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Localized Orbital Studies of Hydrogen Bonding. II. Dimers Containing H_2O, NH_3, HF, H_2CO, and HCN

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Abstract: INDO localized molecular orbitals (LMO's) are utilized for investigating the nature of intermolecular hydrogen bonding in the fully geometry optimized dimers $(HF)_2$, $(H_2O)_2$, $(NH_3)_2$, FH-OH_2, HOH-FH, FH-NH_3, H_2NH-FH, H_2O-HNH_2, HOH-NH_3, HCN-HF, and H_2CO-HF. The results suggest that a reasonable measure of relative hydrogen bond strengths should be the intrabond, two-center, one-electron interference energy connecting the acceptor atom and donated proton. This approach views the net stabilization energy of a hydrogen bonded dimer as arising from a large energy decrease due to formation of the hydrogen bond, modified by smaller energy increases due to internal decreases in monomer bond energies upon formation of the dimer. Hydrogen bond stabilization appears to be closely related to the extent of charge transfer within the hydrogen bonded complex. The calculated transfer of charge can largely be explained in terms of electron density shifts within the acceptor lone pairs, while the decrease in electron density on the proton is discussed in terms of the donor XH bond. The approach presented should be particularly useful for analyzing intramolecular hydrogen bonding systems where the hydrogen bond energy is not simply obtainable from monomer-dimer energy differences.

I. Introduction

There has been considerable literature recently involving the application of quantum mechanics to the study of hydrogen bonding. Most of these investigations have been on the molecular orbital level (*ab initio*[2-15] or semiempirical[2,16,17]) and primarily concerned with elucidating the nature of *inter*molecular hydrogen bonding. Our understanding of the hydrogen bond has been vastly improved by this effort; however, the computational results on systems capable of forming *intra*molecular hydrogen bonds are few in comparison. Pople and coworkers carried out minimal basis *ab initio* calculations on a series of 1,2-disubstituted ethanes;[18] however, their effort was mainly concerned with the possibility of attractive 1,3 interactions in particular molecular conformations and the stability of such conformations relative to those in which hydrogen bonding is unlikely. While these authors concluded that hydrogen bonding stabilizes a configuration, little attempt was made at formulating a quantitative measure of the strength of these hydrogen bonds. Johansson, Kollman, and Rothenberg[19] studied intramolecular hydrogen bonding in ethylene glycol using an STO 3G basis set.

In fact, aside from sheer molecular size, the major difficulty in calculations on intramolecularly hydrogen bonded systems is to find an energy quantity which can be associated with a hydrogen bond energy, at least on a relative scale. For an intermolecular system, the problem is simple since the hydrogen bond energy is just the difference in energy between the dimer and separated monomers. Unfortunately, such a simple approach is not applicable when there is only one molecule, the complex, to consider.

Attempts have been made[16,19] to estimate the energy associated with an intramolecular hydrogen bond using the energy difference between the complex and some "nonhydrogen-bonding" conformation of the same molecule. While there is some merit in this approach, it suffers from the assumption that all of the energy difference between the two conformations may be attributed to the formation of the hydrogen bond.

In the present work an attempt is made, on the basis of calculations on small hydrogen-bonded dimers, to define an energy quantity which correlates with the calculated hydrogen bond energies on the one hand, and which is accessible in a calculation on an intramolecular complex on the other. The intermolecular systems are used as a starting point for the very reason stated above: the energy differences in these cases *are* available for comparison.

To carry out the analysis use is made of localized molecular orbitals[20] (LMO's) obtained from INDO[21] canonical orbitals. Although a semiempirical method is used in the present work to simplify the calculations, the basic approach is extendable to nonempirical methods. The use of localized orbitals aids the calculation and analysis by providing a theoretical description of the bonds in the monomers and of the way in which these bonds change on formation of a hydrogen-bonded complex. Further, since hydrogen bonding is often thought of as interaction between a donor hydrogen and an acceptor lone pair, analysis of the LMO's provides a convenient means of investigating such characteristics as hybridization and availability of lone pairs, hydrogen bond strength *vs.* dipole moment enhancement relationships, and changes in lone pair electron density distributions on hydrogen bond formation.

All of the complexes studied in the present work have been subjected to previous MO calculations, either *ab initio*[2-15] or semiempirical[2,16,17] or both; however, two aspects of the present study seem to be unique. First, little use has been made previously of the application of energy localization to the study of hydrogen bonding, while, as stated above, we feel an analysis using LMO's should be particularly useful. Second, while hydrogen-bond calculations typically include optimization of the *relative* geometries of the monomers in the dimer, relaxation of the *internal* geometry of the monomers on dimer formation is rarely taken into account. The latter is of interest in this study, particularly with regard to the lengthening of the X-H bond of the donor molecule. The specific dimers chosen for this investigation are $(HF)_2$, $(H_2O)_2$, $(NH_3)_2$, $FH\text{-}OH_2$, $HOH\text{-}FH$, $FH\text{-}NH_3$, $H_2NH\text{-}FH$, $H_2O\text{-}HNH_2$, $HOH\text{-}NH_3$, $HCN\text{-}HF$, and $H_2CO\text{-}HF$. (It should be noted that Pople and coworkers[22] have recently considered monomer geometry relaxation in the first nine of these dimers, using the minimal basis STO-3G method.)

II. Method of Calculation

All calculations were carried out using the well-known INDO-MO method in the original parametrization.[21] For each complex, the optimal geometry of the separate monomers was first obtained, these results being used as an initial guess for the internal geometries in the dimers. The initial relative geometry of the two monomers in the dimer was chosen by comparison with previous nonempirical calculations where available and by using intuitive guesses in other cases. In all cases only linear dimers (as opposed to bifurcated, etc.) were investigated since these have been shown to generally be the most stable for these simple systems. Initially, a linear X-H---Y hydrogen bond was assumed; however, all geometric parameters were allowed to vary, and thorough searches were made for local minima within the restriction of a linear complex. The geometry optimizations were carried out using an adaptation of Powell's conjugate directions method[23] using initial (maximum) step sizes of 0.01 Å (0.1 Å) and 0.1° (1.0°).

