

in accord with reality and suffices to give the correct signs and magnitudes for the quadrupole moments in all three  $C_2H_{2n}$  molecules.

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## Perturbation Calculations on the Hydrogen Bonds between Some First-Row Atoms

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**Abstract:** A perturbation theory of intermolecular forces (including exchange) is applied to a hydrogen-bond model system  $A-H\cdots B$ . The parameters in the model are chosen to reproduce recent SCF results for some representative systems. Extrapolation then allows H bonds between the first-row atoms C, N, O, F, and Ne to be dealt with. Optimum orientations of the acceptors  $FH$ ,  $OH_2$ , and  $NH_3$  are determined with respect to the  $A-H\cdots B$  axis (which is kept linear throughout). Equilibrium  $H\cdots B$  distances and H-bond energies are then evaluated for the optimum configurations of these acceptors, as well as for the acceptors  $F^-$  and Ne. It is found that major trends in H-bond stability (as measured by  $-\Delta H$ ) can be reproduced reasonably well, although predictions on individual systems are not always reliable. Acceptor strengths are found to diminish in the order  $N > O > F > Ne$ , and this is ascribed to the decreasing asymmetry of the lone-pair region in these cases. In practice, F is a better acceptor than our results suggest because of its partial charge which here had to be neglected. The importance of a charge is illustrated by the case of  $F^-$ , which is found to form strong H bonds for all donors considered, whereas Ne gives repulsive energies throughout. H bonds involving different proton donors become longer as they get weaker, and in the case of  $C-H$  the  $H\cdots B$  distance may be too long for the interaction to be classified as an H bond. Analysis of the total interaction energy shows that many of the observed trends in stability can be traced to changes in the electrostatic interaction term alone. This term, however, includes more than the dipole-dipole interaction which has traditionally been considered as the term of primary importance.

As a result of extensive experimental and theoretical work,<sup>2-6</sup> reasonably accurate energies of formation and equilibrium conformations are now available for several hydrogen-bonding systems. In view of the difficulties encountered in accurate experimental work, the most reliable results are probably those yielded by accurate SCF calculations<sup>2</sup> (however, see ref 6c), even

though part of the dispersion energy is not obtained in such calculations. Whether we obtain H-bond energies from experiment or from theoretical calculations, the final results in themselves do not tell us where the H-bond stability (as measured by  $-\Delta H$ ) originates from, nor how characteristic differences between different systems should be interpreted. Of course, interpretations tend to be arbitrary, since they are usually based on nonobservable features of the interacting molecules. Nevertheless, they can be useful in organizing the large amount of data available.

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(2) (a) G. H. F. Diercksen, *Chem. Phys. Lett.*, **4**, 373 (1969); (b) D. Hankins, J. W. Moskowitz, and F. Stillinger, *ibid.*, **4**, 527 (1970); *J. Chem. Phys.*, **53**, 4544 (1970); (c) G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, **5**, 570 (1970); (d) P. N. Noble and R. N. Kortzeborn, *J. Chem. Phys.*, **52**, 5375 (1970).

(3) For SCF-LCAO-MO calculations on  $(H_2O)_2$  using a medium or minimal basis set see (a) K. Morokuma and L. Pedersen, *ibid.*, **48**, 3275 (1968); (b) K. Morokuma and J. Winick, *ibid.*, **52**, 1301 (1970); (c) J. Del Bene and J. A. Pople, *Chem. Phys. Lett.*, **4**, 426 (1969); *J. Chem. Phys.*, **52**, 4858 (1970); (d) P. A. Kollman and L. C. Allen, *ibid.*, **51**, 3286 (1969).

(4) For SCF-LCAO-MO calculations on a large variety of simple systems and using a medium-sized basis set of GTO's see (a) P. A. Kollman and L. C. Allen, *ibid.*, **52**, 5085 (1970); (b) *Theor. Chim. Acta*, **18**, 399 (1970); (c) *J. Amer. Chem. Soc.*, in press; (d) *J. Amer. Chem. Soc.*, **92**, 6101 (1970); see also (e) M. Dreyfus and A. Pullman, *Theor. Chim. Acta*, **19**, 20 (1970); (f) E. Clementi, J. Mehl, and W. von Niessen, *J. Chem. Phys.*, **54**, 508 (1971).

