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Theoretical Studies of Hydrogen-Bonded Dimers. Complexes Involving HF, H_2O, NH_3, HCl, H_2S, PH_3, HCN, HNC, HCP, CH_2NH, H_2CS, H_2CO, CH_4, CF_3H, C_2H_2, C_2H_4, C_6H_6, F^-, and H_3O^+

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Abstract: Hydrogen-bonded dimers involving first- and second-row hydrides have been studied theoretically with *ab initio* molecular orbital methods, using a 431G basis set. Certain generalizations about H-bonded dimers found in a previous study[2a] of first-row dimers (those involving NH_3, H_2O, and HF) are supported by this study; others require modification. In addition to studying the dependence of H-bond energy and properties on the row of the periodic table, we examine the dependence of H-bond energies on the "hybridization" of the electron donor, including HCN, H_2CO, H_2CS, HNC, and HCP as electron donors. We have also studied ionic H bonds, "π" H bonds, and H-bonded trimers in an attempt to relate their properties to those of the more conventional H-bonded dimers. Can a C–H bond be an effective H-bond proton donor? We attempt to answer this question by examining the proton donor ability of CH_4 and CHF_3. Electrostatic potentials turn out to facilitate our understanding of H-bond energies and structures, being more useful than Mulliken populations in rationalizing H-bond energies. Finally we address ourselves to the question of predicting dimer H-bond energies from the monomers involved. Using a very simple algebraic model, we are able to predict the H-bond energy of a total 144 H-bonded complexes, using as a basis our theoretical calculations on 25 complexes.

One of us[2a] has previously examined the H-bonded complexes involving HF, H_2O, and NH_3 (altogether nine complexes) and has found that the proton atomic population was a good index with which to predict H-bond *proton donor* strengths. In that same study, *proton acceptor* abilities also correlated with atomic population in NH_3, H_2O, and HF, the Mulliken atomic charges on N, O, and F being −0.91, −0.73, and −0.44, although we noted that the "extent" and ionization potential of the lone-pair electrons on the proton acceptor atom also could be used to understand relative proton acceptor abilities.

In a preliminary attempt to compare first- and second-row hydrogen bonds, we examined[2b] the relative H-bond strengths of dimers involving HF and HCl and concluded that HCl is a better proton donor than HF, but a much poorer proton acceptor. A number of other properties of these complexes were examined and the greater acidity of HCl than HF was clearly evident from the difference in the increase of the X–H distance in $Cl\text{–}H\cdots Y$ and $F\text{–}H\cdots Y$ complexes.

A number of other relevant theoretical studies carrying out systematic comparisons of H-bond energies exist in the literature and many of these have been carried out by Del Bene.[3] She has examined the relative inductive effect of H, CH_3, NH_2, OH, and F and has concluded that the order of proton donor ability in ROH increases as $H < CH_3 < NH_2 < OH < F$, whereas the proton acceptor strength of ROH goes in the opposite direction.

In this paper we address ourselves to the following questions. First, how do the H-bond energies and structure of the first-row hydrides compare with those of the second row and what are the properties of "mixed" first–second row dimers compared to dimers involving both first or both second row hydrides? Second, how do the H-bond energies change when one changes the "hybridization" of the electron donor; the donor atom in the hydrides can be assumed to be sp^3 or even higher in p character; how does one analyze the H-bonding ability of HCN *vs.* H_3N, HCP *vs.* H_3P, H_2CO *vs.* H_2O, and H_2CS *vs.* H_2S? Third, can carbon function as a proton acceptor or a C–H bond as a proton donor in a $X\text{–}H\cdots Y$ hydrogen bond? Fourth, what physical property of the monomers can rationalize the strengths of the H bonds these monomers form? Fifth, are ionic and "π" hydrogen bonds interpretable within the same framework as the neutral hydride H bonds discussed at the beginning of this study? Finally, can one predict *other* H-bond energies using the results of this study?

Computational Details and Monomer Properties

These studies were all carried out within the molecular orbital approximation using the CDC 7600 version of Gaussian 70.[4] These *ab initio* calculations used the well-characterized 431G basis set.[5] The 431G basis appears to have the same defects and virtues of other "double ζ" basis sets, despite the fact that it predicts somewhat higher total energies. One of the major defects of a "double ζ" basis is that it predicts exaggerated bond dipole moments and this leads to a significantly too high dipole moment for the first- and second-row hydrides studied here (Table I). The only saving grace is that the trend in dipole moments (with the exception of NH_3) follows the experimental moments for H_2O, HF, HCl, H_2S, and PH_3. For molecules like HCN, the better agreement with experiment can be rationalized by noting that there are two different bonds, and the errors in the two bond moments appear to be in opposite directions. In some cases, the Mulliken atomic populations predict the opposite polarity to the dipole moment (*e.g.*, PH_3); in general, however, they give one a qualitative feel for the charge distributions in these species. Since our previous study of comparative first- and second-row H bonds employed an STO-3G basis set, which does not exaggerate polarities so greatly, one asks the question: why use a 431G basis rather than STO-3G for this study? These are the only basis sets presently available with which one can carry out systematic comparisons for first and second molecules. In view of the fact that we have employed the STO-3G basis in preliminary studies,[2b] it is worth examining in some detail our reasons for choosing the 431G basis in this study. There are a number of reasons for this. First, the 431G basis consistently overestimates the dipole moment of both first- and second-row hydrides, whereas the STO-3G basis[2b] underestimates the dipole moments of the first row but overestimates the dipole moments of the second. Thus, we expect a more consistent trend of H-bond energies with the 431G basis. Second, we have shown[11] that much of the H-bond energy predicted by the STO-3G basis is observable with no proton donor present, with only the atomic orbitals and not the nuclei of the donor included in the calculation. This defect is shared by all noncomplete basis sets, but Newton and Ehrenson[12] have shown that it is much smaller for the 431G than the STO-3G basis. Third, our studies of amide-H_2O H bonding[13] with both basis sets show that a more reasonable trend in dimerization energies is found with the 431G basis.

Table I. Monomer Energies, Dipole Moments, and Atomic "Charges"

Molecule[a]	E_t, au	μ, D[b]	$q(X)$[c]	$q(H)$[d]
HF	−99.88726	2.28 (1.82)	−0.48	+0.48
H_2O	−75.90739	2.61 (1.85)	−0.78	+0.39
NH_3	−56.10259	2.30 (1.47)	−0.90	+0.30
HCl	−459.56310	1.87 (1.08)	−0.23	+0.23
H_2S	−398.20319	1.77 (0.97)	−0.18	+0.09
PH_3	−342.02516	1.04 (0.58)	+0.06	−0.02
HCN	−92.73130	3.25 (2.98) (3.22)[e]	−0.34	+0.33
HNC	−92.71641	2.66 (2.91)[e]	+0.30	+0.44
HCP	−378.64400	0.524 (0.39)[f]	+0.45	+0.25
H_2CO	−113.69054	3.01 (2.33)	−0.48	
H_2CNH	−93.88119	2.48	−0.55	+0.30
H_2CS	−435.99098	2.13 (1.65)[g]	+0.09	
CH_4	−40.13935			+0.15
CHF_3	−336.33415	2.19 (1.65)		+0.21

[a] Experimental geometries in ref 6. [b] Experimental values in parentheses, unless otherwise noted from ref 7. [c] Mulliken atomic charge on proton acceptor atom. [d] Mulliken atomic charge on proton. [e] See ref 8; this is a very accurate MO + CI study of HNC and HCN. [f] See ref 9. [g] See ref 10.

Of the above reasons for choosing the 431G basis rather than the STO-3G, the first two are by far the more important. Since electrostatic effects are so crucial in representing H-bond energies, the more correct trend in monomer dipole moments found using the 431G basis is an important reason to choose this basis rather than the STO-3G. Even though the STO-3G basis predicts smaller H-bond energies which are more in line with experimental ΔE's (although these are sparse and unreliable for the dimers studied here), much of the stabilization energy calculated with STO-3G is due to a nonphysical and spurious basis set defect.[11,12] We expect that exaggerated electrostatic attractions found with 431G are easier to predict and to compensate for than his basis set defect. We have carried out the counterpoise calculations for $(H_2O)_2$ and $(H_2S)_2$ with the 431G basis and find the "spurious" stabilizations[11] 0.7 and 0.8 kcal/mol, respectively. This energy is far less than for STO-3G, and, encouragingly, is of comparable magnitude for first- and second-row dimers.

