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Commentationes

Semiempirical Quantum Mechanical Studies on Some Hydrogen Bonded Systems

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The CNDO/2 method is used to study the hydrogen bond strength in several representative systems. Enthalpies of hydrogen bond formation are generally predicted fairly well although some exceptions are noted. The proton-proton acceptor distances are predicted to be about 10 percent too small in all cases where comparison with experiment can be made.

Mit Hilfe der CNDO/2-Methode wird in verschiedenen repräsentativen Systemen die Stärke von Wasserstoffbrücken untersucht. Die Enthalpien werden bis auf wenige Ausnahmen recht gut vorausgesagt. In allen Fällen, in denen experimentelle Unterlagen vorhanden sind, werden die Abstände der Proton-Proton-Akzeptoren um etwa 10% zu klein vorausgesagt.

La méthode CNDO/2 est utilisée pour étudier le force de la liaison hydrogène dans quelques systèmes représentatifs. Les enthalpies de formation de la liaison hydrogène sont en général convenablement prédites à quelques exceptions près. La distance entre le proton et l'accepteur de proton est prédite avec une erreur par défaut d'environ 10% dans les cas où le résultat expérimental est connu.

Introduction

An understanding of the factors involved in hydrogen bonding is fundamental to many areas of chemistry and biology. Until quite recently, theoretical elucidation of the hydrogen bond was attempted on the basis of electrostatic interactions, charge-transfer structures in valence bond theory, and the like [1]. It has now become practical, however, to treat hydrogen bonded systems as single large molecules, using either nonempirical or semiempirical quantum mechanical methods, thereby directly computing the enthalpy of hydrogen bond formation. Examples of such recent work are the nonempirical SCF study on water by Morokuma and Pedersen [2], and the semiempirical calculations of Murthy and Rao on water [3], and Pullman and Berthod on formamide [4] using the CNDO/2 method [5—7]. These studies, particularly those made utilizing the CNDO/2 formulation are encouraging and have led us to investigate a wide variety of hydrogen bonded systems with this method. The calculations reported below were all carried out using the original parameterization of Pople, Segal, and Santry [5—7].

Water

The water dimer was studied in the three conformations considered by Morokuma and Pedersen [2], these being designated linear, bifurcated, and cyclic. The linear dimer has also been considered by Murthy and Rao [3]. The geometry of the individual water molecules was taken to be invariant in dimer formation, with an O—H bond length of 0.96 Å and a bond angle of 104.5 degrees.

The geometry of the linear dimer was taken such that one water molecule lies in the $X-Y$ plane, the other lies in the $X-Z$ plane, and the two oxygens and the proton involved in hydrogen bond formation lie on the X-axis. A minimum in the potential curve is obtained at an O—O distance of 2.54 Å, with a stabilization energy of 6.31 kcal/mole. These values are in agreement with those of Murthy and Rao [3] who find an O—O distance of 2.54 Å and a stabilization energy of 6.27 kcal/mole using an H—O—H angle of 107 degrees in the monomer units. The semiempirical results are therefore in much better agreement with the experimental value of the hydrogen bond strength of 5—6 kcal/mole [8] than the SCF study [2] which predicts a stabilization energy of 12.6 kcal/mole. The computed O—O distance is somewhat smaller than the average experimental value of 2.74—2.77 Å in ice [8].

The bifurcated dimer geometry again places one molecule in the $X-Y$ plane and the other in the $X-Z$ plane with the two oxygen atoms lying on the X-axis. A schematic sketch of this conformation is shown in Fig. 3 of Morokuma and Pedersen's paper [2]. The minimum in the potential curve for this system occurs at an O—O distance of 2.41 Å and a predicted stabilization energy of 2.84 kcal/mole. We conclude, as do Pedersen and Morokuma, that this mode of hydrogen bonding is not preferred, being less stable than the linear geometry by 3.47 kcal/mole. The SCF result predicts this difference to be 3.36 kcal/mole, in excellent agreement.

Calculations were performed on the cyclic dimer using the basic geometry found to be most stable by Morokuma and Pedersen. In this conformation, the four atoms involved in hydrogen bonding lie in a plane with an H—O--H angle of 60 degrees. The remaining two protons are located 45 degrees out of and on opposite sides of this plane. The minimum occurs at an O—O distance of 2.67 Å with a stabilization energy of 1.91 kcal/mole, so that this conformation is less favorable to dimer formation than the linear system by 4.40 kcal/mole. This result compares favorably with the *ab initio* difference of 4.82 kcal/mole [2].