(5) Semiempirical MO methods (CNDO/2, extended Hückel) have also been employed. See (a) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 753 (1970), and references therein; (b) J. R. Hoyland and L. B. Kier, *Theor. Chim. Acta*, **15**, 1 (1969); (c) P. Schuster, *Int. J. Quantum Chem.*, **3**, 851 (1969); *Theor. Chim. Acta*, **19**, 212 (1970); (d) A. S. N. Murthy, S. N. Bhat, and C. N. R. Rao, *J. Chem. Soc. A*, 1251 (1970). For VB calculations, see M. Hasegawa, K. Daiyasu, and S. Yomosa, *J. Phys. Soc. Jap.*, **27**, 999 (1969), and references therein.

(6) (a) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960; (b) A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.*, **2**, 69 (1968). (c) Accurate calorimetric experiments have been performed by Drago and coworkers; see G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970), and references therein.

With these problems in mind, we present in this paper the results of some semiempirical calculations on a model system  $A-H\cdots B$ . Certain concepts such as the polarity of the  $A-H$  bond and the hybridization of the lone-pair orbital on B explicitly enter the calculations, thereby allowing an evaluation of their usefulness for interpretative purposes.

Our calculations are based on a perturbation approach<sup>7</sup> in which one calculates the hydrogen-bond energy as the sum of a first-order energy ( $E^1$ ), comprising a *Coulomb* (or *electrostatic*) term and an *exchange* term, and a second-order energy ( $E^2$ ), consisting of *induction*, *second-order exchange*, *dispersion*, and *charge-transfer* terms. In principle, exact eigenfunctions for

(7) (a) J. N. Murrell, M. Randić, and D. R. Williams, *Proc. Roy. Soc., Ser. A*, **284**, 566 (1965); (b) J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **46**, 1768 (1967); see also (c) H. N. W. Lekkerkerker and W. G. Laidlaw, *ibid.*, **52**, 2953 (1970); (d) H. Margenau and N. R. Kestner, "Theory of Intermolecular Forces," Pergamon Press, Oxford, 1969. (e) A full description of the theory as we use it (including explicit expressions for the interaction energy of two closed-shell molecules in terms of MO wave functions for the separate molecules) is available upon request.

the separate molecules should be employed in evaluating the energy terms, but it has been found that useful results can be obtained by using molecular orbital wave functions instead.<sup>8</sup>

All calculations were performed on a linear, three-center many-electron model system A—H···B (section I). In order to prevent a collapse of the system at short H···B distances, all electrons in the system are treated explicitly and no approximations for the many-center integrals are invoked.<sup>9,10</sup> By choosing appropriate values for the parameters in the model, we simulated the various possible hydrogen bonds between C, N, O, F, and Ne (section II). In a number of cases the optimum orientation of the H acceptor was studied, keeping A—H···B linear (section III). Next, for each system we obtained a potential energy curve as a function of the H···B distance, and equilibrium H-bond energies were determined from these curves (section IV). The results of our calculations do not always agree with experiment or SCF calculations. Possible explanations for this are discussed in section IV. A final paragraph summarizes our main conclusions.

At this point, a brief comment on the term "electrostatic energy" is in order. Historically, this refers to the interaction energy as obtained from a set of point charges or multipole moments on the interacting molecules,<sup>11</sup> and in this paper we call this the *multipolar part* of the Coulomb energy.<sup>12</sup> This  $E_{\text{multipole}}$  is an approximation to the full electrostatic energy which, following Coulson,<sup>11</sup> may be defined as the classical interaction energy arising from the unperturbed charge distributions of the separate molecules, *viz.*,  $E_{\text{Coul}} = \langle \psi_0^R \psi_0^T | U | \psi_0^R \psi_0^T \rangle$ , where the  $\psi_0$ 's are separate-molecule ground-state wave functions for molecules R and T and  $U$  is the intermolecular potential. Since these distributions penetrate into one another, this energy is (at the distances we consider) more attractive than the multipolar part alone.