The localized orbitals were obtained by the energy localization technique developed by Edmiston and Ruedenberg[20] and analyzed by the localized charge distribution analysis proposed by England and Gordon.[24] Of particular interest with regard to this analysis is the relationship between the nature of the chemical bond and the two-center, one-electron interference energy. This relationship, first discussed in detail by Ruedenberg[25] and later by England and Gordon[24] and Moffat and coworkers,[26] will be heavily relied upon in the subsequent discussion; thus a preliminary discussion of this interference energy is useful here. As pointed out by Ruedenberg,[25] the electron density, ρ, may be thought of as a sum of quasi-classical and interference contributions

$$\rho = \rho^{\mathrm{QC}} + \rho^{\mathrm{I}} \qquad (1)$$

where the quasi-classical contribution, ρ^{QC}, represents the electronic distribution among the atoms of a molecule in the absence of electronic wave character and sums to the actual electron density (N) in the molecule

$$\int \rho^{\mathrm{QC}}(1)\mathrm{d}V_1 = N \qquad (2)$$

while the interference density, ρ^{I}, takes into account the fact that, quantum mechanically, one adds waves (orbitals) first and not densities. Thus ρ^{I} is purely quantum mechani-

$$\int \rho^{\mathrm{I}}(1)\mathrm{d}V_1 = 0 \qquad (3)$$

cal in nature and sums to zero over all space as it must. As a result of this partitioning of the electron density, the one-electron energy of a molecule may be thought of as a sum of quasi-classical and interference contributions

$$E_1 = E_1^{\mathrm{QC}} + E_1^{\mathrm{I}} = \int \rho^{\mathrm{QC}}(i)\hat{h}(i)\mathrm{d}V_i + \int \rho^{\mathrm{I}}(i)\hat{h}(i)\mathrm{d}V_i \qquad (4)$$

where $\hat{h}(i)$ is the one-electron part of the hamiltonian operator (excluding repulsion operators). Ruedenberg partitioned the pair density in a similar way; however, he draws the pertinent conclusion that the two-center, one-electron interference energy, E_1^{I}, is the "primordial" source of covalent bonding in molecules.[25] This is particularly important since within the INDO approximations, all pair interference energies vanish, the total interference energy reducing to

$$E^{\mathrm{I}} = \sum_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mu}^{\mathrm{A}} \sum_{\mathrm{v}}^{\mathrm{B}} P_{\mu\mathrm{v}}\beta_{\mathrm{AB}}{}^{\circ}S_{\mu\mathrm{v}} = \sum_{\mathrm{A}} \sum_{\mathrm{B}<\mathrm{A}} \beta(\mathrm{A,B}) \qquad (5)$$

where, for a closed-shell, single-determinant wave function

$$P_{\mu\mathrm{v}} = 2\sum_{i}^{\mathrm{occ}} C_{\mu i}C_{\mathrm{v}i} \qquad (6)$$

is the "bond order" between a pair of atomic orbitals χ_μ (on atom A) and χ_v (on atom B), $S_{\mu\mathrm{v}}$ is the corresponding overlap integral, and $\beta_{\mathrm{AB}}{}^{\circ}$ is a semiempirical interference parameter (more commonly referred to as a resonance parameter). E^{I} may be written as a sum of contributions from the occupied molecular orbitals ϕ_i.

$$E^{\mathrm{I}} = \sum_{i}^{\mathrm{occ}} E_i{}^{\mathrm{I}} = \sum_{i}^{\mathrm{occ}} \sum_{\mathrm{A}} \sum_{\mathrm{B}<\mathrm{A}} \beta_i(\mathrm{A,B}) \qquad (7)$$

where

$$\beta_i(\mathrm{A,B}) = 4\sum_{\mu}^{\mathrm{A}} \sum_{\mathrm{v}}^{\mathrm{B}} C_{\mu i}C_{\mathrm{v}i}S_{\mu\mathrm{v}}\beta_{\mathrm{AB}}{}^{\circ} \qquad (8)$$

When the ϕ_i are localized orbitals, $\beta_i(\mathrm{A,B})$ corresponds to the interference energy (constructive or destructive) between a pair of atoms, A-B, within a particular bond or lone pair. Clearly, in this case, by far the greatest amount of constructive interference between a pair of bonded atoms will occur within the corresponding bond orbital. From this point of view, there are two interference energies which one might reasonably expect to correlate with calculated or experimental hydrogen bond energies: the total two-center, one-electron interference energy involving the proton and acceptor atom, $\beta(\mathrm{Y}\cdots\mathrm{H})$, and the interference between the same pair of atoms, but within those LMO's corresponding to the hydrogen bond. A preliminary investigation of the water dimer[16] indicated the former to be a more quantitative estimate of the hydrogen bond energy. A more complete analysis of these two possibilities is given in section V of the present paper.

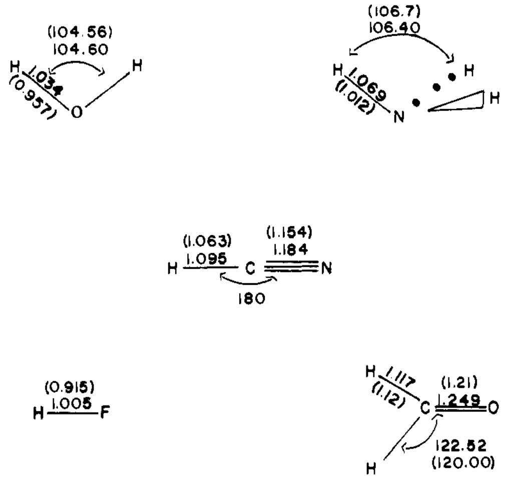

Figure 1. Monomer geometries: bond lengths in Å, angles in degrees. Experimental values in parentheses.

