A Theory of Hydrogen Bond Directionality

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Abstract: A new way of analyzing hydrogen bond structure is presented. This model, which makes use of the symmetry and energy of the molecular orbitals of the fragments which make up the hydrogen-bonded complex, is able to rationalize H-bond directionality in a more satisfactory way than "lone-pair" theory. In fact, the HFHCN dimer is presented as an example where the lone-pair approach to H-bond structure may be in qualitative disagreement with reality.

In ordinary chemical bonding problems, both valence-bond and molecular orbital theories have been very useful in analyzing molecular structure. The valence-bond theory[1] has been most successful when there is a central atom (or atoms) around which the bonding occurs. For example, it has been quite successful in analyzing the structure and bonding in hydrocarbons in terms of the hybridization of the atomic orbitals of each carbon atom. Molecular orbital theory, on the other hand, has been able to provide a coherent understanding of molecular structure in terms of the symmetry and number of valence electrons of the molecule.[2]

The concept of "lone pairs" of electrons, originating in the valence-bond theory of molecular structure, has had some success in rationalizing directionality in hydrogen bonding.[3] The facts that hydrogen fluoride molecules form zig-zag rather than linear chains in the crystal,[4] that HCN crystals contain linear HCN$\cdots$HCN chains,[5] and that hydrogen bonds involving carbonyl "lone-pair" donors often have C=O$\cdots$H angles near 120° are all evidence in support of the view that the proton forming the hydrogen bond is approaching a lone pair of electrons.

However, the lone-pair theory does not allow us to get a better and more detailed understanding of the key features of hydrogen bond structure. A lone pair, or Nyholm–Gillespie, model[6] would predict that a hydrogen bond to a given electron acceptor H—Y always have the same H—Y$\cdots$H angle; this is clearly not the case. Donohue[7] considered many C=O$\cdots$H hydrogen bonds and pointed out the wide scatter in C=O$\cdots$H angles in different H-bonded systems; lone-pair theory predicts that this angle should always be near 120°. So there is a need for a model which rationalizes the facts discussed above and allows at least qualitative predictions of H-bonded structure in related systems.

Components of the Hydrogen-Bond Energy and Their Dependence on H-Bond Directionality

It was shown by Coulson and Danielson[8] and Tsubomura[9] that there are various contributions to the hydrogen-bond energy and that the good agreement with experiment that the previously developed electrostatic theory had found for the H-bond energy was fortuitous. These authors concluded that the main contributions to the hydrogen-bond energy are: (a) electrostatic, which is the interaction between the fixed electron and nuclear charges of the individual molecules; (b) exchange repulsion—the intermolecular "Pauli-principle" repulsion between electrons of like spin; (c) polarization—the attractive interaction between a polarizable charge cloud on one molecule and the permanent multipoles of the other molecule; (d) charge transfer—a quantum mechanical attraction, due to the fact that the wave function for the complex contains a contribution from a term in which charge is transferred from one molecule to the other; and (e) dispersion—the second-order attraction between the fluctuating charges of the two molecules.

Recently, Duijneveldt and others[10] have used the perturbation formalism developed by Murrell, *et al.*,[11] to treat intermolecular interactions in the region of small overlap and have carried out a nonempirical calculation on a three-center, four-electron H-bond fragment to determine the magnitude of the various contributions to the hydrogen-bond energy. The results support the earlier semiempirical estimates made by Coulson and Danielson and Tsubomura. At his calculated equilibrium water dimer geometry, Morokuma's all-electron molecular orbital energy decomposition[12] has shown, in agreement with Coulson and Danielson,[8] that the electrostatic energy (a), the exchange repulsion (b), and the delocalization energy (polarization + charge transfer (c + d) are all of the same order of magnitude as the total hydrogen bond energy, with contributions (a) and (c + d) attractive and (b) repulsive.

How do these different contributions to the hydrogen-bond energy vary with geometry? All the individual contributions to the H-bond energy are very

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(1) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press," Ithaca, N. Y., 1960.

(2) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(3) G. C. Pimentel and A. D. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

(4) M. Atoji and W. N. Lipscomb, *Acta Crystallogr.*, 7, 173 (1954).

(5) W. J. Dulmage and W. N. Lipscomb, *ibid.*, 4, 330 (1951).

(6) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11, 339 (1957).

(7) J. Donohue in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968.

(8) C. A. Coulson and U. Danielson, *Ark. Fys.*, 8, 205, 239 (1955).

(9) H. Tsubomura, *Bull. Chem. Soc. Jap.*, 27, 445 (1954).