Is it reasonable to attempt to describe the electronic structure of second-row atoms without adding d polarization functions to the basis set? In view of the extensive literature on the role of d orbitals in sulfur chemistry, this is an important question. Rothenberg, *et al.*,[14] have studied the molecular properties of SiH_4, PH_3, H_2S, and HCl and conclude that with an extensive sp basis, d functions contribute rather little to the bonding in these hydrides, much less than minimal basis set calculations would have led one to expect. They also find that d functions on the heavy atom and p's on H contribute ~20 kcal/mol to the total energy in these molecules, very similar to the amount Neumann and Moskowitz[15] found for the contribution of d functions on *oxygen* and p functions in hydrogen in H_2O. An important role of the polarization functions in both of these molecules is to reduce the calculated dipole moments to results more in line with experiment.

Petke and Whitten[16] have studied the role of d functions in the bonding of PH_3 and NH_3, although their conclusions must be regarded with caution because the s and p part of their basis set is somewhat more limited than that employed by Rothenberg, *et al.* They do find that d functions play a larger role in P-H than in N-H covalent bonding. However, in the calculation of electrostatic properties (electrostatic potential and dipole moment) they find similar deficiencies in an only sp wave function for both molecules.

The 431G basis used here is far from a *complete* sp basis, but it is a reasonable assumption that, based on the above studies, d functions will contribute similarly to the total energies of first- and second-row *hydrides*. Polarization functions are found to be far more important[17] in SO_2 than SH_2 and thus we expect our calculations for H_2CS and HCP to be less accurate than the corresponding hydrides H_2S and H_3P. However, a description of the relatively weak H-bonded complexes that these molecules form probably depends more on their electrostatic properties than their internal bonding. Our calculations on H_2CS and HCP show that their dipole moments are predicted with similar accuracy (or inaccuracy) as those predicted for H_2CO and HCN.

The polarizabilities for the second-row hydrides are somewhat greater than those of the first row. Since dispersion effects are not included in an SCF calculation, one might question whether this will unbalance the first-second row comparisons presented here. Since dispersion effects

Table II. H-Bond Energies for First- and Second-Row Hydrides[a] (kcal/mol)

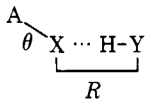
Electron donor	Proton donor HF	H_2O	NH_3	HCl	H_2S	PH_3
HF	7.8 (4.6)	5.4 (3.0)	3.6 (1.3)	4.6	2.5	1.0
H_2O	13.4 (9.4)	8.1 (5.3)	4.1 (2.3)	8.2	3.8	1.1
NH_3	16.3 (11.7)	8.9 (5.8)	4.3 (2.7)	10.8	4.4	1.2
HCl	3.4	2.5	1.3	2.0	1.1	0.4
H_2S	5.8	3.9	2.1	3.5	1.8	0.6
PH_3	6.9	4.0	2.2	4.3	2.1	0.8

[a] Values from ref 2a in parentheses

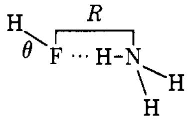
are quite short range (R^{-6}) and the separations larger for second- than first-row complexes, we do not expect large energetic contributions from dispersion attractions. We have no rigorous proof for this conjecture, but the relatively good agreement between the experimental and theoretical results for the energy of dimerization of H_2S offers some support.

We do hope that this study will stimulate more accurate calculations on some of the dimers examined here, since near-Hartree-Fock studies on $(H_2O)_2$ predicted the structure[18] of the complex in near-quantitative agreement with recent experiments.[19] Where it is possible to make comparisons, ($(H_2O)_2$ and $(HF)_2$), it appears that the 431G basis consistently overestimates energies of dimerization and underestimates intermolecular separations. Thus, we hope to correctly predict trends that later more accurate calculations and experiments may confirm.

Dimers Involving HF, H_2O, NH_3, HCl, H_2S, and PH_3. Energies and Geometries. Table II contains the dimerization energies for six hydrides each functioning as a proton donor or acceptor, a total of 36 H-bonded complexes. In each dimer



R and θ were the only geometrical parameters varied in the calculation and the monomer geometries were fixed at the experimental values. The H bond was assumed linear (in all intermolecular interactions so far studied theoretically, where this angle was varied, this is an excellent approximation)[20,21] and the external atoms on Y kept trans to A. For example in



the external hydrogens on nitrogen are fixed by the monomer geometry and θ turns out to be 65° (see Table III) (R = 3.22 Å).

In Table II, the dimerization energies for the first-row hydrides (NH_3, H_2O, and HF) are compared with those found in ref 1 and the order of H-bond energies are the same, even though the energies found with the 431G basis are 1-4 kcal/mol higher. For $(H_2O)_2$ and $(HF)_2$, more accurate calculations[18] find dimerization energies of 4.7 and 4.4 kcal/mol and studies on $(H_2O)_2$[22] indicate that its Hartree-Fock dimerization energy may be near 4.0 kcal/mol. Adding dispersion energy to this may make the experimental energy near 4.8 kcal/mol,[23] but it is not clear whether there are other correlation corrections or significant zero-point energy corrections. Thus, compared to the experimental dimerization energies, we expect our ΔE's calculated in Table II to be about 5-60% too high, with the large errors corresponding to the larger ΔE's.

$H_3N \cdots HCl$ is a much studied complex, Clementi[24] having predicted its existence and properties before experimental observation.[25] For $H_3N \cdots HCl$, $H_3N \cdots HSH$, $H_3N \cdots HF$, and $H_2O \cdots HCl$, we also varied both the position of the proton and the X ··· Y distance. In H_3NHCl the minimum energy geometry occurred for R(N-Cl) = 2.85 Å and r(H-Cl) = 1.67 Å (our predicted r(H-Cl) for HCl monomer is 1.30 Å). These values are very similar to those found by Clementi, *et al.*,[24] but our ΔE is significantly smaller (12.6 *vs.* 19.0 kcal/mol). For $NH_3 \cdots HF$, variation of the H-F distance results in an increase of only 0.03 Å over the monomer HF distance (compared with an increase of 0.37 Å in HCl) and a ΔE = 16.9 kcal/mol, compared with ΔE = 16.3 kcal/mol calculated with fixed H-F distance. For $H_3N \cdots HSH$ we optimized the geometry for both H_2S (r = 1.35 Å, θ = 97°) and the R(N-S) distances in the dimer and found: R(N-S) = 3.50 Å, r(S-H) = 1.36 Å, and ΔE = 4.7 kcal/mol. For $H_2O \cdots HCl$, we optimized both the H-Cl and O ··· Cl distances and found: R(O-Cl) = 3.10 Å, r(H-Cl) = 1.33 Å, and ΔE = 8.3 kcal/mol. From these examples, it is clear that of the 36 dimers in Tables II and III, the geometry and energy of only one ($H_3N \cdots HCl$) is significantly different from the "rigid monomer" values reported in the two tables.

The great difference in the dimerization energies of $H_3N \cdots HF$ and $H_3N \cdots HCl$ determined with the 431G ($\Delta E(H_3N \cdots HF)$ = 16.9 and $\Delta E(H_3N \cdots HCl)$ = 12.6 kcal/mol) and the STO-3G set[2] ($\Delta E(H_3N \cdots HF)$ = 8.5 and $\Delta E(H_3N \cdots HCl)$ = 15.7 kcal/mol) is worthy of mention. The 431G calculation predicts a geometry much closer to that found for $H_3N \cdots HCl$ by Clementi[24] whose basis set was larger and more flexible than either of the basis sets employed here (the total energy for $H_3N \cdots HCl$ in his calculation is about 0.015 au lower than the 431G energy), so we believe the 431G result to be more reliable than STO-

Table III. Geometrical Parameters for First- and Second-Row Hydrides[a] (Distances in Å, Angles in Degrees)

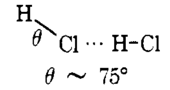
Electron donor		Proton donor HF	H_2O	NH_3	HCl	H_2S	PH_3
HF	R	2.69	2.94	3.22	3.37	3.68	4.05
	θ	42	60	65	39	34	76
H_2O	R	2.64	2.85	3.24	3.17	3.59	4.18
	θ	6	37	53	13	22	52
NH_3	R	2.67	2.93	3.28	3.13	3.52	4.32
	θ^b						
HCl	R	3.42	3.70	4.10	4.05	4.40	4.80
	θ	71	82	55	70	75	87
H_2S	R	3.36	3.66	4.00	4.09	4.39	4.70
	θ	68	78	88	71	73	87
PH_3	R	3.40	3.74	4.06	4.01	4.40	4.80
	θ^b						

[a] R calculated to ±0.05 Å and θ to ±5°. [b] Assumed to be 0.