Calculations were also carried out on two water trimers having linear hydrogen bonding structures. The first of these (Trimer I) considered that both hydrogen atoms of one of the water molecules are hydrogen bonded to the oxygen of the other two waters. A minimum in the potential curve was obtained at an O—O distance of 2.56 Å and a stabilization energy of 11.48 kcal/mole, or 5.74 kcal/mole for each hydrogen bond. The second trimer considered (Trimer II) was taken to have a structure in which the oxygen and one of the hydrogens of a central water molecule are hydrogen bonded to the other water molecules. This arrangement is predicted to be considerably more stable than the other trimer, with a stabilization energy of 13.60 kcal/mole at a O—O distance of 2.52 Å. Thus, the stabilization energy is 6.80 kcal/mole for each hydrogen bond, somewhat larger than that of the linear dimer.

A final calculation was made on a water pentamer in which four waters are arranged tetrahedrally about a central molecule. Such an arrangement occurs in ice. For this system, the bond angle of the central water was changed to a tetrahedral angle. The minimum in the potential curve occurred at an O—O distance (measured from the central oxygen) of 2.56 Å and a stabilization energy relative to five normal water molecules of 23.26 kcal/mole, or 5.81 kcal/mole for each hydrogen bond.

This result is somewhat disturbing in that a significant amount of the ice structure is assumed to exist in the liquid state. Statistical mechanical calculations by Marchi and Eyring [9] based on only the presence of monomer and icelike aggregates yield good agreement for many properties of liquid water. Némethy and Scheraga [10] also predict significant concentrations of water molecules with four hydrogen bonds per molecule. It is probable that the CNDO method is too crude to predict such features quantitatively. Also, the calculations described here are carried out on isolated units and interaction of the polymeric units with other molecules, as occurs in the liquid, cannot be taken into account. The results for water are summarized in Table 1.

Table 1. *Computed results for water*

Polymer	R_0[a]	$\Delta E(R_0+0.05)$[b]	$\Delta E(R_0)$	$\Delta E(R_0-0.05)$	R_{eq}[c]	$\Delta E(R_{eq})$
Linear dimer	2.55	− 6.14	− 6.30	− 6.23	2.54	− 6.30
Bifurcated dimer	2.40	− 2.82	− 2.84	− 2.77	2.41	− 2.84
Cyclic dimer	2.67	− 1.87	− 1.91	− 1.87	2.67	− 1.91
Trimer I[d]	2.55	−11.34	−11.46	−11.04	2.56	−11.48
Trimer II[d]	2.55	−13.02	−13.52	−13.58	2.52	−13.60
Pentamer	2.55	−22.84	−23.16	−22.44	2.56	−23.24

[a] O–O distance in Ångström units.
[b] ΔH in kcal/mole for the reaction $n\mathrm{H_2O} \rightarrow (\mathrm{H_2O})_n$.
[c] Predicted O–O equilibrium separation.
[d] See text for a discussion of the geometry of the two trimers.

Ammonia

The ammonia dimer was studied in two conformations. The first of these considers a linear hydrogen bond to be formed. The geometry is such that the Z-axis is the C_3 symmetry axis for one of the ammonia molecules and one of the hydrogens and the nitrogen of the other molecule lie on this axis. The other two hydrogens of the second ammonia molecule stagger one of the N—H bonds of the first. The experimental geometry of ammonia [11] is used for each monomer and kept fixed during interaction. We predict that the linear dimer is stable toward dissociation into two neutral molecules by 4.06 kcal/mole, the minimum occurring at an N—N distance of 2.77 Å. The experimental hydrogen bond strength is 3.7—4.4 kcal/mole [8].

The second geometry studied assumed that the three hydrogens of one of the ammonia molecules simultaneously hydrogen bond with the nitrogen lone pair of the other. The molecules are oriented in a staggered conformation. It is predicted that this mode of hydrogen bonding is much less favorable. A dissociation energy for the dimer of only 0.29 kcal/mole is found, the equilibrium N—N distance being 2.97 Å. Because of this result and the fact that the bifurcated mode in water was not favored, no further studies were made on NH_3 since the predicted mode of hydrogen bonding will almost surely be the linear one.