III. Results

A. Geometries. The optimized geometries of the five monomers under investigation are compared with experiment in Figure 1. The INDO geometries of these molecules have

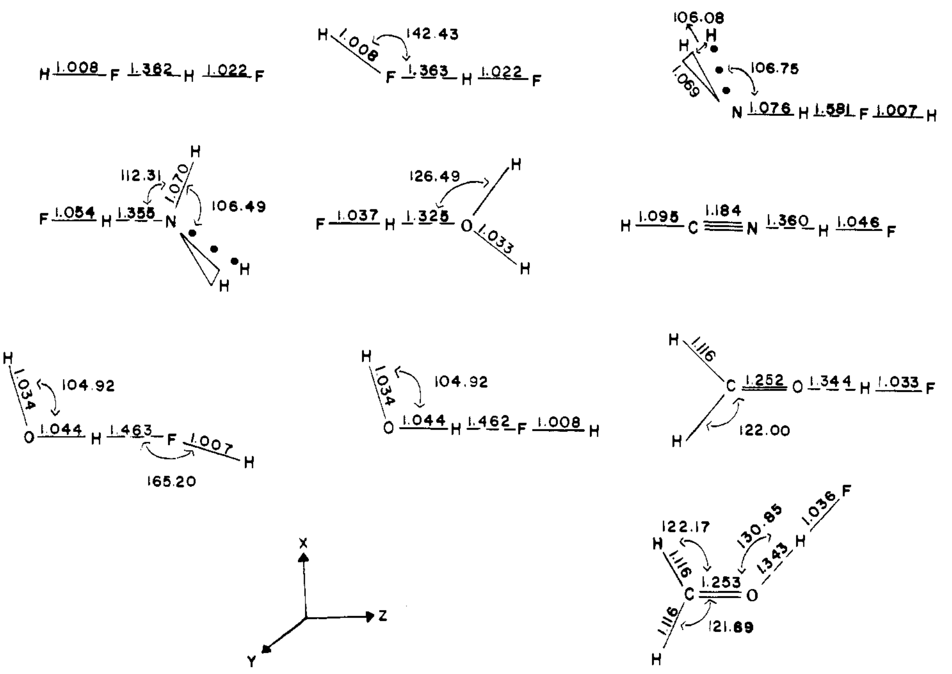

Figure 2. Geometries of dimers containing HF (bond lengths in Å, angles in degrees).

been reported previously[27] and are in reasonable agreement with experiment. The predicted bond lengths are generally off in the second decimal place, while bond angles are reproduced rather well.

The optimal geometries of dimers containing HF are shown in Figure 2. As has been noted previously, the lengths of hydrogen bonds are systematically underestimated by this method,[2] and it appears that the underestimation of the X···Y bond lengths is amplified by complete geometry optimization. In other respects, however, the geometries of these dimers are similar to those predicted by previous calculations. Where HF is the proton donor, the HF bond is seen to lengthen, the effect being greatest in H_3N-HF and smallest in $(HF)_2$. The latter is predicted to have two stable geometries, the bent being slightly (0.23 kcal) more stable than a completely linear molecule although the HFH angle is about 20° larger than that predicted by Klemperer and coworkers.[28] A similar situation is found for H_2CO-HF, where the bent molecule is more stable than linear CO---HF by 0.84 kcal. It should be noted that in $(HF)_2$ and H_2CO---HF, INDO predicts local geometric minima which are not found by *ab initio* calculations. In general, it is found that the present method tends to stabilize locally linear [$(HF)_2$, H_2CO---HF, H_2NH---FH] or locally planar (H_2O---HF) geometries. In subsequent energy analyses of these molecules only the most stable geometry will be considered.

The HCN-HF dimer is predicted to be linear as one would expect. This result is particularly interesting in view of the fact that CNDO, without reoptimization of monomer geometry, predicts an angle of 135° between the two monomers.[3] To test our result, an initial angle of 90° was chosen and a monotonic decrease in energy was found between 90 and 180°. The increase in the H-F bond length on formation of this dimer (0.041 Å) is considerably larger than the 0.007 Å found by Curtiss and Pople.[15]

For H_2NH-FH, the initial HFH angle was taken to be nonlinear and a number of dihedral angles were investigated. In all cases, on geometry optimization the final HFH angle was within 3° of 180° with little effect observed due to internal rotation. Restricting NHFH to linear results in an increase in energy of only 2×10^{-6} au, and in subsequent calculations linearity of HNFH is assumed. Similar results are obtained for HOH-FH, for which the bent trans structure is more stable than the partially linear structure by 0.02 kcal. Here too internal rotation has little effect, although the cis structure is unstable and results in an HFH angle of 180°. Finally, in all dimers involving HF the deviation of the hydrogen bond itself from linearity is negligible.

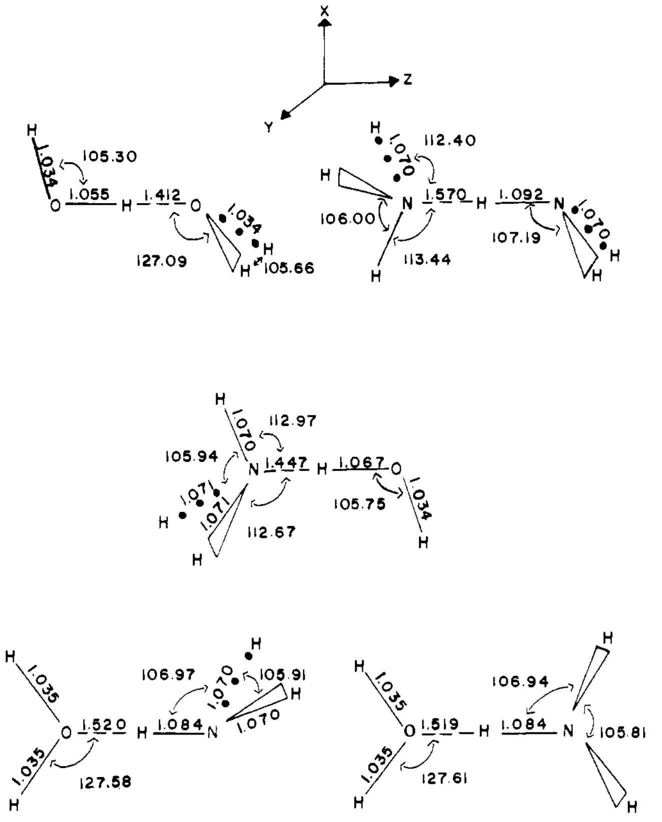

Figure 3. Geometries of $(H_2O)_2$, $(NH_3)_2$, H_2O---HNH_2, and H_3N---HOH (bond lengths in Å, angles in degrees).