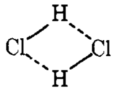
3G. However, $H_3N \cdots HCl$, unlike the other complexes in Tables II and III, involves significant structural reorganization in the monomers and our single determinant wave functions might not represent this properly. These are clearly questions in need of more theoretical and experimental study.

Our calculated ΔE for $(H_2S)_2$ is very similar to the experimental value[26] (1.7 kcal/mol) and Sabin's calculation[27] (2.0 kcal/mol).

We pointed out previously[2b] that the minimum energy for the HCl dimer occurs at a linear



rather than a cyclic (centrosymmetric) structure



This result is also predicted by the 431G basis, the ΔE for the cyclic dimer being 1.7 kcal/mol, compared with 2.0 kcal/mol for the linear structure. Thus, we have further support for the finding of Girardet and Robert[28] that the HCl dimer should be "linear" with θ near 90°.

The minimum energy geometries are interesting for two main reasons. First, the results support the generalization proposed by one of us[2a] that in $X \cdots H\text{-}Y$, the minimum energy ($R(X \cdots Y)$ is mainly determined by H-Y, with the result (for similar X's) being pretty much independent of X. Some examples from the table bear this out for both first- and second-row donors: for $Y = F$, $X = NH_3$, H_2O and HF all yield minimum energy R's between 2.64 and 2.69 Å; for $Y = OH$, $X = NH_3$, H_2O, and HF, $R_{min} = 2.93$, 2.85, and 2.94 Å. For $Y = OH$ and $X = HCl$, H_2S, and H_3P, $R = 3.70$, 3.66, and 3.74 Å, so a switch from a first to a second-row electron donor does have a very drastic effect on R, but once again, within a class of similar electron donors, R_{min} for a given proton donor complex does not change significantly. The reverse is not true; for a given X, changing H-Y has a drastic effect on R (going across a given row in Table III). Thus, we can restate our previous conclusion that in the $X \cdots H\text{-}Y$ dimer, the distance is determined mainly by the properties of H-Y (for a given class of X); though at that minimum energy distance, the nature of X can have a drastic effect on ΔE. The generalizations about the constancy of R for a given H-B can be tested experimentally, once the study of dimers by the technique of supersonic nozzle beams becomes more routine. It should be noted that in both cases, where accurate structures are known for $(H_2O)_2$[19] and $(HF)_2$,[29] more accurate calculations than these predicted the correct $R(X \cdots Y)$ to ±0.05 Å; in both $(H_2O)_2$ and $(HF)_2$ the 431G basis predicts an R about 0.15 Å too short. R for $(H_2O)_2$ is found to be 2.98 ± 0.04 Å;[27] R for $(HF)_2$ is 2.80 Å.[29]

In comparing the θ values for the different dimers, it is clear that there is considerable fluctuation, indicating that this parameter is influenced by the attempt to minimize external hydrogen repulsion rather than any intrinsic "lone pair" directionality. However, it is clear that the θ values for HCl and H_2S as electron donors are significantly greater than those for HF and H_2O, so specific orbital effects do play an important role in determining the minimum energy structure. We shall return to this point later.

When one forms an H-bonded complex between two hydrides, X and Y, is it clear which will be the proton donor and which the acceptor in the minimum energy structure? If X or Y are both in the same row, the choice is rather obvious; $NH_3 \cdots HOH$ and $NH_3 \cdots HF$ will both have NH_3 as electron donor and $H_2O \cdots HF$ will have water as electron donor; $PH_3 \cdots HCl$, $PH_3 \cdots H_2S$, and $H_2S \cdots HCl$ will each have the lower group hydride as electron donor. All of the above is rather obvious from one's intuition on relative acid and base strengths. However, if X and Y are not from the same row, the choice of which is proton donor and which is acceptor is not so obvious. The results are summarized in Table IV and indicate that HCl always prefers to be proton donor to a first-row hydride, PH_3 always prefers to be an electron donor, H_2S prefers to be a proton donor to NH_3 and a electron donor to HF, and $H_2O \cdots HSH$ is approximately equoenergetic to $H_2S \cdots HOH$. All of these predictions can be tested by matrix isolation infrared spectroscopy.

Table IV. Role of Second-Row Dimer (HCl, H_2S, PH_3) in Mixed First-Second-Row Dimers

	NH_3	H_2O	HF
HCl	Proton donor	Proton donor	Proton donor
H_2S	Proton donor	Proton donor ≈ electron donor	Electron donor
PH_3	Electron donor	Electron donor	Electron donor

Other H-Bonded Complexes

When one studies a series of very similar H bonds, as in the hydrides, one can question how "general" the generalizations that emerge really are. Thus, we extended our calculations to a number of other molecules, using FH as our prototype proton donor to NCH, CNH, OCH_2, $NHCH_2$, SCH_2, and PCH, and H_3N as our prototype electron donor to HCN, HNC, $HNCH_2$, HCP, HCH_3, and HCF_3. For all the complexes except $H_2CO \cdots HF$ and $H_2CS \cdots HF$, only $R(X \cdots Y)$ was varied, X and Y being the end atoms in the hydrogen bond; for H_2CO and H_2CS, θ, the angle between the HF bond and the CO (or CS) bond was also varied, keeping HF in the aldehyde plane. The results are presented in Table V. As one can see, the minimum energy X-F distance for $X \cdots H\text{-}F$ varies from 2.64 Å for X = HF to 2.99 Å for X = HNC so one must apply our generalization about the minimum energy distance being constant for similar Y with caution. One does detect a qualitative dependence of $R(X \cdots F)$ on the hybridization of X ($R = 2.64$, 2.67, 2.69 Å) for the sp^3 hybridized electron donors, 2.70 and 2.73 Å for the sp^2 electron donors (H_2CO and CH_2NH) and 2.90 and 2.99 Å for the sp hybridized electron donors (HCN and HNC). Given that one knows what atoms X and Y are in $X \cdots H\text{-}Y$, can one predict the strength of the hydrogen bond, irrespective of what atoms are attached to Y or X? Del Bene[3] has already given some evidence to a *no* answer to the above question, but Table V contains an even more dramatic example of this fact. Com-

Table V. Energies and Geometrical Parameters for Other H-Bonded Complexes

Dimer	R, Å	θ, deg	ΔE, kcal/mol
$F_3C\text{-}H \cdots NH_3$	3.36		7.6
$H_3C\text{-}H \cdots NH_3$	4.02		1.1
$NC\text{-}H \cdots NH_3$	3.15		9.7
$CN\text{-}H \cdots NH_3$	2.88		13.1
$PC\text{-}H \cdots NH_3$	3.29		4.6
$H_2CNH \cdots NH_3$	3.20		5.5
$H_2CHN \cdots HF$	2.70	60	14.7
$H_2CO \cdots HF$	2.73	40	10.0
$H_2CS \cdots HF$	3.46	73	6.1
$HCN \cdots HF$	2.90		8.9
$HNC \cdots HF$	2.99		9.3
$HCP \cdots HF$	3.54		2.1

paring $H_3C-H \cdots NH_3$ and $F_3C-H \cdots NH_3$ one sees that both contain $C-H \cdots N$ bonds. It is clear that one is hard pressed to call the former interaction a hydrogen bond ($R(CN) = 4.02$ Å, $\Delta E = 1.1$ kcal/mol) but the latter one ($R(CN) = 3.36$ Å, $\Delta E = 7.6$ kcal/mol) is clearly a strong one. In addition, when one applies the above generalization that the minimum energy $X \cdots Y$ *distance* is mainly dependent on the nature of the H–Y bond, one must realize that substituents attached to Y (*e.g.*, three fluorines) can have a drastic (0.7 Å) effect on the minimum energy distance.

