The Nature of the Hydrogen Bond. Dimers Involving Electronegative Atoms of the First Row[1a]

Peter A. Kollman[1b] and Leland C. Allen*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received April 3, 1970*

Abstract: Theoretical calculations on the dimers NH_3–NH_3, NH_3–HF, and NH_3–H_2O have been carried out. Ammonia forms much stronger hydrogen bonds with HF and H_2O than with itself. The proton potential surface in NH_3HF has been examined and compared with that calculated for NH_3HCl. Using the results of earlier calculations on $(H_2O)_2$, H_2O–HF, and $(HF)_2$, one finds that the principal features of the hydrogen bonds in these systems can be understood in terms of the degree of positive character of the hydrogen in the bond and the "range" of the electron-donor lone pair.

Theoretical investigations involving O—H···O hydrogen bonds dominate the H-bond literature, but relatively few studies involving N—H···O, N—H···N, N—H···F, N···H—F, and N···H—O systems have been carried out.

One finds experimental evidence of ammonia–ammonia hydrogen bonds from several sources. Pimentel and others[2] studied ammonia dimers in rare gas matrices and found that a linear structure of the ammonia dimer is favored over a cyclic one. Ammonia crystal structure data[3] indicate that an ammonia donates three hydrogens to different neighbors and receives a hydrogen from three different neighbors, thus participating in six hydrogen bonds.

Also of interest are the mixed-dimer systems involving NH_3–HF and NH_3–H_2O. These complexes should have a greater energy of stabilization than the ammonia dimer[4] and therefore are possible candidates for gas-phase structural determination. Clementi[5] has carried out an extensive study of the NH_3HCl system, and it is of interest to compare his results to our calculations on NH_3–HF.

Previous molecular orbital results on experimentally observable H-bond properties have shown the following. Geometry and energy of formation of strong and weak hydrogen-bonded systems are well represented in *ab initio* molecular orbital calculations.[5–12] CNDO (complete neglect of differential overlap) or INDO (intermediate neglect of differential overlap) molecular orbital methods appear to be the most appropriate semiempirical techniques for studies of hydrogen bonding,[4] giving reasonable agreement with experiment for H-bond energies and geometries[13–20] (systematically overestimating the energy and underestimating the X···Y distance). The increased infrared spectral intensity and frequency shift of the X–H stretch and the increase in frequency of the HOH bend have been examined theoretically in some H-bonded systems and have given qualitatively interesting results.[6,10] In both strong (HF_2^-)[11] and weak [$(H_2O)_2$ and $(HF)_2$][10] hydrogen bonds, the electron density around the hydrogen is substantially decreased, demonstrating that much of the nmr downfield shift is probably due to deshielding of the proton rather than the paramagnetic term.[21] CNDO calculations on carbonyl systems show a substantial blue shift in the n–π^* transition upon H-bond formation,[22] and studies on acetylacetone indicate that the proton potential curve may be quite different in the electronically excited state than in the electronic ground state.[23] In this paper we gain further understanding of the nature of the hydrogen bond and the physical effects involved in hydrogen bonding by examining population analyses and molecular orbital energy shifts in dimers involving NH_3, H_2O, and HF.

Description of Calculation

The energy calculations were carried out with the aid of a set of automatic computer programs written at Princeton University. Near Hartree–Fock quality atomic orbitals were used as a basis set: (10s, 5p) Gaussian basis functions on nitrogen, oxygen, and fluorine and 5s Gaussians on hydrogen.[24] In these

---

(1) (a) Research supported by the Chemistry Section of the National Science Foundation under Grant No. NSF-GP-8907; (b) NSF Predoctoral Fellow, 1966–1970.

(2) G. C. Pimentel, M. O. Bulanin, and M. Van Thiel, *J. Chem. Phys.*, **36**, 500 (1962).

(3) See W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 221.

(4) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 753 (1970).

(5) (a) E. Clementi, *J. Chem. Phys.*, **46**, 3851 (1967); (b) *ibid.*, **47**, 2323 (1967); (c) E. Clementi and J. N. Gayles, *ibid.*, **47**, 3837 (1967); the minimum energy is found at R(N–Cl) = 2.8 Å, R(H–Cl) = 1.62 Å; the minimum H–Cl distance in isolated HCl is 1.27 Å; thus, the proton moves 0.35 Å.

(6) P. A. Kollman and L. C. Allen, *ibid.*, **51**, 3286 (1969).

(7) (a) G. Diercksen, *Chem. Phys. Lett.*, 4, 373 (1969); (b) D. Hankins, J. W. Moskowitz, F. Stillinger, *ibid.*, 4, 581 (1970).

(8) J. Del Bene and J. Pople, *ibid.*, 4, 426 (1970).

(9) K. Morakuma and J. Winick, *J. Chem. Phys.*, **52**, 1301 (1970).

(10) P. A. Kollman and L. C. Allen, *ibid.*, **52**, 5085 (1970).

(11) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970).

(12) L. C. Allen and P. A. Kollman, *ibid.*, **92**, 4108 (1970).

(13) P. A. Schuster, *Int. J. Quantum Chem.*, **3**, 851 (1969).

(14) J. R. Hoyland and L. B. Kier, *Theor. Chim. Acta*, **15**, 1 (1969).

(15) T. Miyazaki, H. Oobayashi, and R. Itoh, *J. Phys. Soc. Jap.*, in press.

(16) A. Ockvirk, A. Azman, and D. Hadzi, *Theor. Chim. Acta*, **10**, 187 (1968).

(17) A. Pullman and H. Berthod, *ibid.*, **10**, 461 (1968).

(18) P. Schuster and Th. Funck, *Chem. Phys. Lett.*, **2**, 587 (1968).

(19) A. S. N. Murthy and C. N. R. Rao, *Chem. Phys. Lett.*, **2**, 123 (1968).

(20) P. Schuster, *ibid.*, **3**, 433 (1969).

(21) See G. C. Pimentel and A. D. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, pp 248–251, for a discussion of the possible effects in the nmr shift.

(22) P. A. Kollman, unpublished results.

(23) D. Rauh, personal communication.

(24) The calculations on the NH_3–NH_3 system were carried out using Whitten's lobe function (GLF) for both the s and p bases {J. L. Whitten, *J. Chem. Phys.*, 44, 359 (1966); the calculations on the mixed-dimer systems used Whitten's s basis and Huzinaga's [S. Huzinaga, *ibid.*, 43, 1293 (1965)] p basis (CGF)}. The latter basis gives a lower energy by

calculations the heavy-atom s functions were contracted into three groups, the heavy-atom p functions into one, and the hydrogen s's into one. In one set of NH_3–HF calculations, additional energy-determined coefficients were allowed on the fluorine (4, 2 contraction) in order to better represent the energy of F^- relative to $F(^2P)$. Self-consistent-field calculations were carried out using the Roothaan procedure.[25] For each wave function, molecular orbital energies, energy components, and Mulliken populations[26] were determined.

Geometry and Energy of Formation

The results of calculations on hydrogen fluoride, H_2O, and ammonia are summarized in Table I. The basis set used here predicts monomer geometries in good accord with experimental values, so that the experimental monomer geometry was assumed in the dimer calculations. Even in the strongest dimer previously studied, H_2O–HF,[10] the H–F distance stretches by only 0.011 Å upon H-bond formation, changing the dimerization energy found by bringing rigid monomer fragments together by ~0.4 kcal/mol. Only the NH_3–HF dimer is more tightly bound than H_2O–HF, and in the next section we consider the H–F distance variation for NH_3–HF. A comparison between calculations and experiment on the monomers is given in Table I. An additional support for the adequacy of this basis set to predict dimer properties is found by comparing the water dimer work of Kollman and Allen[6] (using the same quality basis set as found here) with the more extensive SCF calculations of Hankins, *et al.*[7b] and Diercksen.[7a] All three workers find a linear dimer (R = 3.0 Å) to be the most favorable, with the dimerization energy close to 5 kcal/mol (Hankins, 4.72; Diercksen, 4.84; Kollman and Allen, 5.3.).