The geometries of the remaining dimers studied are depicted in Figure 3. Again, the length of the hydrogen bond

Table I. Comparison of INDO, Experimental, and *ab initio* Hydrogen Bond Energies

A[a]	D[b]	ΔE, kcal Exptl[c]			R[e]	q(H)[f]	μ(1p)[g]
		Exptl[c]	*Ab initio*[d]	INDO			
H_3N	HF		11.7	31.9	0.37	0.268	3.64
HCN	HF		5.8	28.3	0.20	0.268	3.28
H_2O	HF		9.4	24.9	0.38	0.268	3.04
H_2CO	HF			22.4		0.268	2.79
H_3N	HOH		5.8	18.2	0.32	0.166	3.64
HF	HF	6.8	4.6	14.9	0.31	0.268	2.55
H_2O	HOH	5.0	5.3	14.1	0.37	0.166	3.04
H_3N	HNH_2	4.4	2.7	9.3	0.29	0.087	3.64
HF	HOH		3.0	7.8	0.38	0.166	2.55
H_2O	HNH_2		2.3	7.4	0.31	0.087	3.04
HF	HNH_2		1.3	3.7	0.35	0.087	2.55

[a] Proton acceptor. [b] Proton donor. [c] Reference 17 of text. [d] From Kollman and Allen, ref 2 of text, except HCN---HF (ref 29 of text). [e] Ratio of *ab initio* and INDO results. [f] Proton charge in free donor. [g] Lone pair dipole moment in free acceptor (D).

is underestimated, the donor X-H bond is lengthened on dimer formation, and the dimers are stable to deviations of the hydrogen bond from linearity.

Except for HCN···HF,[15] STO-3G calculations[22] generally predict little or no stretching of the XH bond on dimer formation. The largest increase calculated in the latter paper is 0.002 Å, and in some cases R_{XH} was found to decrease. Although it is likely that INDO overestimates the increase in R_{XH}, the STO-3G results are not in keeping with decreased XH vibrational frequencies normally attributed to hydrogen bonding.

The structure of the water dimer is identical to that discussed in a previous paper.[16] For $(NH_3)_2$ both eclipsed and staggered geometries were investigated, the latter being more stable by only 6×10^{-6} au. A structure in which the proton donor is planar is less stable by 7.9 kcal. Essentially free rotation is also found for H_3N-HOH. H_2O-HNH_2 has two stable geometries with nearly equal energy: one in which an OH bond bisects the HNH angle and one in which both amino hydrogens are above the HOH plane with C_s symmetry. The former is only 0.02 kcal more stable.

B. Hydrogen Bond Stabilization Energies. The INDO calculated stabilization energies due to hydrogen bonding, ΔE, are listed in Table I for the dimers discussed above. Here ΔE is defined as

$$\Delta E = \sum_i E_i^\circ - E_{\text{dimer}} \tag{9}$$

where E_i° is the energy of the ith isolated monomer. The few experimentally available hydrogen bond energies are also listed in Table I. Since so few of the latter are available, the INDO results are also compared with a series of nonempirical calculations by Kollman and Allen.[2] While more accurate calculations on many of these dimers have been carried out[2,5] those by Kollman and Allen are the most consistent with regard to size of basis set and level of accuracy. The only molecules in Table I not studied by these authors are HCN---HF and H_2CO---HF. For the former we have quoted the result of a recent Gaussian calculation by Johansson, Kollman, and Rothenberg.[29] No *ab initio* calculation on the latter dimer has been carried out to our knowledge.

As has been pointed out before,[2] INDO tends to over-estimate stabilization due to hydrogen bonding. This is consistent with the corresponding under-estimation of intermonomer bond lengths discussed above, and is amplified by the fact that complete relaxation of monomer geometries was allowed in the present dimer calculations. This, of course, will stabilize the dimer relative to the isolated monomers.

Even though the INDO results are too high, the trends predicted by the more accurate calculations are reasonably reproduced, as can be seen from the nearly constant ratios of the two sets of calculations (column 6 of Table I). The only dimer seriously out of order is HCN---HF. The STO-3G calculations[22] predict the same trends and similar magnitudes to those of Kollman and Allen.[2]

Relative hydrogen bond strengths have often been correlated in a qualitative way with the net (positive) charge on the donor proton and the "availability" of the acceptor lone pair. From a purely electrostatic point of view, the greater the positive charge on the proton to be donated, the better the donor. From a valence bond point of view, the more available (less tightly bound) the acceptor lone pair is for bonding, the stronger the hydrogen bond. On this basis one would expect HF to be the best proton donor, and, in fact, this is borne out by comparison of columns 5 and 7 of Table I, where it is seen that the four most stable dimers have HF as the donor, the latter molecule having the largest proton charge. As expected, this approach predicts the donating strength to decrease in the order HF > H_2O > NH_3.

Lone pair availability is a more elusive property; however, a relative measure of this is provided by the lone pair dipole moment, since the more tightly held the lone pair, the smaller its dipole moment is expected to be. As discussed in previous papers,[16,30] localized molecular orbitals[20] provide a means of obtaining lone pair dipole moments, and those for the acceptors are listed in the last column of Table I. As expected, the lone pair availability decreases in the order N > O > F, exactly opposite from the trend of donor proton charge when these atoms are attached to the donated proton in a proton donor. Further, the nitrogen lone pair in NH_3 has a greater dipole moment than that in HCN, while the oxygen lone pair moment is greater in H_2O than in H_2CO. In both cases these results correlate with the calculated trends in ΔE. It is also interesting to note that ΔE seems to be more sensitive to the charge on the donated proton than to the lone pair dipole moment [*e.g.*, $\Delta E(H_2O\cdots HF) > \Delta E(H_3N\cdots HOH)$].

IV. Analysis of Lone Pair and XH Bond LMO's

Two aspects of hydrogen bonding which have received considerable attention are the charge redistribution on formation of the hydrogen bond and the orientation of the acceptor lone pair(s) relative to the position of the proton. Generally, for an X-H---Y hydrogen bond, X gains electron density and H loses electron density on hydrogen bond formation.[2] Further, Del Bene[6] has argued that the relative orientations of the monomers is usually determined by a tendency for the donor proton to be nearly colinear with an acceptor (Y) lone pair (the generalized hybridization model). Some light may be shed on both of these concepts by investigating the changes which occur in the Y lone pair(s) and XH bond orbitals when the hydrogen bond is formed.