It is also clear from the above that there is no reason why carbon cannot participate in reasonably strong H bonds, either as proton donor ($H_3N \cdots HCF_3$) or proton acceptor ($HF \cdots CNH$).

The generalization about the minimum energy $R(X \cdots Y)$ in hydrogen-bonded dimers can now be summarized in the following way. (1) For $X \cdots H-Y$, the minimum energy distance is mainly determined by H–Y, with different X's belonging to the same row of the periodic table having similar R's. (2) There is a small but significant dependence of $R(X \cdots Y)$ on the hybridization of X, $R(X \cdots Y, X = sp^3) < R(X \cdots Y, X = sp^2) < R(X \cdots Y, X = sp)$. (3) Y refers to the *group* to which the proton is attached, not just the atom to which the proton is covalently bonded. Thus for CH_4 and CHF_3 as proton donors, Y = CH_3 for methane and Y = CF_3 for fluoroform.

The use of supersonic nozzle beam techniques[19,29] to study the structures of dimers with a fixed proton donor and varying proton acceptors and a fixed proton acceptor and varying proton donors should allow an experimental test of the above stated generalization.

Interpretation of H-Bond Energies in Terms of Monomer Properties and Charge Redistribution Effects

In a previous study,[2a] Mulliken populations were found to be useful in rationalizing the H-bond energies of the first-row hydrides. How well do Mulliken populations allow us to rationalize the H-bond energies of the larger series of dimers considered here? In these molecules, can one predict proton donor strengths from the positive charge on the proton and electron donor strength from the negative charge on the heteroatom? This prediction works qualitatively for the hydrides, but an important exception are the populations in PH_3, where the phosphorus has a net *positive* population and the hydrogens *negative*, despite the fact that with PH_3, the phosphorus is a very effective electron donor and the hydrogens on PH_3 are capable of forming (weak) $P-H \cdots Y$ hydrogen bonds. In HNC, HCP, and H_2CS we find further cases where the population on the electron donor atoms indicates a net positive charge, whereas these molecules are all effective electron donors. In the case of HNC, much of the positive charge is due to the π electrons (the two π orbitals each have 0.52 electrons on carbon and 1.48 electrons on N). Thus the σ population on the carbon on HNC is −0.66. However, in H_2CS, when one considers only the σ electrons, the net charge on the sulfur is +0.25. Thus, one really would like a more reliable and more basis set independent method for rationalizing H-bond strengths.

Table VI. Energies, Proton Charge, and Electrostatic Potential due to HY in $H_3N \cdots HY$ Complexes

Complex	ΔE, kcal/mol	q(H), e⁻	POT, au[a]
$H_3N \cdots HF$	16.3	+0.48	0.044
$H_3N \cdots HNC$	13.1	+0.44	0.038
$H_3N \cdots HCl$	10.8	+0.23	0.034
$H_3N \cdots HCN$	9.7	+0.33	0.039
$H_3N \cdots H_2O$	8.9	+0.39	0.030
$H_3N \cdots HCF_3$	7.6	+0.21	0.036
$H_3N \cdots HNCH_2$	5.5	+0.30	0.022
$H_3N \cdots HCP$	4.6	+0.25	0.019
$H_3N \cdots HSH$	4.4	+0.09	0.019
$H_3N \cdots HNH_2$	4.3	+0.30	0.017
$H_3N \cdots HPH_2$	1.2	−0.02	0.005
$H_3N \cdots HCH_3$	1.1	+0.15	0.003

[a] Electrostatic potential at fixed distances of 2 Å.

Electrostatic potentials have been found to be very useful in understanding sites of protonation[30] on molecules and here we inquire whether they can be equally useful in rationalizing H-bond energies and directionality. Can one predict the relative strengths of $X-H \cdots NH_3$ hydrogen bonds from the electrostatic potential at a fixed distance from the proton? Since a reasonable H-bond $H \cdots N$ distance is 2 Å, this distance from the proton along the X–H line was chosen to compare different proton donors. As one can see from Table VI, the electrostatic potential at a fixed distance from the proton is quite satisfactory for predicting the $X-H \cdots NH_3$ H-bond strengths for different X. A linear regression of ΔE against q(H) and POT finds the best least-squares lines to be

$$-\Delta E = 26.2(\pm 13.3)q(\mathrm{H}) + 0.4(\pm 3.9) \qquad (1)$$

$$r^2 = 0.66 F_{1,10} = 19.3$$

$$-\Delta E = 326(\pm 86)\mathrm{POT} - 1.0(\pm 2.4) \qquad (2)$$

$$r^2 = 0.88 F_{1,10} = 71.9$$

Although not completely reproducing the order of H-bond strengths, the electrostatic potential is clearly better than the Mulliken populations in ordering H-bond proton-donor abilities.

On the other hand, can one order the relative electron donor abilities of the various molecules by examining the electrostatic potential at fixed distances from the electron donor atom? Table VII contains the values for the electrostatic potential at a fixed distance from first- and second-row electron donors and shows that electrostatic potentials are far more satisfactory than Mulliken populations in predicting relative H-bond electron-donor abilities of molecules. A linear regression of ΔE against q(Y) and POT finds the best least-squares lines to be

$$-\Delta E = -8.0(\pm 4.7)q(\mathrm{Y}) + 6.7(\pm 2.2) \qquad (3)$$

$$r^2 = 0.59 F_{1,10} = 14$$

$$-\Delta E = -201(\pm 26)\mathrm{POT} + 0.6(\pm 1.2) \qquad (4)$$

$$r^2 = 0.97 F_{1,10} = 296$$

Obviously, electrostatic attraction is only one contribution to the total H-bond energy, the others being exchange repulsion, polarization, charge transfer, and dispersion.

Table VII. Energies, Heteroatom Charge, and Electrostatic Potential due to X in $X \cdots H-F$ Complexes

Complex	ΔE, kcal/mol	q(Y), e⁻	POT, au[a]
$H_3N \cdots HF$	16.3	−0.90	−0.075
$H_2CNH \cdots HF$	14.7	−0.54	−0.067
$H_2O \cdots HF$	13.4	−0.78	−0.059
$H_2CO \cdots HF$	10.0	−0.48	−0.049
$HNC \cdots HF$	9.3	+0.30	−0.047
$HCN \cdots HF$	8.9	−0.34	−0.050
$HF \cdots HF$	7.8	−0.48	−0.036
$H_3P \cdots HF$	6.9	+0.06	−0.029
$H_2CS \cdots HF$	6.1	+0.09	−0.024
$H_2S \cdots HF$	5.8	−0.18	−0.026
$HCl \cdots HF$	3.4	−0.23	−0.016
$HCP \cdots HF$	2.1	+0.45	−0.004

[a] Electrostatic potential at 2.12 Å from Y for first row (N, O, F) and 2.65 Å from Y for second row (P, S, Cl).

Table VIII. Angular Dependence of Electrostatic Potential in HF and HCl

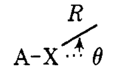
	θ, deg						
R, Å	0	15	30	45	60	75	90
				HF			
1.1	−0.0601	−0.0619	−0.0659	−0.0691	−0.0671	−0.0558	−0.0320
1.9	−0.0439	−0.0438	−0.0431	−0.0411	−0.0368	−0.0291	−0.0172
				HCl			
1.9	−0.0086	−0.0109	−0.0167	−0.0236	−0.0282	−0.0275	−0.0194
2.6	−0.0121	−0.0127	−0.0141	−0.0156	−0.0159	−0.0140	−0.0091
				HF[a]			
1.1	−0.0351	−0.0373	−0.0429	−0.0487	−0.0509	−0.0455	−0.0303
1.9	−0.0238	−0.0238	−0.0238	−0.0231	−0.0210	−0.0169	−0.0110

[a] STO-3G, μ = 1.29 D.