Hydrogen Fluoride

A good deal of experimental work has been carried out on hydrogen fluoride and there is some controversy over the type of polymeric units formed in the gas phase. Vapor density and PVT measurements by Simons and Hildebrand [12] and Long, Hildebrand, and Morrell [13] can be interpreted by assuming the presence of only monomer and hexamer units. The temperature dependence of the equilibrium constant for the assumed reaction 6 HF $\rightarrow (HF)_6$ indicated a ΔH value for this reaction of -41 kcal/mole. The unique stability of a hexamer can be rationalized by assuming the formation of a ring structure.

Electron diffraction studies carried out by Bauer, Beach, and Simons [14] cannot be interpreted by assuming only hexamer and monomer are present. Moreover, there is little or no evidence at all for a ring-hexamer being present in significant concentrations. The electron diffraction data shows a strong peak at about 2.56 Å, small humps at 1.56, 3.42, and 3.95 Å, and a pronounced broad peak at 4.84 Å, which is less intense than that at 2.56 Å. These facts are interpreted as showing the presence of dimer, trimer, and possibly higher polymeric units existing in a zig-zag chain with an F—F distance of about 2.55 Å and an FFF or HFH angle of 140 ± 5 degrees.

Calculations were made on the zig-zag dimer, trimer, tetramer, and hexamer, and also on a ring hexamer. The energy of the dimer was found to be a minimum for an HFH angle of 145 degrees and an F—F distance of 2.43 Å. The stabilization energy due to hydrogen bond formation was found to be 6.92 kcal/mole. The energy is very insensitive to the HFH angle for values larger than the predicted equilibrium angle, the stabilization energy at 180 degrees being 6.84 kcal/mole. Because of this insensitivity, an angle of 145 degrees was assumed for the zig-zag trimer, tetramer, and hexamer. The computed F—F equilibrium separations for these latter three systems were found to be 2.40, 2.39, and 2.37 Å, with stabilization energies of 15.56, 24.82, and 44.10 for trimer, tetramer, and hexamer, respectively. The average hydrogen bond strength is therefore predicted to increase as the number of units in the chain becomes larger.

The ring hexamer was studied at several F—F distances, the minimum energy occurring at a value of 2.34 Å and a stabilization of 56.61 kcal/mole. This value is considerably larger than that found for the chain hexamer, so that on the basis of enthalpic considerations it would appear that the ring hexamer should have considerable extra stabilization over the zig-zag polymer units. Entropy considerations, however, must be taken into account, and this term will eventually become dominant as successive units are added to the polymer. On the basis of the electron diffraction results, it would appear that this occurs at about the tetramer or pentamer and therefore any hexamer formed will be in small concentration except perhaps at low temperatures. Also, ΔS for formation of the ring hexamer will be much more negative than for formation of the open zig-zag chain. A knowledge of the vibrational frequencies of the polymeric forms of HF are necessary for computation of the entropy, and these frequencies are difficult to estimate so that nothing more can be said at the present time due to lack of experimental data.

A summary of the results for HF is given in Table 2. It is seen that the predicted F—F internuclear separations are about 10 percent too low in comparison with the electron diffraction results. Also, the predicted hydrogen bond strengths seem somewhat too large. Since this is also true in water, it is reasonable to assume that this is a general feature of the CNDO/2 method which could probably be corrected by slight changes in parameterization.

Table 2. *Computed results for hydrogen fluoride*

Polymer	R_0[a]	$\Delta E(R_0+0.05)$[b]	$\Delta E(R_0)$	$\Delta E(R_0-0.05)$	R_{eq}[c]	$\Delta E(R_{eq})$
Dimer	2.45	− 6.68	− 6.90	− 6.87	2.43	− 6.92
Trimer	2.40	−15.26	−15.56	−15.18	2.40	−15.56
Tetramer	2.40	−24.05	−24.78	−24.58	2.39	−24.82
Chain hexamer	2.37	−43.16	−44.10	−43.21	2.37	−44.10
Ring hexamer	2.35	−55.16	−56.59	−55.78	2.34	−56.61

[a] F–F distance in Ångström units.
[b] ΔH in kcal/mole for the reaction $n\mathrm{HF} \rightarrow (\mathrm{HF})_n$.
[c] Predicted F–F equilibrium separation.

