*London*), **A18**, 82 (1906).

[24] K. Winkelblech, *Z. physik Chem.*, **36**, 564 (1901).

[25] J. Walker, *ibid.*, **51**, 708 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Inter- and Intramolecular Hydrogen Bonds[1]

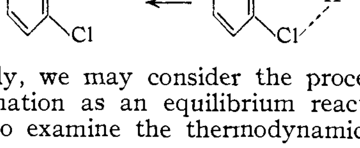
BY H. H. JAFFÉ

RECEIVED SEPTEMBER 24, 1956

The differences in energies of intra- and intermolecular H-bonds are discussed in terms of the entropy changes accompanying H-bond formation.

Since the early work on hydrogen bonds[2] it has generally been accepted that they are usually associated with bond energies in the range of 3 to 7 kcal./mole. These estimates were based almost exclusively on intermolecular hydrogen bonds. In recent years, however, hydrogen bonds have been demonstrated to exist, or at least proposed, for which one would expect appreciably smaller bond energies.[3,4] Most of these cases involve *intra*-molecular hydrogen bonds, many of which could even be demonstrated in solution in polar media,[3] where one might have expected that hydrogen bonding with the solvent might be energetically preferred. It is the purpose of the present paper to call attention to a fundamental thermodynamic difference between *intra*- and *inter*molecular hydrogen bonds which can explain readily why intramolecular H-bonds of much smaller energy than intermolecular ones can be observed.

For the purpose of this discussion, we shall define the process of H-bond formation as the process in which this bond is formed, leaving the molecule (or molecules) otherwise effectively unchanged. For intermolecular H-bonds, this process then is equivalent to association; in case of H-bonds between atoms of the same kind, polymerization or dimerization; in this paper we shall not be concerned with association of more than two molecules, although the arguments presented will hold equally well for more extensive association. For intramolecular H-bonds, the process is represented by reaction 1 (using *o*-chlorophenol as an example) in the forward direction.



(1)

Accordingly, we may consider the process of H-bond formation as an equilibrium reaction, and we wish to examine the thermodynamics of this reaction.

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[1] This work was sponsored by the Office of Ordnance Research, U. S. Army.

[2] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd Ed., 1948, Chapter 9.

[3] D. H. McDaniel and H. C. Brown, *Science*, **118**, 370 (1953).

[4] *E.g.*, H. H. Jaffé, L. D. Freedman and G. O. Doak, THIS JOURNAL, **76**, 1548 (1954).

In order that a H-bond be observable in a given system, it is obvious that the equilibrium constant (K) for the formation process must have a reasonable value, not too much below unity. We might arbitrarily set $K = 10^{-1}$ as the lower limit permitting observation of the H-bond.[5] At room temperature, this would correspond to a maximum value of $\Delta F^\circ \sim + 1.5$ kcal./mole.

Let us consider the entropy change accompanying this process. The entropy change accompanying the dimerization of gas molecules can be estimated. The loss of three translational degrees of freedom should involve a loss of entropy of around 40 e.u. for a moderately sized molecule. The loss of three rotational degrees of freedom will involve a smaller decrease of entropy, which we will estimate at about 10 to 15 e.u. The rotational and translational degrees of freedom lost upon dimerization give rise to six vibrational modes and even though most of these vibrations will have fairly low force constants (there will be only one bond stretching mode for each H-bond and two bending modes), it is doubtful that these vibrations make a very appreciable (positive) contribution to the entropy change. Hence the total entropy change should be about -50 e.u., corresponding to a $T\Delta S$ term of about 15 kcal./mole at room temp., and 20 kcal./mole at the lowest temperatures where moderately sized hydrogen bonded molecules exist in the vapor state. Accordingly it is not astonishing that H-bonded dimers in the vapor phase are rarely encountered, and then only when more than one bond is responsible.

The estimation of the entropy changes in solution or in the liquid phase is much more difficult. The translational motion is no longer free, but in solution or in a liquid, may be viewed either as translation in a cage (small volume) or as a vibration about a pseudo-lattice-site. In either way, the translational entropy should be greatly reduced. Rotation of large molecules in a liquid phase is not free; rather the degrees of freedom corresponding to rotation in the gas are probably best described as librations. As such, their contribution to the entropy will also be greatly reduced. In solutions, a further positive change in the entropy of the solvent, due to the fact that the dimer molecule is solvated by slightly fewer solvent molecules, is probably negligible. Thus we see that we should expect a much smaller entropy change in liquids and solutions. Since the lower limit of energies of observable H-bonds are of the order of 3 kcal./mole we may infer that this figure is the probable entropy change (in terms of $T\Delta S$) for dimerization. This value is certainly not unreasonable in the light of the above discussion.