Table II. Analysis of Acceptor Lone Pair and X–H Bond Orbital

A[a]	D[b]	$\Delta P_H(lp)$[c]	$\Delta P_H(XH)$[d]	ΔP_H[e]	$\Delta P_X(XH)$[f]	ΔP_X[g]	$\Delta\mu(lp)$[h]	α[i]
H_3N	HF	0.1477	−0.1565	−0.0079	0.1442	0.1629	0.85	0.0
HCN	HF	0.1215	−0.1349	−0.0123	0.1201	0.1357	0.77	0.0
H_2O	HF	0.0892	−0.1223	−0.0247	0.1102	0.1265	0.09	60.5
H_2CO	HF	0.0912	−0.1156	−0.0238	0.1077	0.1232	0.58	10.3
H_3N	HOH	0.0836	−0.1246	−0.0399	0.1170	0.0976	0.64	0.1
HF	HF	0.0463	−0.0819	−0.0274	0.0754	0.0868	−0.02	88.4
							0.21	39.2
H_2O	HOH	0.0497	−0.1015	−0.0469	0.0913	0.0758	0.06	64.0
							0.10	57.3
H_3N	HNH_2	0.0402	−0.0829	−0.0421	0.0781	0.0618	0.42	0.0
HF	HOH	0.0121	−0.0659	−0.0389	0.0588	0.0483	0.04	60.6
H_2O	HNH_2	0.0244	−0.0734	−0.0461	0.0649	0.0488	0.06	60.8
HF	HNH_2	0.0093	−0.0477	−0.0357	0.0418	0.0292	0.0	75.2

[a] Proton acceptor. [b] Proton donor. [c] Electron density gained by H-bond proton from acceptor lone pair(s). [d] Electron density lost by H-bond proton in XH bond. [e] Net electron density lost by H-bond proton. [f] Electron density gained by donor atom (X) in XH bond. [g] Net electron density gained by X. [h] Increase in acceptor lone pair dipole moment(s), debye. [i] Angle between hybrid(s) of acceptor lone pair(s) and H---Y bond axis.

Columns 5 and 7 of Table II list the net changes in electron density on atoms H and X, respectively. In agreement with the results of Kollman and Allen[2] the proton generally loses electron density (ΔP_H), while the donor atom generally gains electron density (ΔP_X). While there is no obvious trend in ΔP_H, the electron density gained by X generally decreases in the same order ΔE decreases. In column 3 of Table II, it is seen that, as one would expect, the acceptor atom (Y) loses electron density to H through the Y lone pair(s) [$\Delta P_H(lp)$]. At the same time, the proton loses electron density to X due to a polarization of the XH bond [$\Delta P_H(XH)$]. The latter effect is greater, so the proton loses electron density. Note that the sum of $\Delta P_H(lp)$ and $\Delta P_H(XH)$ is greater than or equal to ΔP_H in all cases, There is a general downward trend in both $\Delta P_H(lp)$ and $\Delta P_H(XH)$ with decreasing ΔE; however, the trend is not strictly followed.

The electron density gained by X due to polarization of the XH bond [$\Delta P_X(XH)$] is listed in column 6 of Table II. Note that this value is generally nearly equal in magnitude and opposite in sign to $\Delta P_H(XH)$. In addition, comparison of columns 6 and 7 indicates that the increase in electron density on X is essentially due to the polarization of the XH bond orbital.

The lone pair dipole moment, $\mu(lp)$, may be taken as a measure of the spatial extent of the lone pair. In Table II, $\Delta\mu(lp)$ represents the change in the dipole moment(s) of the acceptor (Y) lone pair(s). One might expect the lone pair to increase in size to a greater extent, the greater the hydrogen bond stabilization energy, ΔE. While this is often the case, it is not generally true. The reason for the lack of such a general trend may be due to the orientation of the lone pair(s) relative to the proton. Let α be the angle between the H---Y bond axis and the hybrid of the appropriate lone pair(s) on Y. When Y is nitrogen α is generally 0°, indicating the lone pair is oriented directly at the proton. In general, this is not the case for other Y atoms. For example, when the proton acceptor is water, the proton generally lies between the two oxygen lone pairs and α is approximately 60°, and the increase in the spatial extent of the lone pairs is not as great. Thus, $\Delta\mu(lp)$ is seen to decrease with ΔE for lone pairs with similar spatial orientation relative to the proton. In fact, the same is true of $\Delta P_H(lp)$. It should be pointed out in this regard that since INDO tends to overemphasize local planarity or linearity in some of these dimers (see section III), the trends in quantities such as $\Delta P_H(lp)$ and $\Delta\mu(lp)$ may in fact be more regular in STO-3G *ab initio* calculations where there is a great tendency for the proton to be oriented along a particular lone pair.[6]

The value of α is of particular interest in three of these dimers. In H_2CO the oxygen lone pairs make an angle of 60.7° with the CO bond axis (the angle between the lone pairs is 121.4°). In H_2CO---HF this same angle is 60.5°, so that the orientation of the lone pair is essentially unchanged. However, the O---H-F axis makes an angle of only 50.2° with C=O, so that the angle between the lone pair and the hydrogen bond axis is 10.3°. In HF---HOH and $(HF)_2$ it might be expected (see Figure 2) that the proton is lined up along one of the three fluorine lone pairs. This is not the case in either dimer, however. In the former only one lone pair contributes (see section V) to the hydrogen bond, and it is skewed from the H---Y bond axis by about 60°. In the latter, two of the lone pairs contribute with angles of 88.4 and 39.2°. We find that the angle between acceptor lone pairs and adjacent bonds changes by less than 1° in all cases considered upon hydrogen bond formation.

Finally, it should be noted that while the major electron density shifts involve the atoms X, H, Y, changes on other atoms and in orbitals other than XH and the Y lone pairs are also significant and this may partially account for the disruption of some of the trends discussed above.

V. Analysis of the Hydrogen Bonds

As pointed out above, a quantitative theoretical measure of strengths of hydrogen bonds is difficult to obtain for *intra*molecular systems since one does not have separate energies for monomers and complex. A solution to this apparent dilemma would be to isolate some calculable energetic quantity which is both a property of the hydrogen-bonded molecule and a reasonable measure of the hydrogen-bond strength. One such quantity is the bond energy of the hydrogen bond itself, $D_{H\cdots Y}$. An approach for calculating this bond energy has been suggested in a earlier paper,[16] and is described below.