Table I. Monomer Calculations[a]

HF			HF (split fluorine)		
r	θ	E	r	θ	E
0.915		−99.99767	0.915		−100.01146
0.947		−99.99879	0.951		−100.01113
0.979		−99.99725	0.953		−100.01069
			0.990		−100.00753
H_2O			NH_3(CGF)		
0.957	105	−75.97638	1.0116	106.7	−56.14246
0.957	110	−75.97709	1.058	106.7	−56.13480
0.957	115	−75.97631	1.111	106.7	−56.11285
0.990	105	−75.97562	1.0116	113	−56.14660
1.023	105	−75.97007	1.0116	120	−56.14601
NH_3(GLF)			NH_4^+ (C_{3v}, θ = 106.7)		
1.0116	106.7	−56.14176	1.0116		−56.49245
F^- (split F)			F (split F)		
		−99.40738			−99.38629

Atomic Populations

HF		H_2O		NH_3(CGF)		NH_3(GLF)	
F	9.44423	O	8.72979	N	7.90604	N	7.90782
H	0.55577	H	0.635105	H	0.697987	H	0.697393

Comparison with Experiment and More Exact Calculations

		This work	Other	Expt
HF	R	0.944	0.897[b]	0.915
	E_T	−99.99880	−100.07077	−100.530
H_2O	R	0.968	0.953 (assumed)[c]	0.957
	θ	110	105 (assumed)	104.52
	E_T	−75.97737	−76.059	−76.48
NH_3	R	1.002	1.0003[d]	1.012
	θ	115.7	107.2	106.7
	E_T	−56.14726	−56.2219	−56.5818
	ΔE(inversion)[e]	0.8	5.1	5.8

[a] Distances in ångströms, total energies in atomic units, θ in degrees. [b] P. Cade and W. Huo, *J. Chem. Phys.*, **47**, 614 (1967). [c] D. Neumann and J. W. Moskowitz, *ibid.*, **49**, 2056 (1968). [d] A. Rauk, L. C. Allen, and E. Clementi, *ibid.*, **52**, 4133 (1970). [e] Kilocalories per mole.

It is believed[5a,6,27,28] that correlation effects are not of great importance in predicting energies of formation and dimer geometries involving closed-shell reactants and products, but no rigorous test of this conjecture[5] has yet been performed. The reasonable agreement between experiment and SCF-calculated dimerization energies for $(H_2O)_2$ is empirical support for this. An extension of the basis set and inclusion of configuration interaction is likely to change the absolute answers in the systems considered here, but the *trends* found for these chemically similar molecules (H_2O, HF, and NH_3) are likely to be valid.

It should be noted that the monomer dipole moments predicted by these wave functions are greater than the experimental values (calculated NH_3 = 2.31, H_2O = 2.48, HF = 2.12 D; experimental NH_3 = 1.48,[29] H_2O = 1.84,[30] HF = 1.82 D[30]), but there is no obvious correlation between monomer dipole moment and predicted dimerization energy. For example, the basis set used by Del Bene and Pople[8] finds a dipole moment of 1.85 D for H_2O and a dimerization energy of 6.5 kcal/mol; the more accurate (lower energy) water monomer wave function used by Hankins, *et al.*,[7b] predicts a dipole moment of 2.1 D and a dimerization energy of 4.72 kcal/mol.

Our calculations on the ammonia dimer predict a linear structure to be more stable than a cyclic structure, in agreement with Pimentel's[2] interpretation of the infrared spectra of matrix-isolated $(NH_3)_2$. The relative energies of the two structures are in excellent agreement with CNDO results[12] on the same system (see Figure 1 for geometries considered and Table II for dimer results). CNDO results indicate that the bifurcated structure is the least stable; since this semiempirical method tends to overestimate dimerization energies, no *ab initio* calculations have been carried out on the bifurcated structure. Crystal structure studies by Olovsson and Templeton[31a] found an N–N distance in solid ammonia of 3.4 Å, close to our dimer results of 3.49 Å. This agreement may be fortuitous, however, because in the crystal each lone pair is forming three

---

about 0.001 au for NH_3; dimerization energies calculated are invariant to basis set [$(HF)_2$ studies with GLF and CGF both found a dimerization energy of 4.6 kcal/mol].

(25) C. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(26) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(27) K. Freed, *Chem. Phys. Lett.*, **2**, 255 (1968).

(28) L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969).

(29) J. F. Regniew and A. Daum, *C. R. Acad. Sci.*, **255**, 2417 (1960).

(30) R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase," NSRDS-NBS 10, U. S. Government Printing Office, Washington, D. C., 1967.

(31) (a) I. Olovsson and D. H. Templeton, *Acta Crystallogr.*, **12**, 832 (1960). (b) The infrared spectral work by A. Tursi and E. Nixon, *J. Chem. Phys.*, **52**, 1521 (1970), indicates that water dimers in rare gas matrices have a much smaller O–H stretching frequency shift than in ice I. This implies a longer O–O distance in the dimer than in the crystal. For a more detailed description of the $\Delta\nu$ *vs.* $R(X\cdots Y)$ relationships, see L. Bellamy and R. Pace, *Spectrochim. Acta, Part A*, **25**, 319 (1969).

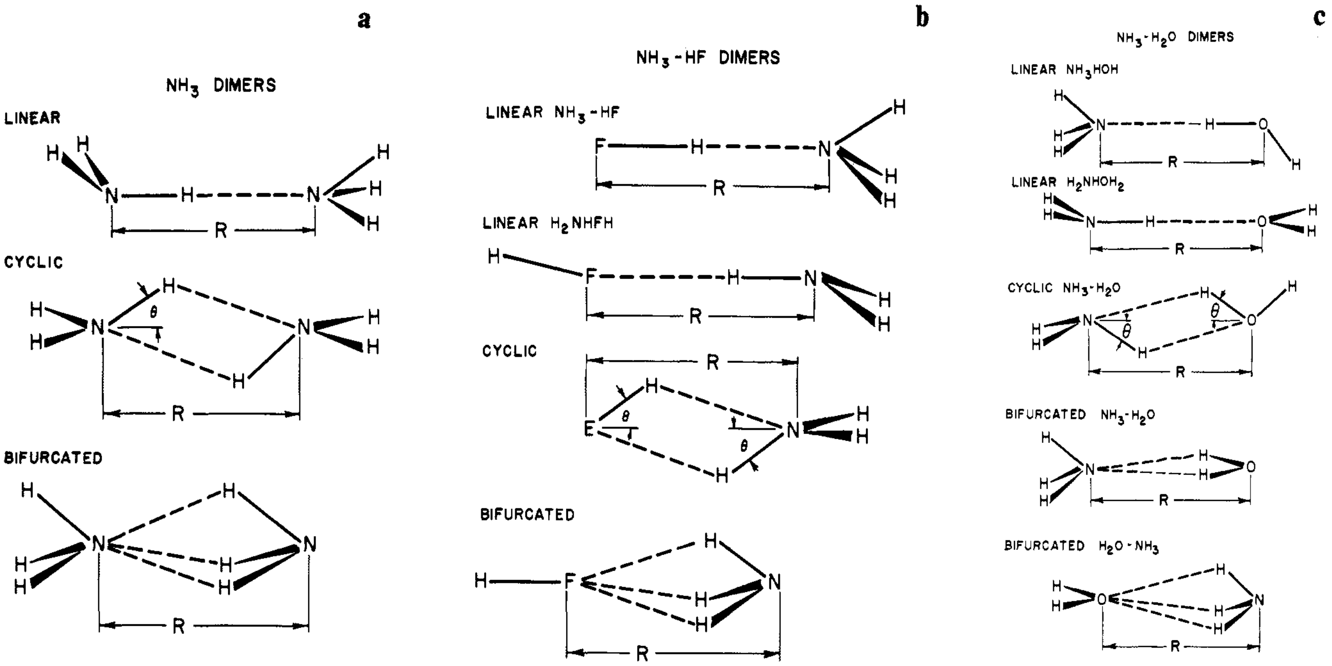


Figure 1. Geometry of dimers considered in this study: (a) $(NH_3)_2$, (b) NH_3-HF, (c) NH_3-H_2O.

hydrogen bonds, in contrast to the dimer, where it is forming one hydrogen bond. It should also be remembered that very accurate SCF calculations[7] on $(H_2O)_2$ find a minimum-energy O–O distance of 3.0 Å in contrast to the ice I distance[31b] of 2.76 Å.