For an intramolecular H-bond in the gaseous or liquid phase, or in solution, the process of H-bond formation (reaction 1) involves no change in the number of "translational" and "rotational" degrees of freedom. The contributions of the various bond stretching vibrations to the entropy of the molecule are undoubtedly so small that even moderate changes in the associated force constants cannot give rise to appreciable entropy effects. Accordingly, using again chlorophenol as an example, it seems evident that the in-plane and out-of-plane bending vibrations of Cl and OH, and the torsional vibration of OH are the only vibrations which could affect the entropy. Altogether, these vibrations do not contribute more than a very few e.u. to the total entropy of the molecule, and while their tightening will lead to a slight decrease in entropy, this decrease is quite insignificant, and can be neglected.

In solution, another possible contribution to ΔS° is due to any change in solvation. The degree of solvation is probably limited by steric relations, and it seems hard to visualize that the number of solvent molecules which can sufficiently closely approach the molecule, is appreciably affected by H-bond formation. Hence, we shall also neglect any contribution to ΔS° from solvation.

Assuming, then, that we can neglect ΔS° for reaction 1, ΔH° and ΔF° are equal, and measurement of either would determine both. Neither of these quantities appear particularly amenable to measurement, and few attempts appear to have been made to determine these quantities for intramolecular H-bonds,[6] and the data obtained invariably refer to the vapor state or to inert solvents. Data in some recent papers,[3,4] however, permit some estimates of ΔF° to be made. For example, in connection with the measurement of the pK's of some *ortho*-substituted benzenephosphonic acids, estimates of the effect of H-bonding on the pK were made, and these are, of course, directly the $-\log K$ applying to eq. 1. The values measured were of the order of 0.25–1.5, and hence lead to enthalpies for reaction 1 of 0.2–1 kcal./mole. These figures are probably slight underestimates, firstly, because the $-\log K$ values were lower limits, and secondly, because ΔS° may well contribute a few tenths of a kcal. However, the arguments seem to show that, in solution, even in highly polar media, extremely weak hydrogen bonds may be observed. Other data of similar nature may be found throughout the modern literature.

It frequently has been pointed out that intramolecular H-bonds are particularly readily formed because other bonds in the molecule constrain the atoms into favorable positions. In this form, this statement, of course, implies the small magnitude of the entropy change. This same constraint also explains certain apparent anomalies, such as the fact that the OH—Cl and OH—Br bonds in *o*-chloro- and *o*-bromobenzenephosphonic acids are of approximately equal strengths, although bromine is generally considered to form much weaker H-bonds than chlorine. The geometry of the molecule, due to the relatively large phosphorus atom, is simply such that the OH—Br distance is much more favorable to H-bonding than the OH—Cl distance, thus overcoming the innate lower H-bonding tendency of Br.

We are now ready to inquire why, even in highly polar solvents, we can find such weak intramolec-

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(5) Some recent techniques such as measurement of heats of solution permit demonstration of appreciably weaker H-bonds; *cf.* S. Searles, M. Tamres, F. Block and L. A. Quarterman, This Journal, **78**, 4917 (1956), and earlier papers by M. Tamres.

(6) *Cf.* L. R. Zumwalt and R. M. Badger, *ibid.*, **62**, 305 (1940).

ular H-bonds, formed apparently in preference to possible much stronger intermolecular bonds. One answer to this question is, of course, contained in the comparison of the entropy changes associated with the formation of the two types of H-bonds.

There seems to be a further reason, however, in steric effects. Consider the H-bonded form of *o*-chlorophenol. There is no reason to believe that both the O atom and the Cl atom could not serve as electron donors for H-bonds with as many as two solvent molecules each (the H-bond O-H—Cl is probably so weak that, at equilibrium, not many molecules would be that highly solvated). In the non-bonded form, sufficient electron pairs are available so that the molecule could act as donor for five, and as acceptor for one further H-bond. For steric reasons such an extensive solvation of the substituted region of the molecule seems out of the question; it appears quite likely that steric hindrance would prevent solvation beyond four solvent molecules in this region, and thus leave both the H-bonded and the non-bonded forms approximately equally solvated. Hence the intramolecular H-bonding provides additional energy over the solvation.