(10) F. B. van Duijneveldt and J. N. Murrell, *J. Chem. Phys.*, 46, 1759 (1967); F. B. van Duijneveldt, *ibid.*, 49, 1424 (1968); J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *Chem. Phys. Lett.*, 2, 565 (1968).

(11) J. N. Murrell, M. Randic, and D. R. Williams, *Proc. Roy. Soc., Ser. A*, 284, 566 (1965); J. N. Murrell and G. Shaw, *Mol. Phys.*, 7, 475 (1967).

(12) K. Morokuma, *J. Chem. Phys.*, 55, 1236 (1971).

sensitive to the X···Y distance between the monomers in an X—H···Y hydrogen bond, much more so than the total H-bond energy. However, in small dimers, for a fixed X···Y distance, exchange repulsion (b) and dispersion (e) are relatively insensitive to H-bond direction. In simple hydrogen-bonded dimers, for example $(HF)_2$ and $(HCN)_2$, both electrostatic (a) and polarization (c) energies favor a linear head–tail H-bonded configuration, H—F···H—F. As we shall see, an explanation of why HCN dimers and polymers are linear ($\theta(\mathrm{C{=}N \cdots H}) = 180°$) and HF dimers and polymers are not ($\theta(\mathrm{H—F \cdots H}) = 104–160°$) is found in the charge-transfer contribution to the hydrogen-bond energy. This charge-transfer energy has been shown to be proportional to the square of the overlap and inversely proportional to the difference in energy between an occupied orbital of the electron donor and an unoccupied orbital of the electron acceptor.[10,11]

Directionality in Hydrogen Bonds. A Comparison of Valence-Bond and Molecular Orbital Approaches on Specific Systems

(a) $(HF)_2$ and Crystalline HF. The H—F···H angle in crystalline hydrogen fluoride is 120°,[4] and accurate molecular orbital calculations by Kollman and Allen[13] and Diercksen[14] have found angles of 160 and 140° for the HF dimer. Using valence-bond theory, one would say that the proton-donor molecule is approaching one of the lone pairs of the proton acceptor. There are two basic difficulties with this argument. First, simple hybridization concepts (sp^3 hybridization around F) and Nyholm–Gillespie electron-pair repulsion ideas (lone pair–lone pair repulsions > lone pair–bond pair repulsions) would predict an H—F···H angle of near 109° for both dimer and polymer. Secondly, charge density maps[15] of the hydrogen fluoride molecule show that the electron density on the side of the fluorine away from the hydrogen is nearly spherically symmetrical, so that from an electrostatic point of view, there is no lone-pair direction favored. The lone-pair effect, if present, must come from a larger charge-transfer contribution in the lone-pair direction than in the direction favored by electrostatic and polarization terms ($\theta(\mathrm{H—F \cdots H}) = 180°$).

This charge-transfer effect can be understood more directly and quantitatively from a molecular orbital point of view. The highest occupied orbital of HF is a π orbital and the lowest unoccupied is a σ^*. Thus, in a linear H—F···H—F approach, the charge-transfer contribution to the hydrogen-bond energy is less because the charge transferred must come from the more strongly bound σ electrons on the proton acceptor to the σ^* orbital of the proton donor. If the H—F···H angle is not 180°, the charge transfer from the highest occupied (π) orbital on the proton acceptor to the σ^* orbital of the proton donor is symmetry allowed.

The calculated minimum-energy angle of 140–160° in the HF dimer is due to a competition between the electrostatic and polarization terms, which favor an angle of 180°, and the charge-transfer term, which favors a much smaller angle.[16] In HF polymers, there is a cooperative "nonlinear" effect in the hydrogen-bond energy and the fluorines approach closer together than they do in the HF dimer.[17] A number of theoretical calculations have noted this nonlinear effect in hydrogen bonds of the type X—H···X—H···X—H, and have also found considerably greater charge redistribution and charge transfer in the polymers than in the hydrogen-bonded dimers.[18] Experimental support for this nonlinear effect is indirect but considerable.[18] As the charge-transfer contribution to the hydrogen-bond energy increases, the minimum-energy F···F···F angle decreases. In HF crystal, this angle is observed to be 120°, and in gas-phase hydrogen fluoride hexamer, the angle is 104°.[21] In the latter case, however, the authors state that "this difference (between 104 and 120°) may be due to the thermal puckering of the extremely flexible ring in the vapor phase," so that in $(HF)_6$, the minimum-energy F···F···F angle is somewhere between 104 and 120°. It should be noted at this point that maximizing the charge-transfer contribution to the energy would lead to an F···F···F angle of 90°, since the most favorable direction for charge transfer is for a hydrogen-bond approach toward the π (highest occupied) molecular orbital of HF. The minimum-energy geometry observed for the hydrogen fluoride polymers is a compromise between electrostatic and charge-transfer contributions.