At short distances, where exchange of electrons between R and T is nonnegligible, the correct wave function to use is  $A\psi_0^R\psi_0^T$  (where  $A$  is an antisymmetrizer) rather than  $\psi_0^R\psi_0^T$ , and one may now define a first-order interaction energy as

$$E^1 = \frac{\langle A\psi_0^R\psi_0^T | H | A\psi_0^R\psi_0^T \rangle}{\langle A\psi_0^R\psi_0^T | A\psi_0^R\psi_0^T \rangle} - E_A^0 - E_B^0$$

If  $\psi_0^R$  and  $\psi_0^T$  are taken to be single-determinant wave functions for the separate molecules, then  $A\psi_0^R\psi_0^T$  is simply a large determinant containing all occupied spin orbitals of R and T, and  $E^1$  is then the electrostatic energy as defined by Kollman and Allen<sup>4b</sup> or the  $E^1$  evaluated by Dreyfus and Pullman.<sup>4e</sup> (In a full SCF calculation on the complex  $E^1$  can be obtained as the first-iteration energy if one starts from separate-mole-

cule MO's as the trial functions.) The latter authors moreover evaluate  $E_{\text{Coul}}$  with the formula given above and define an exchange energy as

$$E_{\text{exch}} = E^1 - E_{\text{Coul}}$$

In the present paper we use an alternative definition for the first-order interaction energy, *viz.*

$$E^1 = \frac{\langle A\psi_0^R\psi_0^T | U | \psi_0^R\psi_0^T \rangle}{\langle A\psi_0^R\psi_0^T | \psi_0^R\psi_0^T \rangle}$$

which for exact eigenfunctions is identical with the  $E^1$  given above. By expanding  $A$  this  $E^1$  may be written as the sum of  $E_{\text{Coul}}$  (see above) and exchange terms, of which we only consider those resulting from a single exchange of electrons (*i.e.*, our  $E_{\text{exch}}$  is not identical with that of Dreyfus and Pullman, even for exact eigenfunctions). If  $\psi_0^R$  and  $\psi_0^T$  are near-Hartree-Fock wave functions, then the two expressions for  $E^1$  give similar answers (at least for the He···He interaction<sup>8</sup>), but for more approximate  $\psi_0^R$  and  $\psi_0^T$ , the results are different.<sup>8</sup>

## I. Model and Formulas

The model system A—H···B that we have used can be described as follows. The donor A—H bond was assigned a bond length of 1.06 Å. It is characterized by a bonding MO  $a_1 = N(t_1 + kh)$  and its antibonding counterpart  $a^*$ . Here  $h$  is a 1s orbital on H ( $\zeta = 1.0$ ),  $k$  is an ionicity parameter, and  $t_1$  is a hybrid of Slater-type 2s and 2p AO's ( $\zeta = 2.0$ ) having an s character  $\chi_A$ . In addition to this orbital, we assume that A carries three bond or lone-pair orbitals  $\phi_i$  ( $i = 2, 3, 4$ ) which are not directly involved in the H-bond formation. Each of these is doubly occupied. In order to describe these, we use three equivalent 2s–2p hybrids ( $a_2, a_3, a_4$ ) which are orthogonal to  $a_1$ . A lone pair on A is then obtained by simply putting two electrons in one of these hybrids. A bond orbital on A (*i.e.*, to an additional H atom, but other substituents have been considered as well; see section II) will have the form  $\phi_i = N_i(a_i + kh_i)$ . In order to avoid the necessity of calculating many-center integrals, we here proceed as follows. In our energy expressions  $\phi_i$  occurs in two different ways. First, we may need the charge density  $2\phi_i^2$  in this orbital. This is approximately equal to a density  $a_i^2 + h_i^2$ , and we consider only the  $a_i^2$  part of this, *i.e.*, H, is assumed not to carry a net charge (the potential due to the H nucleus should then be omitted from the expressions as well). Secondly, we encounter overlap densities such as  $\phi_i b$ , where  $b$  is an orbital on B. These are replaced by the corresponding overlap densities  $a_i b$ ; *i.e.*, exchange effects between  $\phi_i$  and B are assumed to be small, and they are approximated by considering exchange with the  $a_i$  part of  $\phi_i$  only (for simplicity we here put  $N_i = 1$ ).