An examination of the mixed NH_3–H_2O dimer results (Table II) reveals the NH_3HOH structure to be far more stable than the H_2NHOH_2, in agreement with the knowledge that ammonia is a better proton acceptor than water and water is the better proton donor. On the basis of CNDO/2 calculations on NH_3–H_2O dimers,[4] the bifurcated NH_3–H_2O structure would be expected to have a dimerization energy midway between those of the NH_3HOH and H_2NHOH_2 systems, but this system as well as the bifurcated H_2O–NH_3 and cyclic NH_3–H_2O systems have not been examined in this study. It is of interest that in the NH_3HOH system the CNDO/2 method appears to overestimate the dimerization energy (by 80%), in contrast to the much better agreement for H_2O and HF dimers (see Table I of ref 12).

Table II. Dimer Calculations[a]

R	E	R	E	R	E	R	E
NH_3HF linear (split F)		NH_3HF		H_2NHFH (split F)		H_2NHFH	
2.25	−156.16605	2.6	−156.15775	2.75	−156.15034	3.25	−156.14200
2.50	−156.17816	2.7	−156.15870	3.00	−156.15467	3.40	−156.14215
2.75	−156.17713	2.85	−156.15833	3.25	−156.15577	3.55	−156.14208
				3.50	−156.15572		
$(NH_3)_2$ linear (GLF)		$(NH_3)_2$ cyclic (GLF)		NH_3HOH		H_2NHOH_2	
2.8	−112.27842	2.7	−112.27475	2.6	−132.11972	2.80	−132.11659
3.1	−112.28606	3.0	−112.28167	2.85	−132.12695	3.05	−132.12129
3.25	−112.28727	3.3	−112.28385	3.15	−132.12801	3.30	−132.12237
3.4	−112.28767	3.6	−112.28433	3.5	−132.12580	3.55	−132.12228
3.7	−112.28735	3.86	−112.28435				

	Dimerization Energies				
	Optimized R, Å	ΔE, kcal/mol		Optimized R, Å	ΔE, kcal/mol
NH_3HF	2.75 (2.61)[b]	11.7 (15.9)	$(NH_3)_2$ cyclic	3.66	0.63
H_2NHFH	3.45 (3.32)	1.27 (1.41)	NH_3HOH	3.12	5.8
$(NH_3)_2$ linear	3.49	2.71	H_2NHOH_2	3.41	2.28

[a] Distances in ångströms, total energies in atomic units. [b] Values in parentheses are foi calculations with split fluorine.

An examination of the ammonia–hydrogen fluoride system shows the NH_3HF to be a very strongly bound dimer with the ΔE calculated 11.7 kcal/mol. As expected from the previous CNDO results, the linear H_2NHFH is very weakly bound.[32] The cyclic and bifurcated structures of NH_3–HF have been shown[4] to be comparable in stability to the H_2NHFH structure.

---

[32] Only structures with an NFH angle of 180° were considered; it is likely that an optimization of the NFH angle would yield a minimum-energy value of ~130° (staggered with respect to the NH_3 hydrogens) and an additional stabilization of ~0.2 kcal/mol. A similar result has been found previously for the HOHFH dimer (ref 9).

Table III. Proton Transfer[a]

R(N–F)	$r(H_F–F)$	E	Atomic populations H_N	N	H_F	F
2.5	0.915	−156.17816	0.67017	7.92127	0.54185	9.52637
2.5	1.083	−156.18077	0.65302	7.90992	0.48575	9.64527
2.5	1.25	−156.17118	0.63081	7.89308	0.46240	9.75209
2.5	1.369	−156.15870	0.60616	7.87669	0.46251	9.84232
2.5	1.431	−156.14736	0.591243	7.87057	0.47097	9.88473
2.5	1.488	−156.13561	0.58144	7.86905	0.47917	9.90746
4.0	0.915	−156.16104	0.69412	7.91695	0.55706	9.44363
4.0	0.947	−156.16125	0.69389	7.91751	0.53971	9.46111
4.0	0.962	−156.16058	0.69377	7.91781	0.53140	9.46948
4.0	2.915	−156.03845	0.55413	7.86919	0.46962	9.99880
4.0	2.931	−156.03850	0.55246	7.87008	0.47361	9.99893
4.0	2.946	−156.03782	0.54991	7.87167	0.47950	9.99910
4.0	2.988	−156.03507	0.54623	7.87448	0.48753	9.99930

Atomic Populations in Monomers

NH_3		NH_4^+ (C_{3v}) all	(N–H) = 1.01 Å, θ(HNH) = 106.7°	HF	
N	7.90604	N	7.87302	F	9.44423
H	0.697987	H_1, H_2, H_3	0.53322	H	0.55577
		H_4	0.52731		

[a] Distances in ångströms, energies in atomic units.

Proton Transfer. $NH_4^+F^-$?

In the previous section we examined the energy changes as the monomer fragments are brought together with fixed monomer geometries. This is an excellent approximation in all cases studied here, except for NH_3–HF, where we have studied proton transfer from the fluorine to the nitrogen at N–F distances of 2.5 and 4.0 Å using the split (4, 2 contraction) basis on fluorine (Table III). In either case the atomic population shifts show, as the proton is transferred, that most of the charge transferred moves from the hydrogens on the ammonia through the σ framework to the fluorine, with the nitrogen at first more negative than its monomer value and then becoming slightly more positive (less electron density) as the proton is transferred; this is analogous to Clementi's finding on NH_3HCl.[5b]

The minimum-energy proton position for NH_3HF (R = 2.5 Å) is at an F–H distance of 1.0 Å, only stretched by 0.06 Å from the isolated HF bond length (see Table I for a comparison of monomer properties calculated with the experimental properties). This stretch is smaller than that found in NH_3HCl,[5a] where the minimum-energy structure has the proton halfway between its position in isolated H–Cl and in isolated NH_4^+. There is no double minimum in the proton potential well at R(N–F) = 2.5 Å. It is possible that the single-determinant molecular orbital method used here would not show a double minimum because it represents bond dissociation poorly (correlation effects may also be important in determining the shape of the proton well in NH_3HCl). However, a double minimum is evident at R(N–F) = 4.0 Å (*any* proton potential well shows a single minimum at sufficiently short distances and a double well at sufficiently long distances). Valence-bond studies on HF_2^- by Erdahl[33] have revealed that at the minimum-energy F–F distance (2.25 Å) there was no double minimum in the proton potential, but at R = 3.0–3.5 Å a double minimum appeared. (Molecular orbital calculations on HF_2^- [11] indicate that a double well appears near 2.4 Å.) We conclude that many neutral hydrogen bonds with minimum energy at $R(X\cdots Y)$ = 2.6–2.9 Å may have a single minimum in the proton potential well, even though ionic systems (*e.g.*, $DCrO_2$[2]) often have double wells at $R(X\cdots Y)$ = 2.5 Å. Our results indicate that H_3NHF should not be represented as an ion pair, since both monomers retain most of their structural identity on dimer formation. NH_3HCl, as Clementi pointed out, is a much less clear-cut case and can be represented as halfway between $NH_3\cdots HCl$ and $NH_4^+\cdots Cl^-$.