At this point, one can make two tentative generalizations. First, the minimum-energy geometry in H-bonded polymers is a compromise between the electrostatically favored direction ($\theta(\mathrm{H—F \cdots H}) = 180°$) and the charge transfer favored ($\theta(\mathrm{H—F \cdots H}) = 90°$). Secondly, as the F···F distance becomes smaller, the charge-transfer contribution to the hydrogen-bond energy increases and the angle $\theta(\mathrm{H—F \cdots H})$ decreases.

(b) $(H_2O)_2$. Nonempirical molecular orbital studies on water dimer[19,20,22–25] indicate that the minimum energy occurs with the proton-acceptor molecule in the *xy* plane (the *x* axis is the bisector of the HOH angle) and the proton donor molecule in the *xz* plane, with the O–H···O atoms collinear. The angle of ap-

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(13) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970).

(14) G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, **6**, 419 (1970).

(15) R. F. W. Bader, I. Keaveny, and P. E. Cade, *J. Chem. Phys.*, **47**, 3381 (1967).

(16) P. A. Kollman and L. C. Allen, *Theor. Chim. Acta*, **18**, 399 (1970); these authors calculated separately the electrostatic and charge-transfer contributions to the H-bond energy of $(HF)_2$ and $(H_2O)_2$.

(17) See P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 753, 4108 (1970), for molecular orbital calculations on HF polymers. $(HF)_6$, a cyclic polymer, is found to have a smaller F···F distance and more charge redistribution than the HF dimer.

(18) The two articles in ref 17; ref 19 and 20; J. R. Hoyland and L. B. Kier, *Theor. Chim. Acta*, **15**, 1 (1969); and A. S. N. Murthy, R. E. Davis, and C. N. R. Rao, *ibid.*, **13**, 81 (1968), are theoretical calculations which all show this nonlinear effect in H-bond energy and charge transfer as well as shorter X···Y distances in H-bonded polymers than dimers. Infrared spectral studies on methanol dimers and polymers by L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, **22**, 525 (1966), on water dimers and polymers by A. Tursi and E. R. Nixon, *J. Chem. Phys.*, **52**, 1521 (1970), and on HF dimer and polymers by P. V. Huong and M. Couzi, *J. Chim. Phys., Physicochim. Biol.*, **66**, 1309 (1969), all show a larger red shift for the A–H stretch in the polymers than the dimer. The latter authors also note that there is a pressure and temperature range where the dimer is predominant. Since the size of the red shift can be qualitatively correlated with the A···Y distance and A—H···Y hydrogen-bond strength, one can infer shorter A···Y distances and stronger H bonds in these polymers than are found in the dimers.

(19) D. Hankins, J. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.*, **53**, 4544 (1970).

(20) J. Del Bene and J. A. Pople, *ibid.*, **52**, 4858 (1970); in press (HF dimers and polymers).

(21) J. Janzen and L. S. Bartell, *ibid.*, **50**, 3611 (1969).

(22) K. Morokuma and L. Pedersen, *ibid.*, **48**, 3275 (1968).

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

(24) K. Morokuma and J. R. Winick, *ibid.*, **52**, 1301 (1970).

(25) G. H. F. Diercksen, *Chem. Phys. Lett.*, **4**, 373 (1969).

proach, θ, between the proton donor O–H and the bisector of the HOH angle in the proton acceptor is found to be between 25 and 57°,[19,20,23–25] with the external hydrogen of the proton donor trans to the two hydrogens of the proton acceptor. In this configuration, there is a greater tendency toward lone-pair directionality than in $(HF)_2$. The difference in energy between the minimum-energy and the $\theta = 0°$ configuration is 0.3 kcal/mol (1.2 kJ/mol) in the most accurate calculation;[19] in HF dimer, the difference between the minimum-energy and dipole-favored directions is 0.1 kcal/mol (0.4 kJ/mol).[14] Hankins, *et al.*,[19] have shown, however, that if one moves the external hydrogen of the proton donor fragment into the xy plane, one finds an extremely shallow potential curve for variation of θ, even more shallow than that found in $(HF)_2$. (The difference in energy between the $\theta = 0°$ and $\theta = 40°$ configurations is found to be less than 0.05 kcal/mol.) Thus, in water dimer, as in HF dimer, there is no great intrinsic tendency for proton-donor approach along the lone-pair-favored direction. A qualitative rationalization for the fact that the water dimer (with proton donor in the xz plane) has a stronger tendency for θ to be nonzero than in the HF dimer is the intermolecular repulsion among the three hydrogens not involved in the hydrogen bond.[26]