However, there is some evidence that the electrostatic energy[20] (at the minimum energy geometry) is qualitatively similar to the total H-bond energy (this implies that the exchange repulsion energy is about equal to polarization and charge transfer and dispersion at this geometry). It should be emphasized that the electrostatic attraction being discussed here is the total attraction between the calculated charge distributions of the molecules and not just a finite sum of dipole-dipole, quadrupole-dipole, ···, interaction terms. Such a calculation involves a determination of the electrostatic potential due to one molecule and the charge distribution of the other at all points in space (and an integration over all space). In this paper we make no attempt to do such a calculation, since our purpose is to predict relative H-bond dimer energies using only the properties of the *monomers.* Thus, we have evaluated the electrostatic potential for the proton donors and electron donors at a reasonable "representative" point in space, in the hopes that this will predict the relative H-bond strength of a given proton or electron donor. For example, if one wanted to estimate the proton donor ability of a new molecule Y–H, one could calculate its electrostatic potential at 2 Å from the proton; using eq 4 one could predict not only the $\Delta E(H_3N \cdots H\text{-}Y)$ but also whether the molecule would form a stronger or weaker H bond than the other proton donors in Table VI with any other electron donor X.

What can the electrostatic potentials tell us about hydrogen bond directionality;[31] do they predict the angle one expects for a given electron donor? As has been pointed out before, Table III shows a considerable variation in the θ value for a given electron donor but the minimum energy θ for the second-row donor (H_2S and HCl) H bonds is significantly greater than the θ for those involving HF and H_2O as electron donors.

If one examines the electrostatic potential near the electron donor end of the molecule



as a function of R and θ at short R (approximately the same as protonated A–X) the most negative electrostatic potential occurs for θ significantly greater than 0. This is consistent with the results of previous electrostatic potential studies used to predict protonation geometries.[29] However, at distances R more characteristic of H bonds, HF and H_2O show minima in the electrostatic potential near θ = 0 (R = 1.9 Å) but HCl and H_2S (R = 2.6 Å) have minima nearer θ = 45°.[32] Some of these results (for HF and HCl) are in Table VIII. One of us has pointed out[31] that one expects a greater θ in second- than first-row hydrogen bonds and attributed this to charge transfer effects, the highest occupied $\sigma - \pi$ orbital energy difference being greater in the second-row dimers. As one can see from the comparison of the electrostatic potential for HCl and HF in Table VIII, one does not need to invoke charge transfer effects to explain the difference in θ between the first- and second-row H bonds. One can rationalize these results in the following way: the less tightly bound the π orbital is compared to the σ, the more diffuse the charge is at larger θ compared to smaller θ. This causes the electrostatic potential to be greater (in magnitude) for $\theta \neq 0$ (of course at very long distances the minimum in the electrostatic potential will occur at θ = 0), the greater the $\sigma - \pi$ orbital energy difference. Thus the difference in θ for first- and second-row dimers can be rationalized by orbital energy differences, but most of this effect appears to be *electrostatic.* Charge transfer does appear to play a role in the H-bond directionality since for the dimers where there are no important external atom repulsion effects (*e.g.*, $(HF)_2$ and $(HCl)_2$) the minimum energy angle θ is significantly greater than that predicted from the electrostatic potential alone. Further support for this comes from the fact that one finds more charge transfer as θ increases. For example, for $(HF)_2$, R = 2.65 Å, the amount of charge transferred to the proton donor molecule is 0.0278, 0.0313, and 0.0350 electrons at θ = 30, 45, and 60°. Similarly for $(HCl)_2$, R = 4.1 Å, the amount of charge transferred to the proton donor molecule at θ = 30, 60, 75, and 90° is 0.0085, 0.0149, 0.0171, and 0.0182.

Howard[33] predicted that the electrostatic energy was a minimum near θ = 0 for $(HF)_2$. The electrostatic potential of HF with 431G and STO-3G basis sets (Table VIII), whose predicted moment (2.28 and 1.29 D) straddles the true one, supports this prediction.[34]

The orbital energies provide us with a way of rationalizing why ΔE (HCN ··· HF) is less than ΔE(HNC ··· HF) despite the fact that the electrostatic potential (and dipole moment) is greater for HCN. The highest occupied orbital energies for HCN are −0.572 (σ) and −0.497 (2π). For HNC, the σ orbital (ϵ = −0.478) lies lower than the two π orbitals (ϵ = −0.514). The minimum energy electrostatic potential is along the molecular line for both molecules. HNC is a better electron donor than HCN because its highest occupied σ orbital is much less tightly bound than that of HCN ($\Delta\epsilon$ = 0.09 au). Thus, with a fixed proton donor and R(X ··· Y), HNC will have a larger charge transfer energy than HCN. Although we have not separately computed the charge transfer energy for HCN ··· HF and HNC ··· HF, Mulliken populations do support the greater charge transfer in the latter dimer; one finds 0.044 electron transferred to HF in HNC ··· HF (R = 3.0 Å), but only 0.025 electron transferred in HCN ··· HF (R = 2.9 Å).

Certain qualitative features of H-bond complexes pointed out previously[2a,17] have also been found in this study. In A–X ··· H–Y–B, AX loses electrons of HYB. In a X ··· H–Y dimer for fixed H–Y (and similar R(X ··· Y)) the charge transfer and charge redistribution are very sensitive to the nature of X. However, for fixed X *and* fixed R(X ··· Y), the charge redistribution and charge transfer are much less dependent on the nature of HY. These electrons are lost by A and H and gained by Y and B; X usually gains a small number of electrons. The dipole moment of the complex is invariably greater than the sum of the monomer moments. Finally, the orbital energies of AX decrease and those of HYB increase on H bond formation.

The fact that the charge redistribution is much more sensitive to changes in X than to changes in Y–H allows us to speculate why the electrostatic potential at fixed distances from the electron donor correlate better with the H bond energy E (eq 4) than do the potentials near the proton donor (eq 2). This "lone pair" of electrons on X in X ··· H–Y not only has an important electrostatic interaction with the proton, but also plays an important role in the charge transfer and polarization contributions to ΔE. The less tightly bound these electrons are, the larger the electrostatic potential at a long distance from X due to these electrons will be; the less tightly bound the electrons, the larger the electric field they will set up at H–Y and the greater the polarization energy; the less tightly bound the electrons, the easier it will be to transfer part of their charge to H–X and the greater the charge transfer energy.

Because there has been a long history of scientific debate[17] whether the H bond should be characterized as an "electrostatic" or "charge transfer" interaction, we have attempted to see if the amount of charge transfer (measured by Mulliken populations) in these complexes correlates with the H-bond energy. In fact we have carried out a linear regression of ΔE against CT, ΔE against $R(\mathrm{X} \cdots \mathrm{Y})$, and $R(\mathrm{X} \cdots \mathrm{Y})$ against CT. Including all of the neutral complexes discussed so far, one finds correlation coefficients (r^2) of 0.49 for ΔE against CT, 0.66 for ΔE against R, and 0.37 for CT against R. If one separately treats the first- and second-row electron donors, one finds the following for the three regressions: first row, $r^2 = 0.61$ (ΔE *vs.* CT), 0.66 (ΔE *vs.* R), and 0.51 (CT *vs.* R); second row, $r^2 = 0.90$ (ΔE *vs.* CT), 0.65 (ΔE *vs.* R), and 0.51 (CT *vs.* R). It should be clear from the above that ΔE correlates quite poorly in general with the amount of charge transfer, although charge transfer effects appear to play a larger role in H bonds where a second row atom is the electron donor.

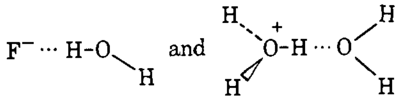
In view of the fact that our basis set exaggerates electrostatic effects, one could not close the debate because of the evidence presented here. However, it should be pointed out that electrostatic effects appear to play the dominant role in determining the *ground state* structure and properties of what have been referred to as "charge transfer" complexes;[35] the evidence presented earlier in this section supports the dominance of electrostatic effects in determining the structure of H-bonded complexes. Charge transfer and polarization effects allow closer penetration of the two monomers than would be expected from van der Waals radii. They are important in understanding spectral properties in H bonds but they appear to play a secondary role in H-bond structure.