Ammonium Ion and Methyl-Ammonium Ion Water Systems

It is of particular interest to examine the interaction of the ammonium and methyl-ammonium ions with water in view of the importance of the quaternary amines in biological phenomena, such as the interaction of many drug molecules with receptor sites. Unfortunately, it is difficult to compare computed and experimental results. The heat of hydration of the ammonium ion is known to be −79 kcal/mole [15]. Pearson and Vogelsong [16] have estimated that the heat of hydration of the tetramethyl ammonium ion is −48 kcal/mole and have concluded on this basis that substitution of a methyl group for a proton raises the heat of hydration of the quaternary amines by 8 kcal/mole for each such group. Thus, these investigators estimate the heat of hydration of $CH_3NH_3^+$ as −71 kcal/mole. An alternate approach is to assume that the interaction energy between a methyl group in the amine and the surrounding aqueous medium is −12 kcal/mole.

Calculations were first carried out on the NH_4^+ ion. It was assumed that because of the large positive charge on the hydrogen nuclei, the initial interactions of this ion with the water lead to the formation of strong hydrogen bonds between these protons and the oxygen atoms of four water molecules. Hydrogen bonding was assumed to be linear with the N—H---O hydrogen bond axis bisecting the HOH angle of the water molecules. The N—H---OH_2 group was assumed to be in a plane. A minimum in the energy was found at an N—O distance of 2.49 Å, the N—H separation being 1.05 Å. The computed stabilization energy of the complex was −89.04 kcal/mole, or −22.26 kcal/mole for each bonded water molecule. An approximate comparison with experiment can be made by assuming that four water-water hydrogen bonds must be broken to form the complex. Assuming a value of 5.5 kcal/mole for the energy of the latter hydrogen bond, the energy for the reaction of NH_4^+ with four waters, ignoring effects other than direct hydrogen bond formation is −67 kcal/mole. We must now include the interaction of the complex with the aqueous medium through various dipole-dipole, dipole-induced dipole, and dispersion terms. It is not unreasonable to assume that these amount to the difference between the computed and experimental heat of hydration, and for later convenience we assume that these interactions contribute -12 kcal/mole.

Calculations were next carried out on the $CH_3NH_3^+-H_2O$ system. The protons bonded to the nitrogen nucleus again carry a large positive charge so that the initial interaction will be the hydration of these nuclei. The heat of formation of this complex was computed to be -62.00 kcal/mole at an N—O separation of 2.48 Å. Additional calculations were then carried out to investigate whether the C—H bonds are enough to lead to direct hydrogen bonding. It was found that this probably does not occur to any great extent, since the C—H—O hydrogen bond is predicted to be less stable than an HO---H bond by about 1 kcal/mole. Entropy considerations, however, may be important here. We feel it is best to assume that the interaction of the methyl group with the water medium is mainly an orientation effect on the surrounding water molecules resulting in a ΔH of -12 kcal/mole from the work of Pearson and Vogelsong. Therefore, we predict the heat of hydration of the methyl ammonium is a sum of four contributions, including the two discussed above, along with the energy required to rupture three water-water bonds (16.5 kcal) and the interaction of the $-NH_3 \cdot (3H_2O)$ portion of the molecule with the aqueous medium. The latter contribution is estimated to be -9 kcal/mole, which is three-quarters of that found for the ammonium ion complex. The total of these contributions is -66.5 kcal/mole. This is somewhat higher than the estimate of Pearson and Vogelsong, due to the fact that the hydrogen bond strength in the methyl-ammonium complex is somewhat weaker than for the ammonium ion. If the latter bond strength is carried over, we would predict a value of -66.9 kcal/mole instead of -62 for the formation of the three N—H---O bonds and a heat of hydration of -71.4 kcal/mole, which is essentially the exact estimate of Pearson and Vogelsong.