Following Ruedenberg,[25] it is assumed that the critical quantity necessary for describing covalent bonding is the two-center, one-electron interference energy [see eq 4–8]. This being the case, it is reasonable to expect the trends in bond energies to be paralleled by these interference energies. It is unlikely, however, that the interference energies will *equal* bond energies.[16,25] Therefore, to obtain a theoretical bond energy for a particular bond A-B, we introduce a normalization factor $N_{AB}{}^{\tau}$, where $N_{AB}{}^{\tau}$ is the ratio of the negative of the total interference energy and the experimental bond energy for the bond in a prototype molecule.

$$N_{AB}{}^{\tau} = -\beta(A,B)/D_{AB}{}^{\text{exptl}} \qquad (10)$$

The calculated bond energy, D_{AB}, for the same bond in any other molecule is then given by

Table III. Prototype Molecules and Normalization Factors[a]

Prototype	Bond A–B	D_{AB}^{exptl}, eV[b]	N_{AB}^{τ}	N_{AB}^{i}
CH_4	C—H	4.508	4.438	4.481
H_2O	O—H	5.161	3.773	3.875
NH_3	N—H	4.467	4.394	4.484
HF	F—H	5.897	3.406	3.338
HCN	C≡N	9.711	6.388	6.601
H_2CO	C═O	7.586	6.198	5.976
C_2H_6	C—C	3.814	8.862	7.811
C_2H_4	C═C	7.068	6.971	6.559
C_2H_2	C≡C	9.970		6.580
CH_3OH	C—O	3.948	8.203	7.365
CH_3F	C—F	4.684	6.628	6.011

[a] All calculations refer to optimized geometries of prototypes. [b] W. J. Moore, "Physical Chemistry," Prentice-Hall, Englewood Cliffs, N.J., 1972, p 72.

$$D_{AB} = -\beta(A,B)/N_{AB}^{\tau} \tag{11}$$

An alternative approach makes use of energy-localized molecular orbitals. It has been shown[30] that the contribution to the total interference energy, $\beta(A,B)$, from the LMO(s) corresponding to the bond of interest, $\Sigma_i\beta_i(A,B)$, provides a qualitative measure of CH bond energies in hydrocarbons. We refer to the latter as *intrabond* interference energies, and these too may be used to obtain calculated bond energies

$$\begin{aligned} N_{AB}^{i} &= -\sum_i \beta_i(A,B)/D_{AB}^{\text{expt}} \\ D_{AB}^{i} &= -\sum_i \beta_i(A,B)/N_{AB}^{i} \end{aligned} \tag{12}$$

where the sum is over all LMO's which can be identified with the bond of interest (*e.g.*, the three equivalent CC banana bonds in acetylene). In the present work, we have investigated the utility of both approaches, the corresponding prototypes, and normalization factors being listed in Table III.

In typical hydrogen-bonded dimers the hydrogen bond is formed from an interaction between the donated proton and the lone pair(s) of the acceptor. Thus, for bond energies calculated from intrabond interferences, a choice must be made concerning which of the acceptor lone pairs contribute to the bond. This is necessary since each LMO contributes some amount of interference (constructive or destructive), however small, to each pair of atoms in the molecule. We take the approach that if α is the angle between the hydrogen bond axis and the direction of the lone pair hybrid, then only those lone pairs having a value of α less than 90° should realistically be thought of as part of the bond. For the present series of molecules this choice is necessary only in H_2CO---HF, $(HF)_2$, and HF---HOH.

Table IV details a comparison of INDO calculated values of D_{AB}^{τ} and D_{AB}^{i} for the hydrogen bonds of the dimers being discussed. A comparison of the trends in these values with the stabilization energies listed in Table I quickly indicates that the *intrabond* interference is a much better general measure of the relative strengths of hydrogen bonds than the total H···Y interference energy. Except for HCN···HF *vs.* H_2O···HF, all trends in ΔE are correctly reproduced by $D_{H\cdots Y}^{i}$. While $D_{H\cdots Y}^{\tau}$ correctly predicts the relative strengths of hydrogen bonds for a *given* donor atom (*e.g.*, H_3N···HF > HCN···HF > H_3N···HOH > H_3N···HNH_2), the relative strengths of bonds involving different donors are not handled properly. These results suggest that a reasonable measure of the relative strengths of *intra*molecular hydrogen bonds should be the intrabond, two-center, one-electron interference energy connecting the acceptor atom and donated proton.

Clearly, there is not a one-to-one correspondence between the (INDO) hydrogen-bond energies, $D_{H\cdots Y}^{i}$, and the hydrogen-bond stabilization energies, ΔE. This is as it should be since *$D_{H\cdots Y}^{i}$ is a measure of the strength of a particular bond (H···Y), while ΔE is a measure of the net stabilization of the dimer relative to the monomers.* Thus, the latter is expected to include destabilizing effects as well as the stabilizing effect due to formation of the hydrogen bond itself. From a purely bond energy point of view, one might expect a more quantitative correlation between ΔE and the *net* change in bond energies, ΔD, on formation of the dimer

$$\Delta D = \sum_i^{\text{dimer}} D_i - \sum_i^{\text{monomers}} D_i \tag{13}$$

the sums being over all bonds in the dimer or monomers. This approach views the net stabilization energy as arising from a large energy decrease due to formation of the hydrogen bond, modified by smaller energy increases due to internal decreases in monomer bond energies on formation of the dimer. Values for ΔD based on both total (ΔD^{τ}) and intrabond (ΔD^{i}) interferences have been calculated for the present series of dimers, the results being listed in Table IV. Here the total interference results do not even consistently reproduce the trends for a given donor atom; however, the ΔD^{i} again reproduce the overall trends in ΔE. Moreover, in view of the approximations involved in the present calculations, the quantitative agreement between ΔE and ΔD^{i} is reasonably good.