Charge Shifts and Molecular Orbital Energy Shifts on Dimer Formation

Atomic populations as well as changes in atomic populations upon dimer formation are reported in Table IV. Even though the Mulliken populations are very basis-set dependent (for example, the atomic population on oxygen in H_2O for this double-ζ-quality atomic basis is 8.73; for a single-ζ Slater orbital basis,[34] it is 8.42), the charge changes upon dimer formation are much less dependent on basis set,[32] and for comparing population changes in different dimers, all studied with the same basis set, the charge changes appear to be a physically meaningful, albeit qualitative tool to analyze the nature of hydrogen bonding.

As the hydrogen bond is formed, the atom donating the lone pair first gains electron density, then loses electron density as more charge is transferred to the electron-acceptor (*i.e.*, proton donor) molecule. The hydrogen in the bond uniformly loses electron density.[35]

---

(33) R. M. Erdahl, Ph.D. Thesis, Princeton University, 1965; copies available from University Microfilms, Ann Arbor, Mich.

(34) K. Morakuma and J. Winick (ref 8) have carried out calculations on $(H_2O)_2$ with a single-ζ Slater orbital basis. The change in atomic population upon dimer formation which they found is very similar to ours [*J. Chem. Phys.*, **51**, 3286 (1969)], even though their atomic populations for the water monomer are quite different.

(35) The population analysis considered here uses monomer fixed geometries. If one allows the H–X bond to stretch as the $Y\cdots X$ distance decreases (considering only the minimum-energy H–X for a given $X\cdots X$ distance), the proton e^- density would undergo a continuous decrease during H-bond formation (see section on proton transfer).

Table IV. Atomic Populations for Dimer Systems

	Population	Δ[a]	Population	Δ	Population	Δ	Population	Δ
H_2NHNH_3								
	$R = 3.7$ Å		$R = 3.4$ Å		$R = 3.25$ Å		$R = 3.1$ Å	
N	7.91737	−0.00955	7.92170	−0.01388	7.92481	−0.01699	7.92886	−0.02104
H[b]	0.67654	+0.020853	0.66912	+0.028273	0.66417	+0.033233	0.65823	+0.03916
H	0.70376	−0.006367	0.70643	−0.009037	0.70846	−0.011067	0.71120	−0.01381
H	0.70376	−0.006367	0.70643	−0.009037	0.70846	−0.011067	0.71120	−0.01381
N	7.91357	−0.00575	7.91436	−0.00654	7.91438	−0.00656	7.91387	−0.00605
H	0.69678	+0.000613	0.69614	+0.001253	0.69562	+0.001773	0.69484	+0.00255
H	0.69411	+0.003283	0.69291	+0.004483	0.69205	+0.005343	0.69090	+0.00649
H	0.69411	+0.003283	0.69291	+0.004483	0.69205	+0.005343	0.69090	+0.00649
NH_3HOH								
	$R = 3.5$ Å		$R = 3.15$ Å		$R = 2.85$ Å			
N	7.91597	−0.00993	7.91846	−0.01242	7.91774	−0.01170		
H	0.69206	+0.005927	0.68844	+0.009547	0.68392	+0.014067		
H	0.69493	+0.003057	0.69220	+0.005787	0.68844	+0.009547		
H	0.69493	+0.003057	0.69220	+0.005787	0.68844	+0.009457		
O	8.74277	−0.01298	8.75334	−0.02355	8.76690	−0.03711		
H[b]	0.61658	+0.018525	0.60617	+0.028935	0.59641	+0.038695		
H	0.64276	−0.007655	0.64919	−0.014085	0.65815	−0.023045		
H_2NHOH_2								
	$R = 3.55$ Å		$R = 3.30$ Å		$R = 3.05$ Å			
N	7.91496	−0.00892	7.91743	−0.01139	7.92239	−0.01635		
H[b]	0.67832	+0.019667	0.67388	+0.024107	0.66577	+0.03247		
H	0.70391	−0.005923	0.70541	−0.007423	0.70846	−0.010473		
H	0.70391	−0.005923	0.70541	−0.007423	0.70846	−0.010473		
O	8.73530	−0.00551	8.73587	−0.00608	8.73604	−0.00625		
H	0.63180	+0.003305	0.63100	+0.004105	0.62944	+0.005665		
H	0.63180	+0.003305	0.63100	+0.004105	0.62944	+0.005665		
NH_3HF								
	$R = 2.85$ Å		$R = 2.7$ Å		$R = 2.6$ Å			
N	7.92584	−0.01980	7.92502	−0.01898	7.92367	−0.01763		
H	0.68360	+0.014387	0.67990	+0.018087	0.67682	+0.021167		
H	0.68360	+0.014387	0.67990	+0.018087	0.67682	+0.021167		
H	0.68360	+0.014387	0.67990	+0.018087	0.67682	+0.021167		
F	9.49210	+0.04787	9.50570	−0.06147	9.51708	−0.07285		
H	0.53126	+0.02451	0.52958	+0.02619	0.52879	+0.02698		
H_2NHFH								
	$R = 3.55$ Å		$R = 3.40$ Å		$R = 3.25$ Å			
N	7.91067	−0.00463	7.91156	−0.00552	7.91273	−0.00669		
H	0.68710	+0.010887	0.68536	+0.012627	0.68314	+0.014847		
H	0.70125	−0.003263	0.70178	−0.003793	0.70248	−0.004493		
H	0.70125	−0.003263	0.70178	−0.003793	0.70248	−0.004493		
F	9.44804	−0.00381	9.44849	−0.00426	9.44894	−0.00471		
H	0.55169	+0.00408	0.55103	+0.00474	0.55023	+0.00554		

[a] Δ is the atomic population difference between monomer and dimer. A negative Δ means an atom gains electron density upon dimer formation; a positive Δ means an atom loses electron density upon dimer formation. [b] Proton forming hydrogen bond.

The heavy atom of the e^- acceptor shows a continuous increase in electron density, even at large distances, before a significant amount of charge transfer has occurred. The charge shift (*not including charge transfer*)[36] on the electron-acceptor fragment is in all cases greater than the charge shift on the electron donor. In the case of the poorest electron acceptor (HNH_2) bonding with the best electron donor (NH_3), the total charge shift in the electron acceptor is 0.0277; in the electron donor the charge shift is 0.0064.

Table V contains the molecular orbital energies for the dimer systems as well as the energy shifts[37] relative to the monomer systems. The electron donor orbitals are tabulated first. As has been noted previously for all the dimers, the molecular orbitals on the electron donor decrease in energy (relative to their monomer values), and all the molecular orbital energies on the electron acceptor are increased. At the minimum-energy geometry, there is sufficiently little mixing between the molecular orbitals of the two monomer fragments that each orbital can still be unequivocally assigned to one fragment or the other. However, when two orbitals of the same symmetry on different fragments approach the same orbital energy value (one from below and the other from above), there is considerable mixing of the coefficients, and the energy of the orbital originally on the electron donor may begin to increase in energy. This occurs in the H_2NHOH_2 dimer, where the energy of the electron-donor (H_2O) orbital (A symmetry), which begins at −0.5374 au when at infinite separation, first decreases upon approach of the electron acceptor. This orbital energy then increases to avoid crossing the A orbital of the

---

(36) Charge shift is defined as the charge redistribution within a monomer fragment. For example, if hydrogen fluoride is the electron donor in a hydrogen bond and the atomic population differences in this fragment are H(+0.0099)–F(−0.0083), the charge shift is 0.0083 electron; the charge transfer is 0.0016 e^- transferred to the electron-acceptor fragment.