It is instructive to estimate the heat of hydration of the di- and trimethyl quaternary amines by extrapolation from the above results. If it is assumed that there is a direct relationship between the gross atomic population of the hydrogens bonded to the nitrogen nucleus and the N—H---O hydrogen bond strength, we would predict the heats of hydration of the di- and trimethyl-ammonium ions to be -58.2 and -52.6 kcal/mole, respectively. It is felt that these values are closer to reality than those predicted by adding 8 kcal/mole for each methyl group present to the ammonium ion result. A summary of computed and predicted results is given in Table 3.

Table 3. *Predicted contributions to the heat of hydration of methyl-substituted ammonium ions*[a]

Quaternary amine	NH—O Hydrogen bonding	Water-water cleavage	$NH—OH_2$ Medium interaction	Methyl group contribution	Total
NH_4^+	-89.0	$+22.0$	-12.0	—	-79.0
$CH_3NH_3^+$	-62.0	$+16.5$	-9.0	-12.0	-66.5
$(CH_3)_2NH_2^+$	-39.2	$+11.0$	-6.0	-24.0	-58.2
$(CH_3)_3NH^+$	-19.1	$+5.5$	-3.0	-36.0	-52.6
$(CH_3)_4N^+$	—	—	—	-48.0	-48.0

[a] All values are in units of kcal/mole.

Methanol

Extensive calculations have been carried out on various methanol dimers since experimental evidence [17–19] seems to indicate that this species has a cyclic structure. The linear dimer was first studied and the predicted hydrogen bond strength was found to be −6.52 kcal/mole at an O—O separation of 2.53 Å, slightly lower than the value of −6.30 kcal/mole found for the linear water dimer. This result is in good agreement with experimental measurements of −4.0 to −6.7 kcal/mole [8]. Internal rotation about O—H---O bond is predicted to be free within perhaps ±0.02 kcal/mole.

The cyclic dimer was next studied thoroughly. Three parameters were considered to be the most important variables. These are the O---H distance, the HO---H angle, α, and the angle, β, between the O—C bond and the plane containing the four atoms participating in the hydrogen bonding. One methyl group is taken to lie above and one below this plane. The minimum energy computed leads to a stabilization of the dimer of 2.55 kcal/mole at an O---H distance of 1.93 Å and an H—O---H angle of 75 degrees, with the O—C bonds lying in the plane. There is no evidence, therefore, that the methanol dimer is cyclic. Since the calculations on water gave a similar result, and these are in agreement with the *ab initio* studies for the relative energies of linear, cyclic, and bifurcated dimers, we feel that the computed result has some merit. It must be realized, however, that the SCF studies on water were made with a small basis set and that configuration interaction will probably be more important in the cyclic dimer than in the linear form. The evidence against the cyclic dimer is, therefore, far from conclusive.

Table 4. *Computed results for methanol*

Polymer	R_0[a]	$\Delta E(R_0+0.05)$[b]	$\Delta E(R_0)$	$\Delta E(R_0-0.05)$	R_{eq}[c]	$\Delta E(R_{eq})$
Linear dimer	2.55	−6.29	−6.50	−6.49	2.53	−6.52
Cyclic dimer $\alpha=60^\circ, \beta=0^\circ$	2.05	−1.93	−1.98	−1.97	2.03	−1.98
Cyclic dimer $\alpha=75^\circ, \beta=0^\circ$	1.95	−2.50	−2.55	−2.54	1.93	−2.55
Cyclic dimer $\alpha=90^\circ, \beta=0^\circ$	2.00	−1.96	−2.04	−2.04	1.97	−2.05
Cyclic dimer $\alpha=75^\circ, \beta=30^\circ$	1.95	−2.31	−2.33	−2.27	1.96	−2.33
Tetramer	2.55	−23.30	−23.90	−23.65	2.54	−23.92

[a] The O—O distance (Å) for the linear dimer and tetramer, and the O---H distance (Å) for the cyclic dimer.

[b] ΔH is kcal/mole for the reaction $n\mathrm{CH_3OH} \rightarrow (\mathrm{CH_3OH})_n$.

[c] Predicted equilibrium separation.

Experimental studies [20] have indicated the presence of a tetramer in methanol vapor with a heat of formation of −24.2 kcal/mole. We assume that this polymer has a cyclic structure involving four hydrogen bonds, with the oxygen atoms lying at the corners of a square. The hydrogen bonding is taken to be of the linear type, and the carbon atoms of the methyl groups are assumed to be in the plane formed by the four oxygen and four hydrogen atoms participating in the hydrogen bonding. The heat of formation of the tetramer was computed to be −23.92 kcal/mole at an O—O separation of 2.54 Å, in good agreement with the experimental result. A summary of the computed results for methanol is given in Table 4.