In addition, electrostatic properties can be employed in a simple, predictive model (eq 2 and 4) for H-bond energies using only monomer properties far more satisfactorily than can "charge transfer" properties which are a more complicated function of overlap and orbital energies of donor and acceptor.

Ionic, π, C–H, and Multiple H Bonds

Up to now, we have limited our analysis to more conventional neutral H-bonded dimers of the type X ··· H–Y, where X was an atom with an available electron pair. Here we attempt to see how the properties of ionic H bonds, π H bonds, and multiply H-bonded systems fit into the concepts we have developed.

Sample examples of ionic H bonds are the



complexes which have been the subjects of previous studies,[34,12] the latter at the 431G level. We attempted to see whether the electrostatic potential at the same positions as studied for the electron donors (2.12 Å) and proton donors (2 Å) in Tables V and VI would allow a qualitative prediction of the observed H-bond energy. Not surprisingly, this turned out to be the case; the electrostatic potential of F^- at 2.12 Å from the fluorine was −0.250 au and the H-bond energy of $\mathrm{F}^- \cdots \mathrm{HOH}$ 39.4 kcal/mol (for H_3N as electron donor, the corresponding values were −0.075 and 8.9 kcal/mol). Comparing HF and H_3O^+ as proton donors to water, the electrostatic potentials and H-bond energies were 0.196 au and 40.1 kcal/mol for H_3O^+, 0.044 au and 13.4 kcal/mol for HF.[37]

Would one expect π H bonds; *i.e.*, can π electrons function as electron donors to partially positively charged protons? We have addressed ourselves to this question using HF as a proton donor to acetylene, ethylene, and benzene.[38] For benzene, we studied the interaction at the STO-3G level[39] and $C_2H_4 \cdots \mathrm{HF}$ was studied at both the 431G and STO-3G levels. Del Bene[40] has also studied π electron donors using molecular orbital methods.

First, we examined (at the 431G level) whether in $C_2H_2 \cdots \mathrm{HF}$ and $C_2H_4 \cdots \mathrm{HF}$ the HF preferred an approach toward the center of the π bond or toward the orbital of one carbon. In both cases, the minimum energy geometry occurred with an F ··· hydrocarbon plane distance of about 3.3 Å. For $C_2H_2 \cdots \mathrm{HF}$ we found ΔE(center of π bond) = 3.2 kcal/mol and ΔE(toward one Cp π) = 2.5 kcal/mol; for $C_2H_4 \cdots \mathrm{HF}$ we found ΔE(center of π bond) = 4.9 kcal/mol and ΔE(toward one Cp π) = 2.9 kcal/mol.

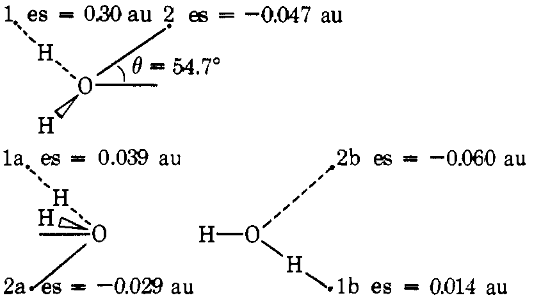
Since benzene-HF is too large to study with our current version of Gaussian 70, we have repeated our potential search for ethylene (center of π bond) ··· HF and found $\Delta E = 1.2$ kcal/mol. For benzene ··· HF, we examined approaches of the HF along the C_6 axis and toward the center of a C–C bond, and both were equally favorable, with $\Delta E = 0.9$ kcal/mol.

Can one rationalize these above calculations with electrostatic potentials? In both C_2H_2 and C_2H_4, the most favorable line of approach (center of π bond) has the more negative electrostatic potential at a given F ··· hydrocarbon plane distance and thus one would expect it to be the more favorable. In benzene, the C_6 axis is favored from an electrostatic point of view, so one might rationalize the fact that the energies for both approaches are equoenergetic by noting that the charge transfer from benzene to HF for the C_6 approach is 0.007 e⁻; for the edge approach it is 0.011 e⁻. Interestingly, these differences in charge transfer are consistent with qualitative arguments about preferential geometry for charge transfer effects,[42] but the calculations are crude enough and the amount of charge transfer small enough that the above argument for the geometrical consequences of charge transfer effects must remain tentative.

If we attempt to put our π electron donors in the same framework as the donors in Table VII, we are faced with the question of how to choose a reasonable out-of-plane distance to examine the potential. Choosing 2.12 Å, somewhat shorter than the observed π ··· H distance, we find the center of π-bond potentials for C_2H_4 and C_2H_2 of −0.016 and −0.026 au; at 2.4 Å the potentials are −0.012 and −0.020 au for the two hydrocarbons. We see that this latter set of potentials, along with the calculated ΔE's (3.2 and 4.9 kcal/mol), fit quite well into Table VII.

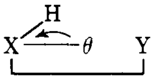
Pimentel[43] and McClellan have pointed out the evidence supporting C-H $\cdots$ X hydrogen bonds, so we examined this point further with electrostatic potentials. Comparing F_3C-H, HOC-H, HCC-H, H_2CHC-H, and H_3C-H, we find the electrostatic potential 2 Å from the proton 0.036, 0.020, 0.011, 0.009, and 0.003. Recalling the H-bond energies previously discussed (7.6 kcal/mol for F_3C-H $\cdots$ NH_3 and 1.1 kcal/mol for H_3C-H $\cdots$ NH_3) we expect an H-bond energy of ~2-3 kcal/mol for HC≡CH $\cdots$ NH_3. We have carried out a calculation for HC≡CH $\cdots$ NH_3 and do find an H-bond energy of 2.7 kcal/mol at a C-N distance of 3.3 Å. Our calculations are consistent with the observation of C-H $\cdots$ X hydrogen bonds in aldehydes and acetylides although our calculated ΔE's are exaggerated.

Given that an H-bonded dimer has been formed, can one predict the energies of further H bonds to this dimer? The electrostatic potentials for H_2O monomer and dimer look as follows, where 1, 1a, and 1b are 2 Å from the appropriate



proton and 2, 2a, and 2b are at 2.12 Å from the oxygen and in the idealized tetrahedral "lone pair" direction. These electrostatic potentials allow us to rationalize the results of calculations[44] which indicate that in the dimer, molecule a (the electron donor) is a better proton donor and poorer electron donor than an isolated H_2O molecule and for molecule b, the reverse is true.

Can intramolecular H bonds be rationalized within the same electrostatic potential framework and compared with intermolecular H bonds? We speculate that they can, when care is taken to evaluate the potential taking into account the constraints imposed by the remainder of the molecule on the H bond. For example, in H bond



if θ is constrained to be a given value ≠180°, the electrostatic potential at the appropriate distance *and* the appropriate angle with respect to the Y-H line should be used to compare this H bond with intermolecular H bonds.[45]

Predicting H-Bond Energies

Can one represent H-bond energies as a product of some function of the proton donor ability and the electron donor ability.

$$\Delta E(X \cdots H\text{-}Y) = f(H\text{-}Y)g(X) \qquad (5)$$

If all bonds were dominated by a dipole-dipole interaction at a fixed $R = \theta$, one would have a basis for the above equation.[46] While there is no rigorous justification for that equation in the general sense, let us consider how well this equation works for our 36 hydride H bonds. One way to approach this would be to optimize the 12 nonlinear parameters (6*f*'s and 6*g*'s) to minimize the deviation between the 36 calculated by 431G and those "calculated" using eq 5. Another, simpler, approach is to determine the *f*'s relative to a standard electron donor and the *g*'s relative to a common proton donor. This approach is illustrated in Table IX (NH_3 as standard electron donor and HF standard proton

Table IX. H-Bond Energies with NH_3 as Standard e⁻ Donor and HF as Standard Proton Donor[a] $f(HF)g(NH_3)$ = 16.3 kcal/mol