Analogously, the acceptor atom B carries four mutually orthogonal 2s–2p hybrid orbitals ( $b_1$ – $b_4$ ). Those which represent lone pairs are doubly occupied and equivalent to each other (each of them has an s character  $\chi_B$ ). The remaining hybrids, if any, are also chosen to be equivalent to each other, and they are used to simulate B–H bonds precisely as described above for the bond orbitals  $\phi_i$  ( $i = 2, 3, 4$ ). The AO's on B are assigned the same orbital exponent as those on A ( $\zeta = 2.0$ ).

(8) (a) G. Shaw, *Int. J. Quantum Chem.*, **3**, 219 (1969); (b) J. N. Murrell and G. Shaw, *Mol. Phys.*, **12**, 475 (1967); **15**, 325 (1968).

(9) F. B. van Duijneveldt and J. N. Murrell, *J. Chem. Phys.*, **46**, 1759 (1967).

(10) J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *Chem. Phys. Lett.*, **2**, 565 (1968).

(11) S. Bratož, *Advan. Quantum Chem.*, **3**, 209 (1966); C. A. Coulson, *Research*, **10**, 149 (1957).

(12) In this paper the multipolar part ( $E_{\text{multipole}}$ ) of  $E_{\text{Coul}}$  was evaluated from point charges on the atoms A and H (which reproduce the A–H dipole moment in our model) and a point dipole and quadrupole on atom B (which reproduce the moments of H in our model). In addition, we define the penetration part of  $E_{\text{Coul}}$  as ( $E_{\text{Coul}} - E_{\text{multipole}}$ ).

For this model system, the first-order contributions to the H-bond energy take the form<sup>7e,12,13</sup>

$$E_{\text{Coul}} = \sum_i n_i (a_i^2 | V^B) + \sum_j n_j (b_j^2 | V^{\text{AH}}) - \sum_{ij} n_i n_j (a_i^2 | b_j^2) + Z_A Z_B R_{\text{AB}}^{-1} + Z_H Z_B R_{\text{HB}}^{-1} \quad (1)$$

$$E_{\text{exch}} = -2 \sum_{ij} \sum_{i'j'} \{ (\rho^{\text{AH}}_{ij} | \rho^{\text{B}}_{i'j'}) + (\rho^{\text{AH}}_{ij} | V^{\text{B}} S_{a_i b_j}) + (V^{\text{AH}} S_{a_i b_j} | \rho^{\text{B}}_{i'j'}) \} \quad (2)$$

where the potentials  $V^{\text{AH}}$  and  $V^{\text{B}}$  and the densities  $\rho$  are defined as follows.

$$V^{\text{AH}}(1) = \sum_i n_i \int a_i^2 (2)r_{12}^{-1} d\tau_2 - Z_A r_{1A}^{-1} - Z_H r_{1H}^{-1} \quad (3)$$

$$V^{\text{B}}(1) = \sum_j n_j \int b_j^2 (2)r_{12}^{-1} d\tau_2 - Z_B r_{1B}^{-1}$$

$$\rho^{\text{AH}}_{ij}(1) = a_i(1)b_j(1) - \sum_{i'} S_{a_i b_j} a_i(1)a_{i'}(1)$$

$$\rho^{\text{B}}_{ij}(1) = a_i(1)b_j(1) - \sum_{j'} S_{a_i b_j} b_j(1)b_{j'}(1) \quad (4)$$

In these expressions  $i, i', j,$  and  $j'$  run from 1 to 4. In the case that  $a_i$  simulates an A-H bond orbital  $\phi_i$ , the occupation number  $n_i$  should be taken to be unity, and it is 2 otherwise (and likewise for  $n_j$ ). Furthermore, we have  $Z_H = 1$ , and since A and B have inner shells of 1s electrons,  $Z_A$  and  $Z_B$  are equal to the respective nuclear charges minus two.