In energy component terms, this can be understood as follows: the most favorable configuration for the electrostatic energy is a compromise between the dipole–dipole-favored direction ($\theta = 0°$) and the direction which minimizes the external H–H repulsion energy ($\theta \neq 0°$). The charge-transfer term, as in $(HF)_2$, is slightly larger for $\theta \neq 0°$ because the most favorable "route" for charge transfer is from the highest occupied orbital of the proton acceptor (b_1) to the lowest unoccupied (a_1) orbital of the proton donor. This transfer is not symmetry allowed unless $\theta \neq 0°$, since the b_1 orbital is antisymmetric with respect to reflection in the xy plane[27] (see Table I for MO energies).

(c) Dimers with NH_3 as Proton Acceptor. In NH_3, the highest occupied orbital is an a_1 orbital, so that both the electrostatic and charge-transfer terms favor $\theta = 0°$ (approach of the proton donor along the C_3 axis). Lone-pair arguments reach the same conclusion.

(d) $H_2CO\cdots HOH$ and $H_2CO\cdots HF$. The highest occupied orbital in formaldehyde is a b_2 orbital (Table I), which is antisymmetric with respect to reflection in the plane bisecting the HCH angle (let this be the xz plane, with the C=O bond in the x direction). No charge transfer from this orbital is symmetry allowed in the dipole-favored approach of the proton donor along the x axis. In this configuration ($\theta(C{=}O\cdots H) = 180°$), charge transfer must come from the more strongly bound a_1 orbital.

Table I. Molecular Orbital Energies (au)

Molecule	Energy	Symmetry
HF[a]	−26.27677	σ
	−1.60276	σ
	−0.75221	σ
	−0.64206	$\pi(2)$
		σ^*
H_2O[b]	−20.55129	a_1
	−1.36302	a_1
	−0.71771	b_2
	−0.56336	a_1
	−0.50592	b_1
		a_1^*
H_2CO[c]	−20.5833	a_1
	−11.3559	a_1
	−1.4261	a_1
	−0.8675	a_1
	−0.7031	b_2
	−0.6389	a_1
	−0.5318	b_1
	−0.4403	b_2
HCN[d]	−15.59783	σ
	−11.29073	σ
	−1.23649	σ
	−0.81288	σ
	−0.58205	σ
	−0.49679	$\pi(2)$
		π^*

[a] Reference 13. [b] Reference 23. [c] A. D. McLean and M. Yoshimine, *IBM J. Res. Develop.*, Supplementary Table of Linear Molecules (1967). [d] S. D. Peyerimhoff, R. J. Buenker, W. E. Kammer, and H. Hsu, *Chem. Phys. Lett.*, **8**, 75 (1971).

However, if the proton donor approaches formaldehyde in the xy (molecular) plane, not exactly along the x axis, charge transfer can take place from the highest occupied b_2 orbital. In formaldehyde–H_2O,[12] the energy difference between the minimum-energy position ($\theta(C{=}O\cdots H) = 116°$) and $\theta(C{=}O\cdots H) = 180°$ is 1.8 kcal/mol (7.5 kJ/mol); this is in contrast to the much smaller difference between the minimum-energy and $\theta(H{-}F\cdots H) = 180°$ configurations in $(HF)_2$ (0.1 kcal/mol). This difference can be rationalized by noting that the difference in MO energy between the b_2 and a_1 orbitals in formaldehyde is 0.20 au,[28] whereas the difference in MO energy between the highest energy occupied π and σ orbitals in HF is 0.11 au.[13] The gain in using the b_2 (rather than the a_1) orbital for charge transfer in H_2CO is considerably greater than the corresponding gain in HF (or H_2O, where the b_1 orbital is only 0.06 au less bound than the a_1[21]).