Proton donor	Electron donor: NH_3	H_2O	HF	PH_3	H_2S	HCl	HNC	HCN	HCP	H_2CO	H_2CS	H_2NCHO	H_2CNH
HF	$f(HF)g(NH_3)$	$0.82g(NH_3)$	$0.48g(NH_3)$	$0.42g(NH_3)$	$0.36g(NH_3)$	$0.21g(NH_3)$	$0.57g(NH_3)$	$0.55g(NH_3)$	$0.13g(NH_3)$	$0.61g(NH_3)$	$0.37g(NH_3)$	16.7	$0.90g(NH)_3$
H_2O	$0.55f(HF)$	7.4 (8.1)	4.3 (5.4)	3.8 (4.0)	3.2 (3.8)	1.9 (2.5)	5.1	4.9	1.2	5.5 (6.3)[b]	3.3	9.2 = 0.55*f* (HF)	8.1
HCl	$0.66f(HF)$	8.8 (8.2)	5.2 (4.6)	4.5 (4.3)	3.9 (3.5)	2.3 (2.0)	6.1	5.9	1.4	6.6	4.0	11.0	9.7
NH_3	$0.26f(HF)$	3.5 (4.1)	2.0 (3.6)	1.8 (2.2)	1.5 (2.1)	0.9 (1.3)	2.4	2.3	0.6	2.6	1.6	4.3	3.8
H_2S	$0.27f(HF)$	3.6 (3.8)	2.1 (2.5)	1.8 (2.1)	1.6 (1.8)	0.9 (1.1)	2.5	2.4	0.6	2.7	1.6	4.5	4.0
PH_3	$0.07f(HF)$	0.9 (1.1)	0.6 (1.0)	0.5 (0.8)	0.4 (0.6)	0.2 (0.4)	0.7	0.6	0.1	0.7	0.4	1.2	1.0
CH_4	$0.07f(HF)$	0.9	0.5	0.5	0.4	0.2	0.7	0.6	0.1	0.7	0.4	1.2	1.0
CHF_3	$0.47f(HF)$	6.3	3.7	3.2	2.8	1.6	4.4	4.2	1.0	4.7	2.8	7.9	6.9
HCN	$0.60f(HF)$	8.0	4.7	4.1	3.5	2.1	5.6	5.4	1.3	6.0	3.6	10.0	8.8
HNC	$0.80f(HF)$	10.7	6.3	5.5	4.7	2.7	7.4	7.2	1.7	8.0	4.8	13.4	11.7
HCP	$0.28f(HF)$	3.7	2.2	1.9	1.6	1.0	2.6	2.5	0.6	2.8	1.7	4.7	4.1
CHOHNH	8.3	6.8 = $0.82g(NH_3)$	4.0	3.5	3.0	1.7	4.7	4.6	0.2	5.1	3.1	8.5 (8.2)	7.5
CH_2NH	$0.34f(HF)$	4.6	2.7	2.3	2.0	1.2	3.2	3.1	0.7	3.4	2.1	5.7	5.0

[a] 431G calculated energies in parentheses. [b] References 13 and 29.

Table X. H-Bond Energies with PH_3 as Standard e^- Donor and HCl as Standard Proton Donor[a] $f(HCl)g(PH_3)$ = 4.3 kcal/mol

Proton	Electron donor					
donor	PH_3	H_2S	HCl	NH_3	H_2O	HF
HCl	$f(HCl)g(PH_3)$	$0.81f(HCl)$	$0.47f(HCl)$	$2.51f(HCl)$	$1.91f(HCl)$	$1.07f(HCl)$
H_2S	$0.49g(PH_3)$	1.7 (1.8)	1.0 (1.1)	5.3 (4.4)	4.0 (3.8)	2.3 (2.5)
PH_3	$0.19g(PH_3)$	0.7 (0.6)	0.4 (0.4)	2.1 (1.2)	1.6 (1.1)	0.9 (1.0)
HF	$1.60g(PH_3)$	5.6 (5.8)	3.2 (3.4)	17.3 (16.3)	13.1 (13.4)	7.4 (7.8)
H_2O	$0.93g(PH_3)$	3.2 (3.8)	1.9 (2.5)	10.0 (8.9)	7.6 (8.1)	4.3 (5.4)
NH_3	$0.51g(PH_3)$	1.8 (2.1)	1.8 (1.3)	5.5 (4.3)	4.2 (4.1)	2.3 (3.6)

[a] 431G calculated energies in parentheses.

Table XI. Scaled H-Bond Energy "Predictions"

Proton	Electron donor												
donor	NH_3	H_2O	HF	PH_3	H_2S	HCl	HNC	HCN	HCP	H_2CO	H_2CS	H_2NCHO	H_2CNH
HF	10.1	8.3	4.8	5.6	4.7	2.8	5.8	5.5	1.7	6.2	4.9	10.5	9.1
H_2O	5.5	(5.0)	3.3	3.2	3.2	2.0	3.2	3.0	0.9	3.4	2.7	5.7	5.0
HCl	8.7	6.6	3.7	4.3	3.5	2.0	5.0	4.7	1.5	5.3	4.2	9.0	7.8
NH_3	2.2	2.5	2.7	1.8	1.7	1.1	1.3	1.2	0.4	1.4	1.1	2.3	2.0
H_2S	3.6	3.1	2.0	2.1	1.8	1.1	2.1	2.0	0.6	2.2	1.7	3.7	3.2
PH_3	1.0	0.9	0.8	0.8	0.6	0.4	0.6	0.5	0.2	0.6	0.5	1.0	0.9
CH_4	0.7	0.6	0.3	0.4	0.3	0.2	0.4	0.4	0.1	0.4	0.3	0.7	0.6
CHF_3	4.7	3.9	2.2	2.6	2.2	1.3	2.7	2.6	0.8	2.9	2.3	4.9	4.2
HCN	6.0	4.9	2.9	3.3	2.8	1.7	3.4	3.3	1.0	3.7	2.9	6.2	5.4
HNC	8.1	6.7	3.8	4.5	3.8	2.2	4.7	4.4	1.4	5.0	3.9	8.4	7.3
HCP	2.9	2.4	1.4	1.6	1.3	0.8	1.7	1.6	0.5	1.8	1.4	3.0	2.6
$CHONH_2$	5.1	4.2	2.4	2.8	2.4	1.4	2.9	2.8	0.9	3.1	2.5	5.3	4.6
CH_2NH	3.4	2.8	1.6	1.9	1.6	0.9	2.0	1.9	0.6	2.1	1.6	3.5	3.1

donor) and Table X (PH_3 as standard electron donor and HCl as standard proton donor).

As one can see from Table IX, once one knows the ΔE for a hydrogen bond between H_3N and H–Y, one can predict the ΔE for H–Y forming a hydrogen bond to other electron donors using simple arithmetic and the above equation. This equation is of course based on the assumption that the hydrogen bonds that H–Y forms all electron donors follow the same order as those formed by H–F and that the relative strength of the X ··· H–Y and X ··· H–F bonds are determined by

$$\Delta E(X\cdots H\text{–}Y) = \Delta E(X\cdots H\text{–}F)\frac{\Delta E(H_3N\cdots HY)}{\Delta E(H_3N\cdots HF)} \quad (6)$$

The "predicted" values for the 25 hydride H bonds not used to calibrate the equation average 3.0 kcal/mol and one can predict the actual 431G energies with an average deviation of 0.6 kcal/mol. Using PH_3 and HCl as standards, one can predict the remaining 25 H-bonded complexes with an average deviation of 0.6 kcal/mol (average ΔE = 4.3 kcal/mol).

Since we have at our disposal the H-bond energies of the other compounds in Table V with NH_3 as electron donor and HF as proton donor, we can extend Table IX to include the other possible dimers and can predict the H bond energies of 119 other H-bonded complexes (Table IX).