Formic Acid and Acetic Acid

The dimerization of organic acids has been extensively studied and much experimental data is available [8]. It is well established that the dimers of both formic and acetic acid are cyclic, with an O—O separation of about 2.70 Å in the gas phase [21], with enthalpies of formation of about −14.2 and −15.0 kcal/mole. Calculations were carried out on both of these acid dimers leading to a computed enthalpy of formation of −22.96 kcal/mole for formic acid and −23.62 kcal/mole for acetic acid. The O—O equilibrium separation in each case was predicted to be 2.42 Å. These results are considerably worse than those described previously and would seem to imply that the parameterization of the CNDO/2 method is somewhat inadequate for prediction of hydrogen bonding in which carbonyl oxygen atoms participate. It is apparent that choosing the same valence-state electronegativities for both an alcohol and carbonyl oxygen atom is not valid. It is also likely that some adjustment should be made in the bonding parameters to further differentiate those two states of oxygen hybridization. This will be extremely important in a consideration of biological phenomena in which carbonyl oxygen can play a significant role in drug-receptor interactions. These effects were not noted by Pullman and Berthod [4] in their study of the dimetrization of formamide since the energy of the dimer was computed with the experimental geometry in which the O—H bond distance is considerably longer than would be predicted by a variation of this distance.

Hydrogen Cyanide

A consideration of dimer formation in HCN resulted in a definite and absolute failure of the CNDO/2 method in its present form. The use of the Pople-Segal parameters for carbon and nitrogen for the state of hybridization present in HCN is inadequate. The calculations predict that HCN will form a "sandwich" dimer with the nitrogen of one HCN molecule directly below the hydrogen of the other and vice versa. The computed enthalpy of dimerization, about −50 kcal/mole, can be compared to the experimental heat of dimerization of −3.3 kcal/mole [22]. It is evident some adjustment in the present method must be made if it is to cope with this and similar systems.

Discussion

The results obtained in this study are, for the most part, quite encouraging. It would seem that the CNDO/2 method in its present form is capable of at least qualitative prediction of hydrogen bonding phenomena except for the carbonyl systems and hydrogen cyanide. The computed hydrogen bond strengths for water