The various second-order terms have only been determined very approximately. First, of the local excitations within the A-H system only the  $a_1 \rightarrow a^*$  transition has been taken into account. No local excitations within B have been considered. The induction energy then reduces to

$$E_{\text{ind}} = -2(a_1 a^* | V^{\text{B}})^2 / \Delta E_{a_1 \rightarrow a^*} \quad (5)$$

The contribution to the second-order exchange energy from the same transition was calculated from

$$E_{\text{exch2}} = 2(a_1 a^* | V^{\text{B}}) \sum_j \{ (\rho^{\text{B}}_{a_1 b_j} | \rho^{\text{AH}}_{a_1 b_j}) + (\rho^{\text{B}}_{a_1 b_j} | S_{b_j a_1} V^{\text{AH}}) + (S_{a_1 b_j} V^{\text{B}} | \rho^{\text{AH}}_{b_j a_1}) + \sum_i (2S_{b_j a_i} a_i^* a_1 - S_{b_j a_i} a_i^* a_i | \rho^{\text{B}}_{a_1 b_j} + S_{a_i b_j} V^{\text{B}}) \} / \Delta E_{a_1 \rightarrow a^*} \quad (6)$$

To allow for some of the polarization of B in the field of the A-H bond, a charge-transfer energy corresponding to the transitions from the lone pairs  $b_j$  of B to the orbital  $a^*$  was calculated from

$$E_{\text{ct}} = -2 \sum_j^{\text{lone pairs}} (\rho^{\text{B}}_{b_j a^*} | V^{\text{AH}}) \{ (\rho^{\text{B}}_{b_j a^*} | V^{\text{AH}}) - \sum_i (a_i a^* | \rho^{\text{B}}_{a_i b_j} + S_{a_i b_j} V^{\text{B}}) \} / \Delta E_{b_j \rightarrow a^*} \quad (7)$$

In eq 6 and 7 the densities  $\rho$  are given by the simplified expressions

$$\rho^{\text{B}}_{a_1 b_j}(1) = a^*(1)b_j(1) - S_{a_1 b_j} b_j^2(1)$$

$$\rho^{\text{AH}}_{a_1 b_j}(1) = a_1(1)b_j(1) - S_{a_1 b_j} a_1^2(1) \quad (8)$$

$$\rho^{\text{B}}_{a_i b_j}(1) = a_i(1)b_j(1) - S_{a_i b_j} b_j^2(1)$$

(13) The following notations are used:  $S_{a_i b_j} = \int a_i(1)b_j(1)d\tau_1$ ;  $(a_i^2 | V^{\text{B}}) = \int a_i^2(1)V^{\text{B}}(1)d\tau_1$ ;  $(a_i^2 | b_j^2) = \iint a_i^2(1)b_j^2(2)d\tau_1 d\tau_2$ ;  $(\rho^{\text{AH}}_{ij} | \rho^{\text{B}}_{ij}) = \iint \rho^{\text{AH}}_{ij}(1)r_{12}^{-1} \rho^{\text{B}}_{ij}(2)d\tau_1 d\tau_2$ .

These differ from the complete expressions in ref 7e in that summations of the type  $-\sum_{j'} S_{a_i b_j} b_j b_{j'}$  have been replaced by the principal term  $-S_{a_i b_j} b_j^2$ . This reduces the computation time considerably, and we verified that it does not affect the results significantly.

In view of the approximate nature of these calculations, no attempt has been made to calculate precise values for the excitation energies  $\Delta E$  in (6) and (7). As before,<sup>14</sup> we used  $\Delta E_{a_1 \rightarrow a^*} = 0.20$  au (1 au = 627 kcal/mol) and  $\Delta E_{b_j \rightarrow a^*} = 0.11 + 0.37\chi_B$  au. The  $\chi_B$  dependence of  $\Delta E_{b_j \rightarrow a^*}$  accounts for the fact that charge-transfer to  $a^*$  is facilitated by decreasing the lone-pair s character on B.