A number of examples will illustrate the usefulness and limitations of this approach: $(HCN)_2$ is predicted to have a ΔE of 5.6 kcal/mol, about 40% higher than the experimental value.[47] Thus, we are limited in this approach by the accuracy of our wave functions for the molecules with which we calibrate the equation. We predict the energy of the $H_3CH \cdots OH_2$ H bond to be 0.9 kcal/mol;[48] one expects this value to be an upper bound for the nondispersion part of this interaction. This illustrates quite clearly the weakness of the $CH_4 \cdots H_2O$ interaction.[49]

It also should be pointed out that one does not need to have calculated $\Delta E(H_3N \cdots HY)$ or $\Delta E(X \cdots HF)$ to use Table IX in a predictive way. This is illustrated by the entries for formamide as a proton donor and acceptor where we had previously calculated[13] $\Delta E(HNHCHO \cdots HOH)$ and $\Delta E(CHOHNH \cdots OH_2)$. These calculations[13] allow us to predict the H-bond energies for formamide interacting with all the other dimers in Table IX by using eq 7 and 8.

$$\Delta E(H_2NCHO\cdots HY) = \Delta E(H_2NCHO\cdots HOH)\frac{\Delta E(H_3N\cdots HY)}{\Delta E(H_3N\cdots HOH)} \quad (7)$$

$$\Delta E(X\cdots HNHCHO) = \Delta E(H_2O\cdots HNHCHO)\frac{\Delta E(X\cdots HF)}{\Delta E(H_2O\cdots HF)} \quad (8)$$

Using these relations, we predict the ΔE for linear formamide dimer in very good agreement with the actually calculated value (8.5 "predicted" *vs.* 8.2 kcal/mol).[13]

It is clear from Table IX that the "predictions" are limited by the accuracy of the calibration calculations, our 431G basis set giving us too large H bond ΔE's. We now attempt a strictly empirical adjustment of the entries in the table based on $\Delta E(H_2O)_2$ = 5.0 kcal/mol[17] and $E(H_2S)_2$ = 1.7 kcal/mol.[24] We thus scale all our X = first row, H–Y = first row H bonds by 5.0/8.1 = 0.62, do not change our X = second row, H–Y = second row H bonds, and scale mixed-first-second-row dimers by 0.81. Thus, Table XI contains reasonable predictions for H-bond energies (where we have directly calculated ΔE's, these have been scaled; where there are none, we have used eq 5 to predict the ΔE). One could go one step further for molecules for which we know only the 431G electrostatic potential at the reference point. First, use either eq 2 or 4 (depending on whether one is examining an electron or proton donor) to predict ΔE for this molecule complexing with HF (if electron donor) or ammonia (if proton donor). Then use this information to predict the ΔE's for this molecule complexing with all the rest of the proton or electron donors in Table IX, and scale appropriately for Table XI. We will leave this as an exercise for the interested reader.

The use of empirical models to "predict" H-bond energies has been extensively developed by Drago and coworkers[50] using known H-bond solution enthalpies. Although not capable of "predicting" enthalpies to experimental accuracy,[51] it appears to do a respectable job in ordering the relative enthalpies of different complexes. The "model" proposed here goes one step further; by using eq 2 and 4, one should be able to predict H-bond energies for new compounds prior to any measurements.

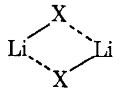
Summary and Conclusions

We have been able to predict a large number of H-bond geometries and *relative* energies for complexes which should be amenable to experimental observation, either by matrix isolation ir[52] or by supersonic nozzle beam methods.[27,28] The former method can tell in a given mixed X ··· Y dimer which is the proton donor and, from the observed ir frequencies, qualitative information about the strength of the interaction. The latter method has succeeded in predicting H-bond geometries very well. One might be able to evaluate relative H-bond energies with the beam method, but absolute H-bond energies are difficult to determine for weak H-bonded complexes.

Thus far, we have discussed experimental H-bond energies very little because for the complexes studied here, these energies are probably less reliable than very accurate calculations (such as carried out in ref 16) and empirical estimates of dispersion, correlation, and zero point energy corrections, although in those few dimers where accurate calculations and reliable experimental ΔE's are available (*e.g.*, $(HCOOH)_2$),[53] the agreement between theory and experiment is quite good. Thus, there is a need for more accurate calculations and experiments on the systems studied here. It should be emphasized that a series of very accurate calculations on a number of proton donors with a single electron donor (*e.g.*, NH_3) and a number of electron donors with a single proton donor (*e.g.*, HF) would allow us to reconstruct Table IX and predict with more confidence the remaining 144 entries in the table.

We have found that electrostatic potentials appear to be a useful tool in understanding and rationalizing H-bond energies and geometries. In cases where electrostatic potentials predicted the opposite order of H-bond energies (*e.g.*, HCN ··· HF and HNC ··· HF), an analysis of the charge transfer effects were useful in giving a qualitative rationale for the greater ΔE of the HNC ··· HF complex. In this study, we examined electrostatic potentials at a number of chosen points to try to correlate these with H-bond energies; a more rigorous approach is to evaluate the total electrostatic energy and other energy components separately for a number of H-bond complexes such as has been carried out in Morokuma's group.[54] Since it is clear that the 431G basis exaggerates the electrostatic attractions in H bonds, it remains for more rigorous calculations to show whether the use of electrostatic potentials proposed here will be generally useful. The fact that the electrostatic potential appears to dominate many structural and energetic features of H-bonded complexes predicted with STO-3G (which underestimates polarity) and 431G (which overestimates polarity) gave support to the hope that these potentials will be useful at any level of calculation.

Finally, one might ask whether the above has given a useful hint on how to define a hydrogen bond. There are two criteria one might reasonably use: (1) a cut-off ΔE for X ··· H–Y complex formation and (2) a requirement that the X ··· Y distance be shorter than the sum of the van der Waals radius of X, H, and Y by a nonnegligible amount. Both of the above would be fraught with arbitrariness, so one might settle for something less ambiguous: an AX ··· HYB system is held together by a H bond if the electrostatic potential surrounding X is negative, H is positive, and the X, H, and Y are approximately colinear. Intramolecular H bonds pose a problem with the above, as do certain crystal H bonds which appear to be reasonably strong despite their nonlinearity. The linearity requirement would separate H bonds from Li bonds,[55] since Li–X systems prefer cyclic



to linear Li–X ··· Li–X geometries. The electrostatic requirement would differentiate the H bonds discussed here from diborane and metal H bridges, since these latter are of low polarity or $X^{\delta+} \cdots {}^{\delta-}H\text{–}{}^{\delta+}Y$ polarity. Comparing the simple hydrides examined in this study, we see that the electrostatic potentials 2 Å from the protons (Table VI) follow a nearly linear trend in both the first and second rows of the periodic table: F–H (0.044), HO–H (0.030), H_2N–H (0.017), and H_3C–H (0.003); and Cl–H (0.034), HS–H (0.019), and H_2P–H (0.005). Thus we predict that B–H and Si–H groups will (unless there are very electronegative substituents attached to the B or Si) have electrostatic potentials 2 Å from the proton along the bond axis that are *negative* (~ -0.010). We expect (and eq 2 predicts) that B–H and Si–H groups will *not* form a hydrogen bond with a lone pair donor molecule.

The trend for the electron donors is not so linear and systematic (see Table VII), but we expect that the rare gas atoms, Ne and Ar, will have electrostatic potentials very near zero and eq 4 will predict negligible H-bond energies for these rare gases as electron donors to HF. A recent *ab initio* study by Losonczy, *et al.*,[56] on Ne ··· HF (ΔE = 0.23 kcal/mol) is consistent with this. In addition, eq 4 predicts repulsive interaction of the electrostatic potential near lone pair on the electron donor is positive and an *ab initio* study by Newton and Ehrenson[12] finds that the structure $H_3O^+ \cdots HOH$, with the water proton approaching the hydronium ion "lone pair", is unstable with respect to H_3O^+ and H_2O.

Thus the electrostatic potential is a powerful tool in understanding H bonds. First it allows semiquantitative predictions of H-bond energies for monomers prior to experimental measurement (eq 2 and 4), and, secondly, it is a useful organizing concept for all X:H–Y interactions, allowing us to predict whether one should call the interaction a "hydrogen bond". Clearly, $H_3O^+ \cdots HOH$ is formally a O: H–O interaction but is incapable of forming a hydrogen bond.

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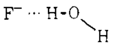

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