The second highest energy occupied molecular orbital in formaldehyde is a b_1 ("π") orbital, which indicates that charge transfer would also be larger for a proton-donor approach somewhere in the xz plane than for an approach along the x axis, where charge transfer is only symmetry allowed from the a_1 orbital. Once again, the minimum energy for approach in the xz plane would be a compromise between the dipole-favored direction (along the x axis) and the charge-transfer-favored one (not directly along the x axis).[29]

No accurate calculations for $H_2CO\cdots HF$ have been carried out, but from the above arguments, it would be

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(26) At the minimum-energy O–O distance, the configuration in which the external hydrogens are cis to each other is less stable than the $\theta = 0°$ configuration (where the cis and trans configurations are the same). On the other hand, the configuration in which the external hydrogens are trans is more stable than the $\theta = 0°$ configuration. Thus, much of the tendency for the water dimer to be more stable in a $\theta \neq 0°$ configuration is due to the fact that the intermolecular hydrogen repulsions are minimized in such a configuration.

(27) In this case, the symmetry argument is not rigorous, since the dimer is not a member of the C_{2v} group, even for a proton-donor approach along the x axis. Here it is most meaningful to consider the orbitals of the H–O fragment, since this is the "route" through which the charge transfer occurs.

(28) S. D. Peyerimhoff, R. J. Buenker, W. E. Kammer, and H. Hsu, *Chem. Phys. Lett.*, **8**, 75 (1971).

(29) The difference in energy in the formaldehyde–water dimer between the O–H approach along the x axis and an approach of 30° in the xz plane is only 0.14 kcal/mol, whereas a similar change of approach of 30° in the xy plane results in an energy change of 0.5 kcal/mol.

Table II. CNDO/2 Study of HF···HCN[a]

HF···HCN			HCN···HF		
R(F···C), Å	θ, deg	E, au	R(N···F), Å	θ, deg	E, au
2.5	0	−47.56456	2.3	0	−47.58597
2.5	10	−47.56442	2.5	0	−47.59001
2.5	20	−47.56404	2.5	10	−47.59001
2.5	30	−47.56342	2.5	20	−47.59008
2.5	45	−47.56227	2.5	30	−47.59013
2.75	0	−47.57235	2.5	45	−47.59016
3.0	0	−47.57283	2.5	60	−47.59009
3.0	30	−47.57264	2.5	90	−47.57966
3.0	60	−47.57215	2.75	0	−47.58407
3.2	0	−47.57235	3.0	0	−47.57813

[a] E(HF) = −28.41819 au, E(HCN) = −19.15247 au. Monomer geometries taken from experiment; see "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11** (1958), and *Chem. Soc., Spec. Publ., Suppl.*, **No. 18** (1965).

expected to have a similar structure and potential surface as $H_2CO\cdots H_2O$.

(e) HCN Dimer and Polymer. The HCN crystal structure indicates that H bonds in this solid are linear.[5] Infrared studies on the HCN dimer in inert matrices indicate that $(HCN)_2$ is linear or near linear (no rotational fine structure was observed in the infrared modes of the dimer).[30]

In HCN, unlike HF, both the highest occupied and lowest unoccupied orbitals are of π symmetry (Table I).[31] Thus, both electrostatic and the energetically most favorable charge transfer favor a linear H-bonded system.[32]

A point made in the introduction should now be emphasized. The charge-transfer energy depends on the square of the overlap between the occupied orbitals of the electon donor and the unoccupied orbitals of the acceptor *as well as* the difference in energy between the orbitals. In HCN, unlike the molecules discussed up to now, the highest occupied and lowest unoccupied molecular orbitals are not centered on the electronegative atom in the hydrogen bond. Both the π and π^* orbitals in HCN contain nearly equal contributions from the nitrogen and carbon AO's;[31] thus, the overlap between the π and π^* orbitals on the two monomers would be much smaller than in the case of X—H···Y, when the highest occupied and lowest unoccupied molecular orbitals are effectively localized on X and Y. In HCN dimer, the largest charge-transfer contribution to the H-bond energy probably comes from the highest occupied σ and the lowest unoccupied σ^* orbital, because the greater overlap between these two makes up for the greater difference in energy between σ and σ^* than π and π^*.

(f) HCN···HF and HF···HCN. In the hydrogen bonds discussed to this point, the lone-pair arguments of the valence-bond theory, although founded on questionable premises, predict the same qualitative results as the MO method. One would like to consider dimers where the two models would predict different qualitative results. HF···HCN and HCN···HF are examples where such a situation might occur.

Lone-pair hybridization arguments would predict the dimer in which HF is functioning as proton acceptor to have a H—F···H angle near 120° and the dimer in which HCN is the proton acceptor to be linear.