As in our model there are no antibonding orbitals on B, the dispersion energy has been calculated using London's formula<sup>15</sup>

$$E_{\text{disp}} = -D R_{\text{AB}}^{-6} \quad (9)$$

If atomic units are used throughout,  $D$  takes on values in the range 30–100 au, depending on the interaction considered. However, we have used a constant value of 73.2 au. It should be noted that  $D$  is probably a function of the molecular distance, showing a decrease as the molecules get close together.<sup>16</sup>

## II. Choice of Parameters

A few parameters in our model remain to be specified before actual calculations can be carried out, *viz.*,  $k$ ,  $\chi_A$ , and  $\chi_B$ . If the H-bonding system that we wish to describe with our model involves simple hydrides only (*e.g.*,  $\text{HOH} \cdots \text{NH}_3$ ), the most straightforward procedure is to take these parameters from localized orbitals obtained in minimal-basis SCF calculations on the molecules involved. Such localized orbitals are usually more complex than the ones we employ, but neglecting small terms in the published results<sup>17,18</sup> and after renormalization one arrives at the parameter values shown in Table I (columns 1–4).

Table I. Parameters Characterizing the A-H Bond and the B Lone Pair(s)

	Ref 17		Ref 18 <sup>a</sup>	Present work <sup>b</sup>		
	$\chi_B$	$\chi_A$	$k$	$\chi_B$	$\chi_A$	$k$
CH <sub>4</sub>		0.31	0.90	0.89	0.31	0.95
NH <sub>3</sub>	0.34	0.20	0.90	0.84	0.33 <sup>c</sup>	0.20
H <sub>2</sub> O	0.39	0.13	0.82	0.79	0.33	0.13
HF	0.32	0.04	0.85		0.29	0.04

<sup>a</sup> In ref 18  $\chi_A = 0.25$  (assumed) throughout. <sup>b</sup>  $k$  was taken 0.05 lower for A-H bonds that are more acidic than in the hydrides (such as the C-H bond in chloroform, the N-H bond in *N*-methyl-aniline, and the O-H bond in phenol). <sup>c</sup> For nitriles we use  $\chi_B = 0.67$ .

It is seen that in the A-H bonds the ionicity parameter  $k$  varies rather little, while the s character  $\chi_A$  decreases sharply going from CH<sub>4</sub> to HF. At the same time the

(14) F. B. van Duijneveldt, *J. Chem. Phys.*, **49**, 1424 (1968).

(15) F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

(16) (a) J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **49**, 4731 (1968); (b) H. Kreek and W. J. Meath, *ibid.*, **50**, 2289 (1969); *Mol. Phys.*, **19**, 513 (1970).

(17) C. Edmiston and K. Ruedenberg, "Quantum Theory of Atoms, Molecules and the Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, p 263, and references therein.

(18) J. Krell, Ch. Zuhrt, and L. Züllicke, *Chem. Phys. Lett.*, **4**, 261 (1969).

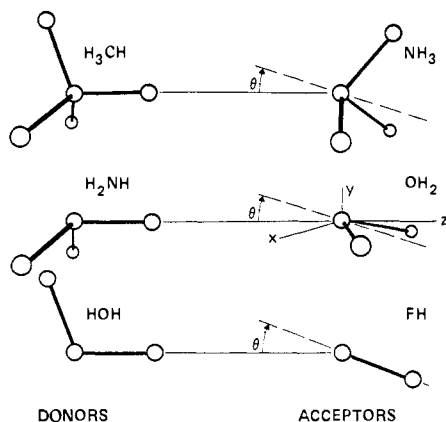


Figure 1. Donor and acceptor orientations. The donor orientations are kept fixed, and in all cases the  $yz$  plane is a symmetry plane for the donor. The acceptor orientations are shown for  $\theta = +20^\circ$ , and the molecular axis lies in the  $yz$  plane. Rotations about  $y$  are also considered and the molecular axis then lies in the  $xz$  plane (*i.e.*,  $\theta = 0^\circ$ ). Of all H atoms shown, only the donor H atom is explicitly included in the calculations.