Acknowledgment.—The author is indebted to Dr. Robert J. Good for several interesting discussions concerned with this work.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Polarized Electronic Absorption Spectrum of Amides with Assignments of Transitions[1]

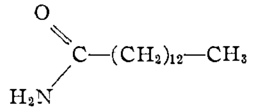
BY DON L. PETERSON[2] AND WILLIAM T. SIMPSON

RECEIVED NOVEMBER 2, 1956

The polarized electronic spectrum of myristamide is obtained to 1600 Å. It is analyzed into n-π; NV_1; Rydberg (2p, 3s) and NV_2 transitions. Emphasis is on obtaining and interpreting the NV_1 transition moment direction.

Introduction

In this investigation the polarized electronic spectrum of myristamide



in the region between 2300 and 1600 Å. was obtained. Starting from the long wave length end there are characterized n-π and NV_1 transitions, a first member of a Rydberg series, and part of the NV_2 transition.

The main result of the paper is considered to be the determination of the direction of polarization of the NV_1 transition, appearing at 1850 Å. In the work on myristamide this direction could not be determined uniquely owing to unfavorable crystal symmetry.[3] Two possible orientations were obtained: one inclined away from the nitrogen–oxygen axis 9.1°, toward the carbon–nitrogen axis; and the other 26.7°, toward the carbon–oxygen axis.[4]

Several methods were employed in an attempt to select the correct direction. The work of Ward on N-acetylglycine was considered first.[5] In addition, an attempt was made to use the results of a π-electron calculation with full configurational interaction in the framework of the ASMO method. During the final stages of this research the crystal structure of N,N′-diacetylhexamethylenediamine was found reported in the literature.[6] This substance has only one molecule per unit cell, a circumstance which made it possible unambiguously to determine the correct polarization direction. The 9.1° value proves to be the correct one, which, gratifyingly was the value selected by the theoretical calculation, and also turns out to be allowed by Ward's experiments.[7]

The theoretical work in this paper is based on calculations described in a collateral paper on the allyl system, particularly allyl anion.[8] Much of the interpretation of the experiments depends on results described in a paper on the nature of resonance force transfer of excitation energy in molecular crystals.[9] Use will also be made of earlier research in which the spectrum of amides in the gas phase down to *ca.* 1300 Å. has been recorded.[10]

I. Experimental

The instrument used in these studies is the same as described elsewhere[11] except for a sliding vane valve situated between the slit compartment and tank.[12]

The calculation of the optical densities of the sample at the various wave lengths was complicated by the fact that there was marked reciprocity failure. Time sensitometry, using numbers of flashes as abscissas, gave characteristic curves which had the usual straight line portion, but with a definite decrease in slope when the intensity was reduced. It was found possible, after a certain amount of trial and error, to assign every density, *D*, at a given number of flashes, *n*, an effective gamma determined empirically,

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[1] This research was supported in part by The Air Research and Development Command under Contract No. AF 18(600)-375.

[2] National Science Foundation Predoctoral Fellow, 1954–1955.

[3] The crystal structure was determined by J. D. Turner and E. C. Lingafelter, *Acta Cryst.*, **8**, 549 (1955), and refined by R. F. Adamsky and E. C. Lingafelter, private communication.

[4] These possibilities were briefly reported in a Communication to the Editor, D. L. Peterson and W. T. Simpson, THIS JOURNAL, **77**, 3929 (1955).

[5] J. C. Ward, *Proc. Roy. Soc.* (*London*), **A228**, 205 (1955).

[6] M. Bailey, *Acta Cryst.*, **8**, 575 (1955).

[7] Our first interpretation of Ward's results, given in ref. 4, proved to be incorrect.

[8] H. D. Hunt, D. L. Peterson and W. T. Simpson, *J. Chem. Phys.*, in press.

[9] W. T. Simpson and D. L. Peterson, *ibid.*, in press.

[10] H. D. Hunt and W. T. Simpson, THIS JOURNAL, **75**, 4540 (1953).

[11] R. C. Nelson and W. T. Simpson, *J. Chem. Phys.*, **23**, 1146 (1955).

[12] D. L. Peterson, Thesis, University of Washington, 1956.