On the other hand, the MO theory would predict the HF···HCN dimer to be linear, because both the highest occupied orbital of HF and the lowest unoccupied orbital of HCN are of π symmetry. Thus, both electrostatic (dipole–dipole) and charge-transfer contributions to the H-bond energy would favor an H—F···H angle of 180°. In H—C≡N···HF, the highest occupied orbital of the electron donor is π and the lowest unoccupied orbital of the proton donor is σ^*. Thus, one might expect θ(C≡N···H) to be less than 180°. In this case (HCNHF), the electrostatic energy favors a linear dimer, whereas the lowest energy charge-transfer term favors a nonlinear dimer.[33]

Semiempirical molecular orbital calculations using the CNDO/2 method[34] on the hydrogen-bonded configurations of HCN···HF are presented in Table II. As one can see, the most stable structure with HF as proton donor occurs at θ(C≡N···H) = 135° and the most stable structure with HCN as proton donor occurs at θ(H—F···H) = 180°. This result, although in line with the predictions of the molecular orbital model proposed in this paper, is unfortunately not definitive. First, the CNDO method finds the highest σ orbital less tightly bound than the π, in disagreement with more accurate calculations.[31] Secondly, there is *less* charge transfer in HCN···HF as θ is made less than 180° due to "back-bonding" from the HF into the π^* orbitals of HCN. This spurious extra stabilization in dimer calculations has been observed before.[35] An *ab initio* molecular orbital calculation on the potential surface of this dimer would be of great interest. Although there is no experimental evidence on the structure of HCNHF, mixed-crystal structure data or a matrix IP study might give insight into the H-bonded structure.

(g) Other H-Bonded Systems. Dreyfus and Pullman[36] have found that θ(C=O···H) in linear formamide dimer is near 120° and that the difference in

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(30) C. M. King and E. R. Nixon, *J. Chem. Phys.*, **48**, 1685 (1968).

(31) A. D. Mclean and M. Yoshimine, *IBM J. Res. Develop.*, Supplementary Table of Linear Molecules (1967).

(32) A. I. M. Rae, *Mol. Phys.*, **16**, 257 (1969).

(33) Again, one must also consider charge transfer originating from the more strongly bound σ orbitals of HCN and HF. As one changes θ from 180°, the overlap between the σ^* orbital of the proton donor with the σ orbital of the proton acceptor will decrease and the σ^*–π overlap will increase. If the total charge surrounding the outside of the electron-donor atom is roughly spherical (a good guess for HF,[15] but more questionable in HCN,[32] then charge transfer increases as θ increases, because the charge transfer comes increasingly from the more weakly bound π orbital. If, however, the decrease in overlap overcomes the more favorable energy denominator, charge transfer will start to decrease.

(34) See J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966), for a description of this method and ref 17 and 18 for applications of CNDO/2 to hydrogen-bonding problems.

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

(36) M. Dreyfus and A. Pullman, *ibid.*, **19**, 20 (1970).

energy between this configuration and the configuration in which $\theta = 180°$ is 1.5 kcal/mol (6.3 kJ/mol), similar to what Morokuma found in $H_2CO \cdots HOH$.[12] Dreyfus and Pullman note that in formamide, the highest occupied orbital is mainly an oxygen lone pair of "local" b_2 symmetry (as seen in formaldehyde) and that the charge-transfer contribution to the H-bond energy is 30% greater at $\theta = 105°$ than at $\theta = 180°$. This demonstrates that one need not have rigorous symmetry orbitals to apply the basic principles discussed above.[37]

Donohue[7] has presented a number of crystal structure examples where carbonyl groups and water molecules are functioning as electron donors. He presents many examples of H_2O functioning as double proton donor and single proton acceptor, with the "environment" around the oxygen approximately planar trigonal. It is difficult to give detailed structural predictions for the minimum-energy positions of the water in cases where it is functioning as the water of hydration to some larger, more complicated molecule. In these cases, the large molecule is the more important in determining the lowest free energy structure. The structure of the simplest hydrate (HNO_3–H_2O) presented by Donohue is not difficult to rationalize as near trigonal planar around the oxygen, because in that crystal one is dealing with something more like H_3O^+ ion (which is planar, or nearly so) than a neutral H_2O molecule. In general, however, the results of the molecular orbital studies on water dimer discussed above are consistent with Donohue's finding a great variety of directionality of proton approach toward H_2O. If one removes the effect of external hydrogen repulsion, the H-bond energy stays practically the same during considerable changes in the direction of proton-donor approach. Recall that Hankins, *et al.*,[19] found very little change in the hydrogen-bond energy for a change of θ from 0 to 40°.