(37) See P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1140 (1970).

Table V. MO Energies (au)

Monomers and Atoms

NH_3(CGF)	NH_3(GLF)	HF	H_2O	LiF[a]
−15.46579	−15.46733	−26.17998	−20.45630	−25.6275
−1.11769	−1.11832	−1.56652	−1.32241	−2.4705
−0.60364	−0.60408	−0.71667	−0.68330	−1.1808
−0.60364	−0.60408	−0.61744	−0.53805	−0.2927
−0.40109	−0.40133	−0.61744	−0.48549	−0.2927
				−0.2817

Li_2[a]	H_2[a]	H(^{2}S)	Li(^{2}S)	F(^{2}P)	O(^{3}P)
−2.4760	−0.5922	−0.4998	−2.4761	−26.3798	−20.66617
−2.4760			−0.1962	−1.5713	−1.2425
−0.1884				−0.7266 (3)	−0.6295 (3)

Dimers

E	Δ[b]	*E*	Δ	*E*	Δ
		H_2NHNH_3			
R = 3.1 Å		*R* = 3.4 Å		*R* = 3.7 Å	
−15.41692	0.05041	−15.43127	0.03606	−15.43963	0.02770
−1.07767	0.04065	−1.08708	0.03124	−1.09323	0.02509
−0.56900	0.03508	−0.57600	0.02808	−0.58145	0.02263
−0.56745	0.03663	−0.57271	0.03137	−0.57747	0.02661
−0.36133	0.04000	−0.37139	0.02994	−0.37764	0.02369
−15.48109	−0.01376	−15.47794	−0.01061	−15.47588	−0.00855
−1.13480	−0.01648	−1.13019	−0.01187	−1.12754	−0.00922
−0.62034	−0.01626	−0.61614	−0.01206	−0.61360	−0.00952
−0.61987	−0.01579	−0.61570	−0.01162	−0.61321	−0.00913
−0.41720	−0.01587	−0.41601	−0.01468	−0.41351	−0.01218
$\langle\Delta_{don}\rangle = -0.01563^{c}$		$\langle\Delta_{don}\rangle = -0.01217$		$\langle\Delta_{don}\rangle = -0.00972$	
$\langle\Delta_{acc}\rangle = 0.04055^{d}$		$\langle\Delta_{acc}\rangle = 0.03134$		$\langle\Delta_{acc}\rangle = 0.02514$	
$\lvert\langle\Delta\rangle\rvert = 0.02809^{e}$		$\lvert\langle\Delta\rangle\rvert = 0.02176$		$\lvert\langle\Delta\rangle\rvert = 0.01743$	
		NH_3HF			
R = 2.6 Å		*R* = 2.7 Å		*R* = 2.85 Å	
−26.04847	0.13151	−26.06774	0.11224	−26.09055	0.08943
−1.47878	0.08774	−1.48922	0.07730	−1.50220	0.06432
−0.65690	0.05977	−0.65901	0.05766	−0.66392	0.05275
−0.52996	0.08748	−0.54114	0.07630	−0.55470	0.06274
−0.52996	0.08748	−0.54114	0.07630	−0.55470	0.06274
−15.51953	−0.05374	−15.51331	−0.04752	−15.50561	−0.03982
−1.17045	−0.05276	−1.16462	−0.04693	−1.15243	−0.03974
−0.65502	−0.05138	−0.64966	−0.04602	−0.64298	−0.03934
−0.65502	−0.05138	−0.64966	−0.04602	−0.64298	−0.03934
−0.45485	−0.05376	−0.45379	−0.05270	−0.45006	−0.04897
$\langle\Delta_{don}\rangle = -0.05260$		$\langle\Delta_{don}\rangle = -0.04784$		$\langle\Delta_{don}\rangle = -0.04144$	
$\langle\Delta_{acc}\rangle = 0.09080$		$(\Delta_{acc}\rangle = 0.07996$		$\langle\Delta_{acc}\rangle = 0.06640$	
$\lvert\langle\Delta\rangle\rvert = 0.07170$		$\lvert\langle\Delta\rangle\rvert = 0.06390$		$\lvert\langle\Delta\rangle\rvert = 0.05392$	
		NH_3HOH			
R = 2.85 Å		*R* = 3.15 Å		*R* = 3.50 Å	
−20.37933	0.07697	−20.40456	0.05174	−20.42361	0.03269
−1.26581	0.05660	−1.28076	0.04165	−1.29389	0.02852
−0.63628	0.04702	−0.64428	0.03902	−0.65500	0.00830
−0.49632	0.04173	−0.50290	0.03515	−0.51212	0.02593
−0.42993	0.05556	−0.44561	0.03988	−0.45849	0.02700
−15.49489	−0.02910	−15.48683	−0.02104	−15.48025	−0.01446
−1.14824	−0.03055	−1.13987	−0.02218	−1.13296	−0.01527
−0.63426	−0.03062	−0.62612	−0.02248	−0.61929	−0.01565
−0.63315	−0.02951	−0.62564	−0.02200	−0.61892	−0.01528
−0.42475	−0.02366	−0.42645	−0.02536	−0.42106	−0.01997
$\langle\Delta_{don}\rangle = -0.02869$		$\langle\Delta_{don}\rangle = -0.02261$		$\langle\Delta_{doa}\rangle = -0.01613$	
$\langle\Delta_{acc}\rangle = 0.05558$		$\langle\Delta_{acc}\rangle = 0.04148$		$\langle\Delta_{acc}\rangle = 0.02849$	
$\lvert\langle\Delta\rangle\rvert = 0.04213$		$\lvert\langle\Delta\rangle\rvert = 0.03205$		$\lvert\langle\Delta\rangle\rvert = 0.02231$	
		H_2NHFH			
R = 3.25 Å		*R* = 3.4 Å		*R* = 3.55 Å	
−15.44480	0.02099	−15.44714	0.01865	−15.44898	0.01681
−1.09874	0.01895	−1.10048	0.01721	−1.10195	0.01574
−0.58625	0.01739	−0.58787	0.01577	−0.58919	0.01445
−0.58122	0.02242	−0.58396	0.01968	−0.58606	0.01758
−0.38321	0.01788	−0.38493	0.01616	−0.38633	0.01476
−26.19129	−0.01131	−26.19004	−0.01006	−26.18898	−0.00900
−1.57939	−0.01287	−1.57782	−0.01130	−1.57655	−0.01003
−0.73420	−0.01753	−0.73133	−0.01466	−0.72922	−0.01255
−0.63071	−0.01327	−0.62910	−0.01166	−0.62780	−0.01036
−0.63060	−0.01316	−0.62902	−0.01158	−0.62773	−0.01029
$\langle\Delta_{don}\rangle = -0.01363$		$\langle\Delta_{don}\rangle = -0.01185$		$\langle\Delta_{don}\rangle = -0.01045$	
$\langle\Delta_{acc}\rangle = 0.01953$		$\langle\Delta_{acc}\rangle = 0.01749$		$\langle\Delta_{acc}\rangle = 0.01587$	
$\lvert\langle\Delta\rangle\rvert = 0.01658$		$\lvert\langle\Delta\rangle\rvert = 0.01467$		$\lvert\langle\Delta\rangle\rvert = 0.01316$	

Table V. (*Continued*)