total lone-pair  $s$  character increases from 0.34 for  $\text{NH}_3$  to 0.96 for  $\text{HF}$ . The values of columns 1–4 were obtained using Slater orbital exponents for the atoms C, N, O, and F. However, we used  $\zeta_A = \zeta_B = 2.0$  throughout. The effect of this is that in a C–H bond too little charge is placed near the H, so in order to maintain the correct polarity, our  $k$  value for  $\text{CH}_4$  should be a little higher than in columns 3 and 4. Similarly, for the F–H bond our  $k$  value should be lower than in columns 3 and 4. Of course, these arguments do not tell us precisely which  $k$  and  $\chi$  values we should employ. Trial calculations showed that our results were not sensitive to the  $\chi_A$  values, and we have since used the values of column 2 for this parameter. On the other hand, the results turned out to be very sensitive to the parameters  $k$  and  $\chi_B$  and thus we decided to use empirically determined values for some of these. First, we took  $\chi_B = 0.33$  for  $\text{NH}_3$  and assumed that this value can also be taken to represent amines and pyridine.<sup>19</sup> Likewise, we took  $\chi_B = 0.33$  for  $\text{H}_2\text{O}$ <sup>20</sup> as well as for ethers (ketones have a somewhat higher lone-pair  $s$  character). Next, experimental H-bond energies for systems involving these acceptors and the donors phenol and *N*-methylaniline were used to select  $k$  values for acidic O–H and N–H bonds, respectively. Values of 0.7 and 0.8 were found to be fairly satisfactory. By inference we used  $k = 0.9$  for acidic C–H bonds such as in chloroform and perhaps toluene. Normal A–H bonds such as in the simple hydrides, methanol, and alkylamines were assigned  $k$  values 0.05 higher than the corresponding acidic A–H bonds. This leads to  $k$  values of 0.95 for C–H, 0.85 for N–H, 0.75 for O–H,<sup>21</sup> and by inference 0.65 for F–H. It is seen that these values differ from those of columns 3 and 4 in the sense that was indicated above. Finally, we took  $\chi_B = 0.29$  for F acceptor atoms (this will be discussed in the next section) and  $\chi_B = 0.67$  for the N

(19) A change in the groups bonded to atom B will, of course, influence its net charge, and this might have a significant effect on the H-bond energy. However, except in the case of  $\text{F}^-$  net charges on B have been neglected throughout.

(20) J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *Theor. Chim. Acta*, **19**, 83 (1970).

(21) In ref 20, where only the case of  $(\text{H}_2\text{O})_2$  was considered, we arbitrarily assumed  $k = 0.70$  for the O–H bond in  $\text{H}_2\text{O}$ .

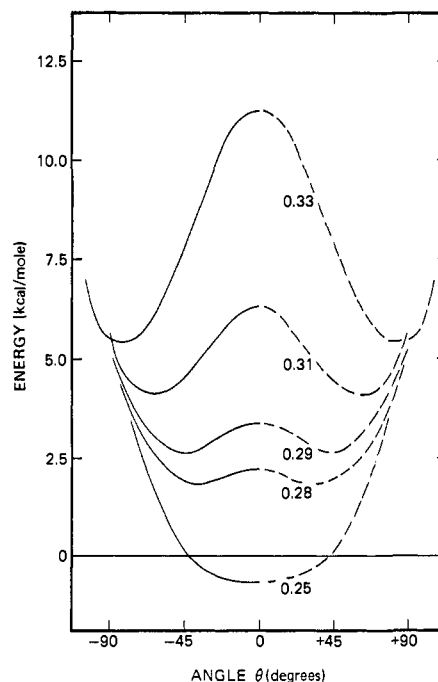


Figure 2. The H-bond energy of  $\text{FH}\cdots\text{FH}$  as a function of the acceptor angle  $\theta$  and of the acceptor lone-pair  $s$  character  $\chi_B$  ( $k = 0.65$ ,  $R_{\text{HFB}} = 1.85 \text{ \AA}$ ). The actual results were not entirely symmetrical around  $\theta = 0^\circ$  because of the approximate nature of eq 8.

atom in nitriles, since these presumably have a much higher lone-pair  $s$  character than amines.