In examining the carbonyl electron donors presented by Donohue, one is not able to present *a priori* predictions of the exact structure in these large molecules. However, this author would like to make a very qualitative observation about Donohue's Figure 4. Of the ten singly H-bonded structures, the first four, which have an average H-bond distance ($O \cdots Y$) of 2.80 Å, an average out-of-carbonyl-plane distance of 0.80 Å, and an average $C{=}O \cdots H$ angle of 145°, have a larger charge-transfer contribution (from the more weakly bound b_2 and b_1 orbitals of the C=O fragment) than the last six, whose average H-bond distance is 2.94 Å, average out-of-plane distance 0.38 Å, and average $C{=}O \cdots H$ angle 164°. As Coulson and Danielson pointed out,[8] longer H bonds are essentially electrostatic, and one would expect $C{=}O \cdots H$ angles near 180° and small out-of-plane distances for these. Thus, one would expect that in carbonyl hydrogen bonds, the longer bonds would tend to have $C{=}O \cdots H$ angles closer to 180°, and, the shorter the $O \cdots H$ distance, the more this angle would deviate from 180°. As has been emphasized above, in explaining the H-bond direction in a specific system, one must consider both the "external atom" interactions and the difference in energies among the highest occupied b_1, b_2, and a_1 orbitals of the carbonyl group.

The fact that the $H{-}Cl \cdots H$ angle in the hydrogen chloride crystal is 107° and the $H{-}Br \cdots H$ angle in solid HBr is 97°[38] can be rationalized in valence-bond language in terms of the increasing p character of the halogen lone pairs. This decrease in $\theta(H{-}X \cdots H)$ as one goes down the periodic table (recall that in HF crystal, this angle is 120°) can also be understood in terms of the increasing energy gap between the highest occupied π and σ orbitals of the H—X molecule. The σ–π gap in HF is 0.11 au; in HCl, it is 0.15 au.[39] The highest occupied orbital in HCl, which is of π symmetry, has a calculated ionization potential of 0.476 au,[39] which is lower than that of HF.

Thus, as one goes down the periodic table in the H–X series, one can make two generalizations. First, the *relative* charge-transfer contribution to the hydrogen-bond energy increases, due to the lower IP of HX. Secondly, the *directionality* imposed by this charge transfer increases, due both to the greater energy gap between the highest occupied π and σ orbitals and to the relatively smaller contribution of the electrostatic term to the overall H-bond stabilization.

A similar trend is expected for hydrogen bonding in $(H_2S)_2$ relative to $(H_2O)_2$. This difference in energy between the b_1 and a_1 orbital is 0.11 au in H_2S[40] compared to 0.06 au in H_2O, so that the charge-transfer directionality imposed in the H_2S dimer should be stronger than that found in H_2O.

It has been noticed[41] that in some situations the hydrogen bond is not exactly linear, *i.e.*, in $X{-}H \cdots Y$ the hydrogen is not exactly on the $X \cdots Y$ line. A small deviation from linearity is not surprising in these molecular crystals, if it allows some other intermolecular repulsion to be reduced. What about deviation of the hydrogen bond from linearity in $(HF)_2$ when $\theta(H{-}F \cdots H) = 180°$? This deviation would make the most favorable charge transfer (π–σ^*) symmetry allowed, but would cause a considerable loss in electrostatic attraction between the fragments. This change in $\theta(F \cdots H{-}F)$ very far from 180°, unlike the corresponding change in θ, would decrease the total overlap between the occupied orbitals of the proton acceptor and the σ^* of the proton donor, thus decreasing the charge transfer as well. Therefore, in systems with no other intermolecular repulsions to consider, the H bond prefers to be linear. The calculated small deviations from $X \cdots H{-}Y$ linearity by Del Bene and Pople[20] in $(HF)_2$ and $(H_2O)_2$ are probably due to a decrease in hydrogen–hydrogen repulsion brought about by a small deviation from $\theta = 180°$.

(h) Donor–Accepted Complexes. Benzene–Br_2. It should be pointed out that considerations similar to those employed in this paper have been most useful in giving further insight into the structures and properties of other donor-acceptor complexes; benzene–Br_2 is an excellent example. If charge transfer were the most important contribution to the stabilization of this complex, one would expect the Br_2 axis to lie parallel to the ben-

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[37] In the formamide linear dimer, there are significant changes in the repulsion and electrostatic terms as one changes θ; this is due to interactions between the non-H-bonded carbon and nitrogens in this dimer.

[38] D. F. Hornig and W. E. Osberg, *J. Chem. Phys.*, 23, 662 (1955).