The last two columns of Table IV list the increase in the XH bond length (ΔR_{XH}) and the concomittant decrease in the HX bond energy, due to formation of the dimer. One might expect the lengthening of the donor XH bond length to be proportional to the strength of the hydrogen bond. Indeed, this is generally found to be the case; however, there are exceptions. This would indicate that a degree of caution is necessary when correlating these two quantities experimentally. Finally, as one might expect, most of the destabilization in ΔD^{i} relative to $D_{H\cdots Y}^{i}$ is due to the weakening of the XH bond. In fact it is interesting to note that even

Table IV. Calculated Bond Energies for Hydrogen-Bonded Dimers[a]

A[b]	D[c]	$D_{H\cdots Y}^{\tau}$	$D_{H\cdots Y}^{i}$	ΔD^{τ}	ΔD^{i}	ΔR_{XH}, Å[d]	ΔD_{HX}^{i}
H_3N	HF	34.9	40.0	10.6	23.9	0.049	−14.8
HCN	HF	32.4	36.1	12.9	23.1	0.041	−12.6
H_2O	HF	34.2	36.3	18.3	24.8	0.032	−10.2
H_2CO	HF	31.6	34.5	14.7	24.3	0.031	−9.5
H_3N	HOH	23.9	27.0	9.3	18.7	0.033	−6.5
HF	HF	26.7	25.8	16.0	18.0	0.017	−5.7
H_2O	HOH	23.2	23.9	13.5	17.7	0.022	−4.6
H_3N	HNH_2	14.6	15.9	6.1	11.7	0.023	−2.8
HF	HOH	16.7	14.9	10.9	10.7	0.010	−2.3
H_2O	HNH_2	14.5	14.2	7.8	10.2	0.015	−2.1
HF	HNH_2	9.8	8.0	6.3	5.6	0.007	−1.0

[a] Energies in kcal/mol. [b] Proton acceptor. [c] Proton donor. [d] $\Delta R_{HX} = R_{HX}(\text{dimer}) - R_{HX}(\text{monomer})$.

Table V. Charge Transfer and Dipole Moment Enhancement

A^a	D^b	Δq^c Allen^d	INDO	$\lvert\Delta\mu\rvert^e$	$\Sigma\Delta q_{lp}$ (Y)^f	$\Delta\mu_{lp} + \Delta\mu_{XH}{}^g$
H_3N	HF	0.0313	0.1550	1.65	0.1677	1.27
HCN	HF	0.0061	0.1234	1.69	0.1325	1.05
H_2O	HF	0.0176	0.1018	1.24	0.1038	0.86
H_2CO	HF		0.1004	1.45	0.1004	0.89
H_3N	HOH	0.0100	0.0986	1.11	0.1077	1.09
HF	HF	0.0040	0.0594	0.82	0.0567	0.52
H_2O	HOH	0.0064	0.0607	0.79	0.0650	0.69
H_3N	HNH_2	0.0036	0.0546	0.66	0.0609	0.71
HF	HOH	0.0016	0.0289	0.47	0.0167	0.35
H_2O	HNH_2	0.0017	0.0317	0.43	0.0370	0.41
HF	HNH_2	0.0005	0.0129	0.23	0.0144	0.14

[a] Proton acceptor. [b] Proton donor. [c] Charge transferred from acceptor to donor. [d] Reference 2 of text. [e] Debye. [f] Charge lost by acceptor atom in lone pair LMO's. [g] See text.

Table VI. Comparison of Experimental and INDO Monomer Dipole Moments

Molecule	μ, D Expt	INDO
HCN	2.99[a]	2.50
H_2CO	2.34[b]	2.04
H_2O	1.85[c]	2.14
HF	1.82[d]	1.99
NH_3	1.47[e]	2.03

[a] B. N. Battacharya and W. Gordy, *Phys. Rev.*, **119**, 144 (1960). [b] J. N. Shoolery and A. H. Sharbaugh, *ibid.*, **82**, 95 (1951). [c] G. Birnbaum and S. K. Chatterjie, *J. Appl. Phys.*, **23**, 220 (1952). [d] R. Weiss, *Phys. Rev.*, **131**, 659 (1963). [e] D. K. Coles, W. E. Good, J. K. Bragg, and A. H. Sharbaugh, *ibid.*, **82**, 877 (1951).

though ΔR_{HX} does not decrease monotonically with ΔE, the absolute value of $\Delta D_{HX}{}^i$ does.

VI. Dipole Moment Enhancement and Charge Transfer

One of the manifestations of the formation of a hydrogen-bonded complex is the concomittant rearrangement of electron density relative to the monomers. Numerous authors have discussed the relationship between the amount of charge transferred from proton acceptor to donor and the hydrogen bond stabilization energy, ΔE.[2,6,17,31-33] Bratoz[33] has argued for a charge-transfer mechanism of hydrogen bonding, while accurate molecular orbital calculations indicate roughly equivalent charge transfer and electrostatic contributions.[32] Kollman and Allen[2] argue against the importance of charge transfer based on their partitioning of electron density rearrangements into charge transfer and polarization contributions. However, a comparison of the latter authors' calculated charge transferred from acceptor to donor in the molecules considered here (reproduced in column 3 of Table V) with their calculated ΔE's (Table I) indicates that the trends in the two calculated properties are, in fact, rather similar. Also listed in Table V are the corresponding values of Δq calculated by INDO. It is not surprising that the latter are somewhat larger than those calculated nonempirically; however, there is a general downward trend in Δq with decreasing ΔE, although there are exceptions. Similar results were recently obtained by Ratajczak[17] using CNDO/2. While these trends certainly do not prove a causal relationship between ΔE and Δq, they do support the notion that charge transfer and hydrogen bond stabilization are closely related.

The relationship between ΔE and charge transfer may be further investigated by considering the enhancement of the dipole moment on formation of the dimer. Del Bene has discussed the relative orientation of monomer dipoles in the context of her generalized hybridization model.[6,34] Of more direct interest to the present study is the work of Ratajczak and Orville-Thomas[31] who have extended Mulliken's charge transfer theory[35] to hydrogen-bonded complexes and derived a relationship between the enthalpy of hydrogen-bond formation and that part of the corresponding dipole moment enhancement due to charge transfer, $\Delta\mu_{ct}$, where

$$\Delta\mu = \mu(\text{complex}) - \Sigma\mu_i(\text{monomers}) = \Delta\mu_{ct} + \Delta\mu_{pol} \quad (14)$$

Here, μ(complex) is the dipole moment of the hydrogen-bonded complex, the sum is over the dipole moments of the *noninteracting* momomers in the dimer geometry, and $\Delta\mu_{pol}$ is the dipole enhancement due to internal rearrangement of electron density within the monomers. Ratajczak and Orville-Thomas found the latter term to be small relative to $\Delta\mu_{ct}$, and, based on the charge transfer argument, obtained the relationship

$$\Delta H \propto (\lvert\Delta\mu_{ct}\rvert)^{1/2} \quad (15)$$

Inferred experimental values of $\Delta\mu_{ct}$ were found to give a reasonable fit to this expression.