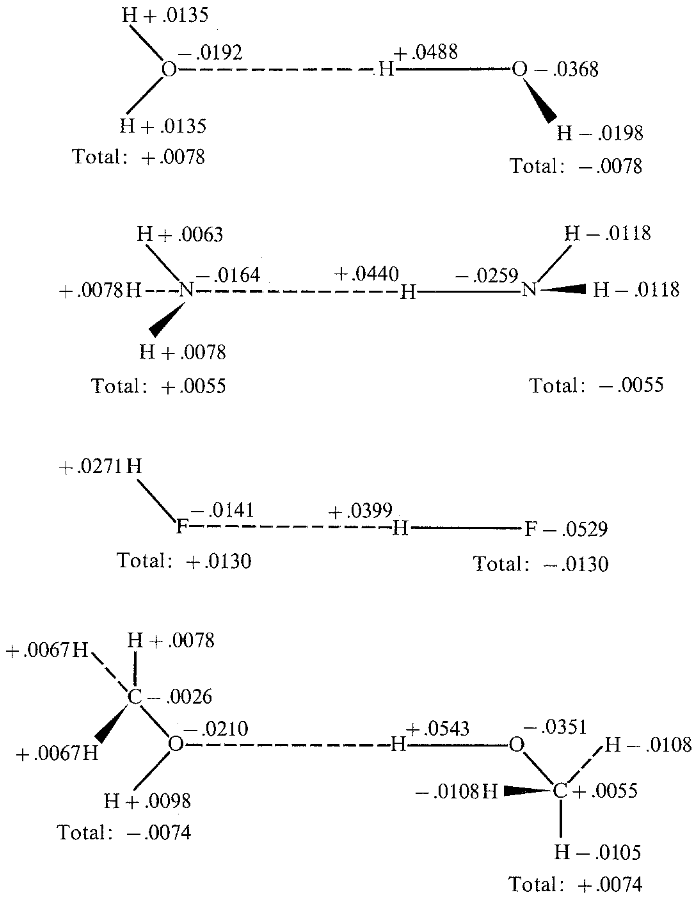

Fig. 1. Charge shift in dimer formation

and methanol are reasonable, although probably a little large. Likewise, the O---H equilibrium distances seem too small by about 10 percent. Some slight adjustment in parameterization could probably be made to overcome these shortcomings. The computed results for NH_3 are in good agreement with experiment so that no adjustment of the nitrogen parameters in the ammonia valence state seem to be called for. The case of HF is similar to that of water and methanol, in that equilibrium distances are too small and hydrogen bond strengths too large. An adjustment of the fluorine bonding parameter should result in better agreement with available data.

Further work should be carried out on the organic acids in which the use of a single oxygen parameterization is definitely not a good assumption. Also, the HCN calculations indicate additional study of the valence-state electronegativity and bonding parameters for highly unsaturated molecules.

Figs. 1 and 2 give a summary of the charge shifts which are predicted to occur in hydrogen bonding for several of the systems studied. A positive value indicates an electron deficiency at the nucleus in question in comparison with the free molecule. Examination of the total charge shifts from the dimers of H_2O, NH_3, HF, and CH_3OH indicates that there is a small amount of charge transferred from the acceptor to the donor molecule, and that, in general, the trend appears to indicate that the amount of charge transfer is related to the hydrogen bond strength. A much larger charge transfer has been noted by Morokuma and Pedersen [2] in their SCF calculations. The results computed here would seem to indicate that the approach of a proton will tend to give slightly larger weight to ionic configurations in the acceptor and donor of the type $H^{+}\text{—}X^{-}\text{---}H$ and $H\text{—}X\text{--}H^{+}\text{—}X^{-}$, and a small amount of charge transfer structures such as $H\text{—}X^{+}\text{---}H\text{—}X^{-}$, $H\text{—}X^{+}\text{---}H\text{—}X\diagup^{H^{-}}$, etc. The latter structure appears to be fairly important in water and ammonia.

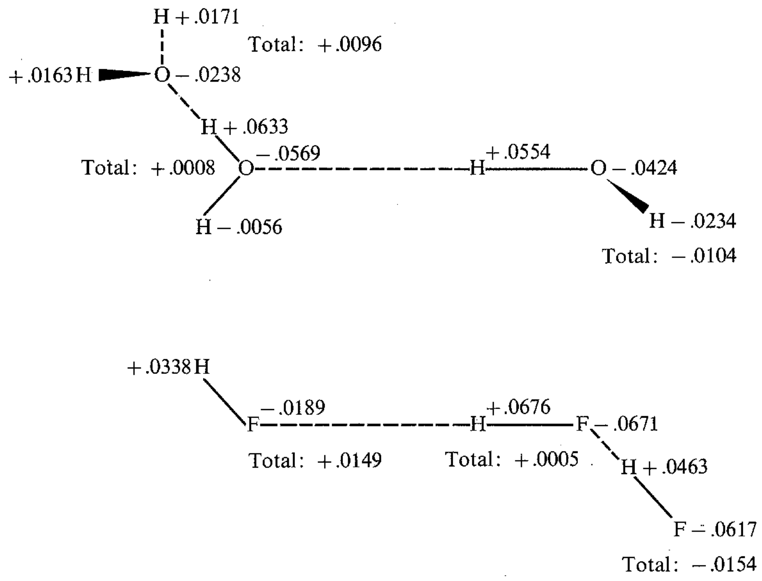

Fig. 2. Charge shift in trimer formation

The charge shifts in the trimers of water and HF are larger than in the dimers and a greater amount of charge transfer is noted. This transfer is from the molecule acting solely as an acceptor to the molecule acting solely as a donor. The central molecule which acts as both donor and acceptor is more highly polarized than in the free state but is otherwise unaffected by the charge transfer.

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Note Added in Proof: After this manuscript was completed Murthy, Davis, and Rao published a study of hydrogen bonding in methanol and formic acid [Theoret. chim. Acta (Berl.), **13**, 81 (1969)]. We find general agreement between our results and theirs for methanol but we cannot reproduce their values for the cyclic dimer of formic acid.

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