[39] P. E. Cade and W. M. Huo, *ibid.*, 47, 649 (1967).

[40] S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Amer. Chem. Soc.*, 92, 3243 (1970).

[41] W. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

zene plane, so that charge transfer from the highest occupied benzene MO (of E symmetry) to the lowest unoccupied MO of Br_2 (σ_u) would be symmetry allowed. In fact, the minimum energy of the complex occurs with the Br_2 along the C_6 axis,[42] where any charge-transfer stabilization must come from the more strongly bound MO (A symmetry) of benzene. This configuration, however, maximizes the polarization stabilization (benzene quadrupole–Br_2 polarizibility), which appears to be the dominant attractive term.[43] This is strong evidence that charge transfer is not the key stabilizing effect in this complex. However, these two structures of benzene–Br_2 are likely to have a considerably different exchange repulsion and dispersion energy, so that in this case (unlike the H-bonded systems discussed above), the minimum energy is not mainly a compromise between electrostatic and polarization and charge-transfer terms.

Conclusions

A simple molecular orbital approach can give insight into the geometry of hydrogen-bonded systems. As has been shown above, the minimum energy often occurs at a position which is a compromise between the electrostatic and charge-transfer forces. Since each of these components is harder to predict quantitatively (being very sensitive to the basis set employed in the calculation[44] than the total H-bond energy, it is doubtful whether quantitative *a priori* predictions of the magnitude of the different energy components in more complex H-bonded systems are possible at present. However, proper consideration of the difference in the molecular orbital energy between the highest occupied orbitals of different symmetry (as in $(HF)_2$ and $H_2CO\cdots HOH$), the angular dependence of the electrostatic energy, and nonbonded hydrogen repulsions (as found in $(H_2O)_2$) should be useful in understanding structural differences in related hydrogen-bonded systems.

In this paper, it has been shown that in certain cases, the molecular orbital theory and the lone-pair (VB) theory predict different H-bonded structures. This is because the valence-bond theory of H-bond structure considers only the orbital structure of the electron donor and the molecular orbital theory considers the nature of the orbitals on both electron donor and acceptor.

Finally, what further insight into the role of charge transfer in hydrogen bonding has been achieved? Bratoz[45] and Puranik and Kumar[46] have developed a simple, empirical charge-transfer model for the hydrogen bond, with the justification that the hydrogen-bond energy often varies inversely as the lowest ionization potential of the electron donor. On the basis of the above discussion, the following comments are pertinent. First, certain hydrogen bonds, such as chloroform–benzene,[47] may have the proton donor approaching along the C_6 axis of the benzene, where charge transfer from the highest occupied "E" orbital is not symmetry allowed. Charge transfer should play very little role in the stabilization of such complexes and, in any case, should not depend on the lowest ionization potential of the electron donor, but the second lowest. Secondly, the fact that phosphines typically form weaker hydrogen bonds than amines[48] despite the lower ionization potential of the highest occupied a_1 orbital of the former does not imply that charge transfer is unimportant in phosphine H bonds. It is likely that the relative contribution of charge transfer to electrostatic stabilizations is greater for phosphines, even though the *total* H-bond energy is smaller.[49]

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(42) O. Hassel and K. Stromme, *Acta Chem. Scand.*, **12**, 1146 (1958); **13**, 178 (1959).

(43) J. L. Lippert, M. W. Hanna, and P. J. Trotter, *J. Amer. Chem. Soc.*, **91**, 4035 (1969).

(44) Compare the water dimer results of ref 12 and P. A. Kollman and L. C. Allen, *Theor. Chim. Acta*, **18**, 399 (1970).

(45) S. Bratoz, *Advan. Quantum Chem.*, 3, 209 (1967).

(46) P. G. Puranik and V. Kumar, *Proc. Indian Acad. Sci.*, **58**, 29, 327 (1963).

(47) M. D. Johnston, F. P. Gasparro, and I. D. Kuntz, *J. Amer. Chem. Soc.*, **91**, 5715 (1969).

(48) A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.*, **2**, 1 (1968).

(49) NOTE ADDED IN PROOF. Recently, Johanssen, Kollman, and Rothenberg (submitted to *Chem. Phys. Lett.*) have carried out *ab initio* calculations on the HCNHF and HFHCN dimers, finding both to have a minimum energy linear configuration. In both structures, the charge-transfer term appears to slightly favor the nonlinear arrangement, but the electrostatic contribution is clearly dominant in these long H bonds (R = 3.0–3.2 Å).