E	Δ^b	E	Δ	E	Δ
$R = 3.05$ A		$R = 3.30$ Å		$R = 3.55$ Å	
−15.42498	0.04081	−15.43433	0.03146	−15.43905	0.02674
−1.08369	0.03400	−1.08990	0.02779	−1.09339	0.02430
−0.59530	0.00834	−0.58561	0.01803	−0.58289	0.02075
−0.57282	0.03082	−0.57854	0.02510	−0.58166	0.02198
−0.36841	0.03268	−0.37485	0.02624	−0.37828	0.02281
−20.46996	−0.01366	−20.46715	−0.01085	−20.46565	−0.00935
−1.33852	−0.01611	−1.33743	−0.01232	−1.33284	−0.01043
−0.69926	−0.01596	−0.69568	−0.01238	−0.69383	−0.01053
−0.53171	+0.00634	−0.54253	−0.00448	−0.54622	−0.00817
−0.50248	−0.01699	−0.49857	−0.01308	−0.49656	−0.01107
$\langle\Delta_{\mathrm{don}}\rangle = -0.01128$		$\langle\Delta_{\mathrm{don}}\rangle = -0.01062$		$\langle\Delta_{\mathrm{don}}\rangle = -0.00991$	
$\langle\Delta_{\mathrm{acc}}\rangle = 0.02933$		$\langle\Delta_{\mathrm{acc}}\rangle = 0.02572$		$\langle\Delta_{\mathrm{acc}}\rangle = 0.02332$	
$\lvert\langle\Delta\rangle\rvert = 0.02030$		$\lvert\langle\Delta\rangle\rvert = 0.01817$		$\lvert\langle\Delta\rangle\rvert = 0.01662$	

[a] See ref 19. [b] Δ = molecular orbital energy of dimer minus molecular orbital energy of isolated monomer. [c] $\langle\Delta_{\mathrm{don}}\rangle$ = average MO energy change for electron-donor orbitals. [d] $\langle\Delta_{\mathrm{acc}}\rangle$ = average MO energy change for electron-acceptor orbitals. [e] $\lvert\langle\Delta\rangle\rvert$ = average absolute value of molecular orbital energy change.

electron acceptor (NH_3), whose energy was −0.60364 at infinite separation and began to increase as the two fragments approached each other. If one considers the average molecular orbital energy change for the different dimers at the *equilibrium geometry*, this energy change is a good indication of the relative dimerization energies.[37]

It is of interest to compare the molecular orbital changes upon covalent bond formation to those in donor–acceptor complexes. In those orbitals which do not mix substantially (mainly the 1s orbitals), one finds an increase in molecular orbital energy in LiF (both fluorine and lithium 1s), HF (fluorine 1s), and H_2O (oxygen 1s). The water 2s orbital is lowered in energy and the fluorine 2s raised upon bond formation.[38]

Cyclic systems (with a center of symmetry) are also of interest. In the cyclic dimer systems examined [$(H_2O)_2$,[6] $(HF)_2$,[10] and $(LiF)_2$[37]] all the molecular orbitals are raised in energy. All of the orbitals in Li_2 are raised in energy relative to 2Li, whereas the H_2 molecular orbital is lower in energy than the orbital on H.

The Mechanism of Hydrogen Bonding

(a) Hydrogen Bonding Involving a Fixed Electron Acceptor (Proton Donor), X–H. Certain interesting features emerge when one compares the hydrogen bonding for the first-row "electronegative" hydrides (Tables VI and VII) with a given electron acceptor, X–H. First, the minimum-energy X—H···Y distance is practically the same no matter what the electron donor Y is. Thus the system H_2N—H···Y has its minimum energy at R = 3.49, 3.41, and 3.42 Å for Y = NH_3, H_2O, and HF, respectively. However, all the other variables in the table for H_2NH as electron acceptor change as one changes the electron donor. As would be expected, the amount of charge transfer increases as the electron donor changes from HF to H_2O to NH_3, whose "lone-pair" ionization potentials are 16.38,[39] 12.61,[40] and 10.16[40] eV, respectively.[41] The amount of charge shift on the electron donor is relatively constant for all three complexes (for the H_3NHNH_2 it is 0.0064 electron, for H_2OHNH_2 it is 0.0058 electron, and for $HFHNH_2$ it is 0.0042 electron), but the charge shift on the electron acceptor changes drastically (for H_3NHNH_2 it is 0.0277 electron, for H_2OHNH_2 it is 0.0222 electron, and for $HFHNH_2$ it is 0.0123 electron) as one changes the electron donor. Thus, one sees that the electron-donor molecule causes much more charge redistribution on the electron acceptor than the electron acceptor causes on the donor.

(b) Hydrogen Bonding Involving a Fixed Electron Donor (Proton Acceptor), Y. Considering a given electron donor, one finds that the minimum-energy separation between monomers changes dramatically as the electron acceptor is changed (for H_3N–HF, H_3N–HOH, and H_3N–HNH_2, the minimum-energy separations are R = 2.75, 3.12, and 3.49, respectively). This trend can be understood by assuming that the closeness of approach of the proton donor to the base is mostly a function of the positive character of the hydrogen (the proton atomic population is 0.556 in HF, 0.635 in H_2O and 0.698 in NH_3). The more positive the proton, the closer it can approach the electrons of the lone pair before repulsive effects outweight this electrostatic attraction.

Naturally, if there is a drastic change in X···Y distance, there will be a large change in charge redistribution, but if one considers a common electron donor with different electron acceptors at the *same X···Y distance* (not necessarily the minimum-energy distance), one finds that the charge shifts and charge transfer are very much the same. This indicates that a change in electron acceptor has a relatively small effect on overall charge redistribution. For example, at R = 3.2 Å for H_3NHOH, the total charge shift is 0.0395 and the charge transfer is 0.0078. For H_3NHNH_2 at the same distance, the charge shift is 0.0414 and the charge transfer is 0.0071. This is further support for the fact that the electron donor plays a much greater role in the charge redistribution than the electron acceptor.

(c) Contributions to the Total H-Bond Energy. A division of the total SCF energy into electrostatic plus exchange and charge-redistribution energy [for $(HF)_2$ and $(H_2O)_2$]^{42} indicates that the consideration of just the first two terms yields a potential curve which is

---

(38) These trends of orbital shifts in H bonding are compatible with the idea behind 1s ESCA shifts. A fragment which gains electrons has its 1s (and other) orbitals raised in energy; the fragment which loses charge has its 1s lowered in energy [see M. Schwartz, C. Coulson, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 447 (1970)].

(39) F. H. Field and J. R. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(40) M. Al-Jobury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

(41) Calculated ionization potentials (using Koopmans' theorem) for these wave functions are 16.79 for HF, 13.21 for H_2O, and 10.91 for NH_3.

(42) P. A. Kollman and L. C. Allen, *Theor. Chim. Acta*, **18**, 399 (1970).