Since dipole moments at the present level of approximation are generally in reasonable agreement with experiment (see ref 36 and Table VI), it is of interest to examine the relationship, if any, between the INDO calculated ΔE and $\Delta\mu$. The latter are listed in Table V, where it is seen that, with the exception of $H_2CO\cdots HF$ and $HCN\cdots HF$, the two properties follow the same trends. Omitting the latter two complexes, a linear least-squares fit of ΔE as a function of $(\lvert\Delta\mu\rvert)^{1/2}$ yields a correlation coefficient of 0.970. This is greater than the corresponding correlation coefficient obtained by Ratajczak and Orville-Thomas, even though the present calculations do not separate the charge transfer and polarization contributions to $\Delta\mu$. This implies that the former contribution to $\Delta\mu$ is considerably greater than the latter. It should be noted, however, that this does not necessarily imply that polarization of electron density within the monomers is small. As pointed out, for example, by Kollman and Allen,[2] there is significant internal rearrangement of electron density. This is also clear from our discussion of the polarization of the XH bond orbital. What is indicated is that there are other internal polarizations occurring and that their overall effect on $\Delta\mu$ is small.

Since one of the major perturbations on the monomers due to complex formation is the spreading of the acceptor lone pair(s) onto the donated proton, it is likely that the transfer of electron density occurs largely within the acceptor lone pairs. To test this hypothesis, we have listed in Table V the electron density lost by the acceptor atom in these lone pairs on formation of the dimer. These may be compared with the electron density gained by the donated protons within the lone pairs (Table II). As expected, the total electron density lost by the acceptor atom within the lone pair LMO's is virtually the same as the total Δq and follows the same trends. The charge gained by the donated proton (Table II) is generally somewhat smaller, indicating that other small electron density shifts are involved. Even so, the calculated transfer of charge can largely be explained in terms of electron density shifts within the acceptor lone pairs.

The major effects of hydrogen-bond formation occur within the lone pairs of the acceptor and the XH bond of the donor. While, as discussed above, other changes must also take place, it is of interest to determine if the dipole enhancement is explainable in terms of changes in the lone pair and XH dipole moments. As outlined earlier[30] the molecular dipole moment may be expressed in terms of a vector sum of the dipole moments of the individual localized charge distributions.[24]

$$\mu = \sum_i \mu_i \quad (16)$$

Hence, the enhancement of the dipole moment may be thought of as a similar vector sum.

$$\Delta\mu = \sum_i \Delta\mu_i \quad (17)$$

Since $\Delta\mu$ is a vector sum, it is not sufficient to compare magnitudes μ_i in the dimer and noninteracting monomers. Instead we have calculated for each case the projection of each bond or lone pair moment on the molecular dipole axis $[\mu_i(\mu)]$, since the sum of such projections yields the magnitude of the molecular dipole moment

$$\mu = \Sigma\mu_i(\mu) \quad (18)$$

and the magnitude of $\Delta\mu$ is just

$$\Delta\mu = \Sigma\Delta\mu_i(\mu) \quad (19)$$

The last column of Table V lists the sum of such differences for the X–H bond and acceptor lone pairs only. Comparison of these values with $\Delta\mu$ indicates that while the major enhancement of the dipole moment arises from increases in these XH and lone pair moments, there are often other changes occurring as well, as pointed out in section III. These latter changes are significant enough that changes in the lone pair and XH moments do not reproduce the trends in ΔE nearly as well as does $\Delta\mu$ itself, so a simple explanation of dipole moment enhancement in terms of bond moment changes does not appear to be available. This is not entirely surprising since changes occurring in other parts of the molecule are not negligible.

VII. Conclusions

At the present level of approximation it appears that a reasonable measure of the relative strengths of hydrogen bonds is provided by the normalized intrabond interference energies, D^i, while, in the particular case of intermolecular dimers studied in the present work, the hydrogen-bond stabilization energies (ΔE) are reasonably well reproduced by ΔD^i. From this we conclude that ΔE may be regarded as being the result of a stabilization due to the formation of the hydrogen bond itself, modified by a destabilization due to the weakening of internal bonds in the monomer, principally the donor XH bond.

The loss of electron density on the proton may be similarly viewed as a combination of effects. On the one hand the proton gains electron density as a result of a spreading of the acceptor lone pair(s) onto the donor molecule. The greater effect, however, is the polarization of the donor XH bond, the net effect being a loss of electron density by the proton and a concomitant gain by the donor atom X.

An investigation of the relationship between ΔE and the dipole moment enhancement, $\Delta\mu$, supports the importance of charge transfer, as proposed by Ratajczak and Orville-Thomas;[31] however, no simple interpretation of $\Delta\mu$ in terms of localized orbital moments was found. This is undoubtedly due, at least in part, to nonnegligible electron density shifts on atoms not directly involved in the hydrogen bond.

It should be reiterated that the approach outlined in the present paper is, in principle, general and not limited to a particular level of approximation. The results obtained with INDO are encouraging; however, a true test of the model requires application of the localized orbital approach using nonempirical wave functions, and such calculations would be most welcome. This is particularly true with regard to the hybridization model of Del Bene,[6] since localized orbitals allow a measure of the orientation of acceptor lone pairs relative to the hydrogen-bond axis at a level of calculation which predicts more accurate intermolecular geometries. In more complicated dimers than those discussed here, such as NH_2OH---OH_2 and NH_2OH--H_2CO, Del Bene has suggested[34] that the most stable intermolecular geometry is influenced by long range attractive interactions between protons of the acceptor molecule and an electronegative atom of the *donor*. It would be interesting to investigate the corresponding long range interference energies in such systems.

Finally, the correlation of the trends in D^i and ΔE is encouraging and will be utilized in future papers on intramolecular hydrogen bonds.

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