Table VI. Comparative Analysis of H-Bond Energies and Electron Distribution

System	R, Å	ΔE, kcal/mol	Charge changes[a] X	Charge changes[a] H	Charge changes[a] Y	Total charge shift	Charge shift on e^- donor	Charge shift on e^- acceptor	Charge transfer
NH_3 as Electron Donor									
N_2NHNH_2	3.49	2.7	−0.0064	+0.0277	−0.0136	0.0331	0.0064	0.0277	0.0036
H_3NHOH	3.12	5.8	−0.0123	+0.0299	−0.0249	0.0422	0.0123	0.0299	0.0100
H_3NHF	2.75	11.7	−0.0192	+0.0256	−0.0569	0.0448	0.0192	0.0256	0.0313
NH_3 as Electron Acceptor									
NH_3NHN_2	3.49	2.7	−0.0064	+0.0277	−0.0136	0.0331	0.0064	0.0277	0.0036
H_2OHNH_2	3.41	2.3	−0.0058	+0.0222	−0.0103	0.0280	0.0058	0.0222	0.0017
$HFHNH_2$	3.45	1.3	−0.0042	+0.0123	−0.0054	0.0165	0.0042	0.0123	0.0005
H_2O as Electron-Pair Donor									
H_2OHNH_2	3.41	2.3	−0.0058	+0.0222	−0.0103	0.0280	0.0058	0.0222	0.0017
H_2OHOH	3.0	5.3	−0.0116	+0.0275	−0.0219	0.0391	0.0116	0.0275	0.0064
H_2OHF	2.72	9.4	−0.0176	+0.0245	−0.0421	0.0433	0.0174	0.0259	0.0176
H_2O as Electron-Pair Acceptor									
H_3NHOH	3.12	5.8	−0.0123	+0.0299	−0.0249	0.0422	0.0123	0.0299	0.0100
H_2OHOH	3.00	5.3	−0.0116	+0.0275	−0.0219	0.0391	0.0116	0.0275	0.0064
$HFHOH$	3.08	3.0	−0.0083	+0.0148	−0.0106	0.0231	0.0083	0.0148	0.0016
HF as Electron-Pair Donor									
$HFNHN_2$	3.45	1.3	−0.0042	+0.0123	−0.0054	0.0165	0.0042	0.0123	0.0005
$HFHOH$	3.08	3.0	−0.0083	+0.0148	−0.0106	0.0231	0.0083	0.0148	0.0016
$HFHF$	2.88	4.6	−0.0133	+0.0137	−0.0177	0.0270	0.0133	0.0137	0.0040
HF as Electron-Pair Acceptor									
H_3NHF	2.75	11.7	−0.0192	+0.0256	−0.0569	0.0448	0.0192	0.0256	0.0313
H_2OHF	2.72	9.4	−0.0176	+0.0245	−0.0421	0.0433	0.0174	0.0259	0.0176
$HFHF$	2.88	4.6	−0.0133	+0.0137	−0.0177	0.0270	0.0133	0.0137	0.0040

[a] Where the respective atoms are connected as X···H—Y.

Table VII. Summary of Trends in H Bonding

Electron donor	Electron acceptor NH_3	Electron acceptor H_2O	Electron acceptor HF	Electron donor	Electron acceptor NH_3	Electron acceptor H_2O	Electron acceptor HF
	Heavy-Atom Distances, Å				Energies of Dimerization, kcal/mol		
NH_3	3.49	3.12	2.75	NH_3	2.7	5.8	11.7
H_2O	3.41	3.00	2.72	H_2O	2.3	5.3	9.4
HF	3.45	3.08	2.88	HF	1.3	3.0	4.6
	Charge Shifts, e^-				Charge Transfer, e^-		
NH_3	0.0331	0.0422	0.0448	NH_3	0.0036	0.0100	0.0313
H_2O	0.0280	0.0391	0.0433	H_2O	0.0017	0.0064	0.0176
HF	0.0165	0.0231	0.0270	HF	0.0005	0.0016	0.0040

similar in shape to the total energy curve but has a minimum at an X···Y distance approximately 0.3 Å longer. Dreyfus and Pullman[43] further divided the total energy, considering electrostatic, exchange-repulsion, and charge-redistribution energies separately. They found that the electrostatic (attractive) and exchange (repulsive) energy changes are a much more sensitive function of intermolecule distance than the changes in the charge-redistribution term. The minimum-energy geometry [R(X···Y)] was 0.15–0.35 Å shorter than the minimum energy in the coulomb plus electrostatic potential curve (see Table VIII for a summary of the results). These results seem to indicate that a fixed-charge model gives reasonable minimum-energy separation (although ~0.3 Å too long) and hydrogen-bond energy (although underestimated) for these *weak* H-bonded systems. In systems where there is substantial geometrical reorganization (*e.g.*, Clementi's NH_3HCl),[5a] a simple electrostatic plus exchange repulsion model would do a much poorer job.

Table VIII

System	E + X[a] R, Å	E + X[a] ΔE, kcal/mol	Total SCF R, Å	Total SCF ΔE, kcal/mol
$(H_2O)_2$[b]	3.1	5.5	2.85	7.7
$(HF)_2$[b]	2.9	5.3	2.75	6.9
$(Formamide)_2$[c]	3.2	4.5	2.85	8.0

[a] Electrostatic + exchange repulsion. [b] Reference 42. [c] Reference 43.

(d) Charge Transfer in Hydrogen Bonding and Connection with Previous Models. The role of charge transfer in hydrogen bonding has been discussed by many authors. Coulson[44] and Morakuma and Winick[9] point out that at long X···Y distances the hydrogen bond is essentially electrostatic, whereas at shorter X···Y distances charge transfer becomes important. Other authors correlate various hydrogen-bond properties with the ionization potential of the long pair,

---

(43) M. Dreyfus and A. Pullman, *Theor. Chim. Acta*, **19**, 20 (1970).

(44) C. A. Coulson in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, New York, N. Y., 1959, p 339.

stating that the main features of hydrogen bonding can be understood in terms of a charge-transfer mechanism.[45] Our quantitative calculations allow us to qualify and reconcile these points of view. There are three important effects in play: static attraction plus exchange repulsion, charge shift (charge redistribution within monomer fragments), and charge transfer. Charge shift is appreciable and, for all the dimers studied here except NH_3HF and H_2OHF, it is at least four times as large as the charge transfer at the minimum-energy $X\cdots Y$ distance. For NH_3HF and H_2OHF, the amount of charge transfer has become of the same order as the charge shift. Thus, while charge transfer is an important effect when the $X\cdots Y$ distance is short (<2.8 Å) *and* when the lone-pair ionization potential of the electron donor is sufficiently small (for example, at $R = 2.85$ Å the amount of charge transfer in HFHF is 0.0042; at the same $X\cdots Y$ distance in NH_3HF, it is 0.0234), the charge shift is larger than charge transfer in weak hydrogen bonds and of comparable importance in moderately strong H bonds (NH_3–HF). Charge shift is very dependent on the range of the lone-pair electron distribution (nitrogen has a longer range $2p_z$ orbital than fluorine) because the less tightly held the lone-pair electrons, the closer they get to the electron acceptor and the more they cause redistribution of the charge within the electron acceptor. Bratoz[45] has postulated that many of the phenomena associated with H bonding can be explained by charge transfer and has supported his view with evidence that the strength of the H bond varies inversely as the ionization potential of the lone pair. In contrast to this, it is our finding that the major physical effect for moderate-to-weak H bonds is in fact charge shift rather than charge transfer. However, *charge shift* also varies inversely as the ionization potential of the lone pair, and this then explains the observed empirical observations.

It is important to also make connection with the long-standing valence-bond models of Coulson and Danielson and Tsubomura.[44] They note that the relative weights of valence-bond structures (1) $X—H\cdots Y$, (2) $X^-H^+\cdots Y$, and (3) $X^-H—Y^+$ change as a hydrogen bond forms. The findings of the present work imply that the *change* in the relative contributions of structures 1 and 2 to the overall wave function is a larger effect in moderate-to-weak hydrogen bonds than the *total* contribution of structure 3 to the wave function.

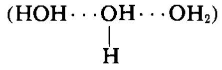
(e) MO Energy Shifts. The advantage of analyzing hydrogen bonding in terms of MO energy shifts (as discussed in the previous section) is that these shifts measure change in the system as a whole and are not dependent on whether or not one can rigorously abstract a three-atom, four-electron "hydrogen bond." One can also understand the individual donor and acceptor shifts in terms of the concepts discussed in this section (see Table IX).

With the exception of $(HF)_2$ and HFHOH, the average electron-acceptor molecular orbital energy shifts exceed those on the electron-donor fragment, supporting the view that the electronic structure of the electron acceptor is perturbed much more by the presence of the electron donor than *vice versa*. A common electron acceptor (HF) causes similar average changes in the MO energies of the various electron donors NH_3 (-0.045), H_2O (-0.043), and HF (-0.040), whereas a common electron donor (NH_3) causes very different changes in the MO's of HF (0.076), H_2O (0.043), and NH_3 (0.031).

Table IX

System		Av ΔMO (electron donor)	Av ΔMO (electron acceptor)	Av |ΔMO|	ΔE
NH_3	HF	−0.045	+0.076	0.0605	11.7
NH_3	HOH	−0.023	+0.043	0.033	5.9
NH_3	HNH_2	−0.012	+0.031	0.0215	2.7
H_2O	HF	−0.043	+0.057	0.050	9.4
H_2O	HOH	−0.026	+0.040	0.033	5.3
H_2O	HNH_2	−0.010	+0.024	0.017	2.3
HF	HF	−0.040	+0.036	0.038	4.6
HF	HOH	−0.024	+0.024	0.024	3.0
HF	HNH_2	−0.012	+0.017	0.0145	1.3

(f) Extension to Multiply H-Bonded Systems. It is of importance to consider the applicability of these results to multiply H-bonded systems. Hankins, *et al.*,[7b] find that the minimum-energy O–O distance in the water trimer is 3.0 Å, the same as in the dimer, but that the hydrogen-bond energy in certain trimers (those with the central water donating and accepting one hydrogen bond, as in I) is more than twice the dimer H-bond energy, whereas in other structures (*e.g.*, $H_2O\cdots HOH\cdots OH_2$) the H-bond energy is less than that for two dimers. Del Bene and Pople[8] found similar results with a contraction of the O–O distance in water polymers relative to the dimer, as did Allen and Kollman[12] for $(HF)_2$ $(HF)_4$, and $(HF)_6$. These results can be rationalized as follows. In the favorable water trimer and the HF linear trimer, the third H bond is formed by a hydrogen already more positive than the hydrogen in the HF monomer ($F^{\delta-}—H^{\delta+}\cdots F^{\delta-}—H^{\delta+}\cdots \lessdot F\cdots H$), thus allowing a closer approach of the H–F fragments, a larger hydrogen-bond energy, and greater charge redistribution. In the unfavorable water trimer, the third water is approaching **a** hydrogen which is *less* positive than in the water monomer ($H_2O\cdots H^{\delta+}—O^{\delta+}—H^{\delta-}\cdots OH_2$) and less H-bond energy is gained.


$$(HOH\cdots\underset{\mathrm{H}}{\underset{|}{O}}H\cdots OH_2)$$
I

(g) Extension to Other Molecules. Another aspect of population-analysis results must be stressed. The charge change upon H-bond formation is as large in the external parts of the molecules as it is in the three-atom fragment $X—H\cdots Y$, which is usually taken as the basic framework of a hydrogen bond (see Table IV). This means that one must consider the atoms directly attached to X and Y in order to understand the variation in strength of different hydrogen bonds. Thus NCl_3 is clearly going to be a poorer electron donor than NH_3, both because its dipole moment is smaller (less electrostatic attraction) and because the nitrogen lone pair is closer to the nitrogen and more tightly bound (less charge shift and charge transfer). 1,4-Dioxane (which has a total dipole moment of 0.4 D) forms strong hydrogen bonds because the *local* dipole moment (around

---

[45] See ref 21 and S. Bratoz, *Advan. Quantum Chem.*, 3, 209 (1966), for further discussion of charge transfer effects.

the oxygen) is high and because the oxygen lone-pair ionization potential and range in dioxane are comparable to those in water. Therefore, it appears that most hydrogen bonds can probably be understood in terms of the electrostatics and charge shift of the X—H···Y fragment plus the atoms immediately attached to X and Y.

Finally, one must consider how applicable the results of sections a and b are to other molecules in the periodic table. We have rationalized the proton-donating strengths of NH_3, H_2O, and HF on the basis of the amount of positive character of the hydrogen. But, why does HCl form a stronger H bond with ammonia than does HF? Certainly "the positive character of the hydrogen" does not tell the whole story as far as proton-donor ability is concerned. The H–X force constant is important because a smaller force constant allows the bond to stretch more upon approach of the base. If one examines Clementi's[5a] results for NH_3HCl, one finds that 7.5 of the 19.5 kcal of stabilization of the dimer is due to the H–Cl elongation (bringing the fragments together with monomer distances fixed results in a 12-kcal/mol stabilization). In addition, chlorine has a greater electron affinity than fluorine, and thus one would expect a greater stabilization through charge transfer in NH_3HCl than in NH_3HF. These last two statements rationalize the NH_3HCl case, but in order to test their validity in general, it will be necessary to carry out molecular orbital studies on hydrogen bonds involving the third row of the periodic table (PH_3, H_2S, HCl).

We have been able to understand the relative electron-donating abilities of NH_3, H_2O and HF on the basis of the greater radial extent and lower ionization potential of the lone pair of NH_3. However, as one goes down the periodic table, the ionization potential decreases (for HF it is -0.617 au, in HCl[5a] it is -0.472 au) and the "extent" of the lone pair increases. Experimental evidence[46] also indicates that electron-donor strengths increase in the order HI < HBr < HCl. Thus electron-donor ability must depend on the electronegativity of Y (it must have electrons available to function as an electron donor) and on its ability to donate these electrons. (Clearly, the nitrogen "lone pair" in NH_3 is much more available than in NCl_3 because, as Clementi has pointed out,[5b] the loss of electrons in the NH_3 fragment when $H_3N{:}HCl$ is formed occurs mainly at the three hydrogens. Thus chlorine is less likely to donate electrons than hydrogen.) Also, one would expect the oxygen in OF_2 to be a very poor electron donor. Even though it is very electronegative, the available electrons would be attracted by the fluorines and would not be available to attract an approaching H–X. Therefore, for an atom in a molecule to function as an electron donor in hydrogen bonding, it must have sufficient electron density to attract the approaching proton. To form very strong H bonds (as in the case of NH_3HCl), the electron donor must be able to draw on the electron reservoir of atoms covalently bonded to it, since its high electronegativity makes it energetically unfavorable for it to give up very much of its charge.

Conclusions

Ab initio calculations on the ammonia dimer have supported the experimental evidence that the linear structure is the more stable structure. Examination of ammonia–water and ammonia–hydrogen fluoride dimers shows that NH_3–HF is a very strongly bound complex, and perhaps amenable to gas-phase structural determination, but its ΔE(formation) is much less than that of HCl.

A comparative analysis of hydrogen bonding in the first-row species NH_3, H_2O, HF has revealed that most of the X···Y distance dependence in different H-bonded systems is determined by electrostatic considerations, with the amount of positive character of the H atom in the hydrogen bond being the crucial factor. At the particular X–Y separation, the range of the lone pair is the key to delocalization and charge-transfer parts of the total bond energy, the total charge shift and the charge transfer, and a further small shortening of the minimum-energy X–Y separation. The electron acceptor is the more important fragment in the initial electrostatic attraction, and the electron donor is the more important fragment in the charge-shift and charge-transfer effects in hydrogen bonding.

Finally, we have attempted to understand hydrogen bonding in other systems by comparing the trends found in the H bonding involving second-row hydrides (HF, H_2O, NH_3) with those expected as a function of the row in the periodic chart *and* as other atoms are substituted for A and B on the basic A—X—H···Y—B framework.

Acknowledgment. The authors appreciate the services made available by the Princeton University Computer Center (supported in part by National Science Foundation Grants No. GJ34 and GU3157). One of us (P. A. K.) thanks the NSF for fellowship support. The referees comments were very much appreciated.

---

(46) M. T. Bowers and W. Flygare, *J. Mol. Spectrosc.*, 19, 325 (1966).