### III. Optimum Acceptor Orientations

Even if we keep  $\text{A-H}\cdots\text{B}$  linear, there may still be a number of orientations of the acceptor molecule with respect to the  $\text{A-H}\cdots\text{B}$  axis for which stable H bonds can be formed. In a later section we shall calculate the H-bond energy as a function of  $R_{\text{HFB}}$  but, at it is impracticable to do this for all the possible stable orientations, such calculations were carried out only for the optimum acceptor orientations (as determined at  $R_{\text{HFB}} = 1.85 \text{ \AA}$ ) whose determination will now be discussed briefly.

**FH as Acceptor.** In complexes where FH is the acceptor, one may ask whether in the optimum orientation the FH axis coincides with the  $\text{A-H}$  axis or not (*i.e.*, whether  $\theta$  in Figure 1 is zero or not). If the donor has axial symmetry, then the dipole-dipole interaction favors  $\theta = 0^\circ$ , but it may be that other energy terms cause the optimum  $\theta$  ( $\theta_{\text{opt}}$ ) to be nonzero (for example, because of some preference of the  $\text{A-H}$  bond to line up with one of the F lone pairs). In fact, in crystalline HF one observes  $\theta = 60^\circ$ ,<sup>22</sup> while recent SCF calculations gave  $\theta_{\text{opt}} = 20^\circ$ , with an extremely small dependence on  $\theta$ .<sup>4a</sup>

Using our model, we studied this question for the system  $\text{FH}\cdots\text{FH}$ . Taking  $k = 0.65$  and a variety of  $\chi_B$  values, the results are as shown in Figure 2 (the maximum possible  $\chi_B$  value is  $1/3$  in this case). It is seen that on increasing  $\chi_B$  from 0.25 to 0.33 the optimum geometry changes from  $\theta_{\text{opt}} = 0^\circ$  to  $\theta_{\text{opt}} = 90^\circ$ , respectively. In addition, the H-bond energy decreases and at this  $\text{H}\cdots\text{B}$  distance there is no stability at all from  $\chi_B \approx 0.26$  upward. Inspection of the separate energy

(22) M. Atoji and W. N. Lipscomb, *Acta Crystallogr.*, **7**, 173 (1954); see also the gas-phase work by J. Janzen and L. S. Bartell, *J. Chem. Phys.*, **50**, 3611 (1969).

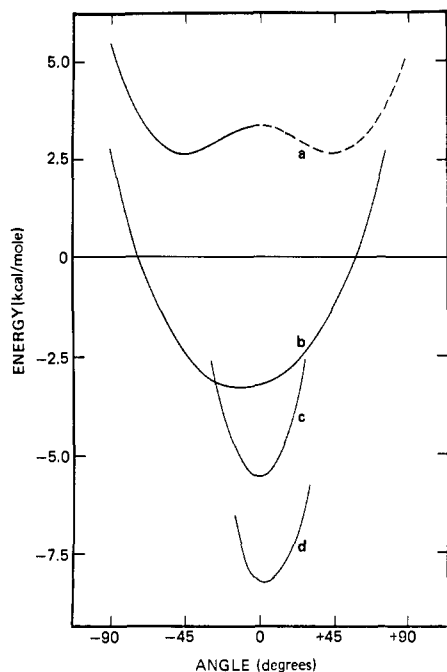


Figure 3. Dependence of H-bond energies on the acceptor orientation: (a) FH...FH, rotation around  $x$ ; (b and c) OH...OH<sub>2</sub>, rotations around  $x$  and  $y$ , respectively; (d) OH...NH<sub>3</sub>, rotation around  $x$ . The  $k$  values are 0.65, 0.75, 0.70, and 0.70;  $\chi_B$  values are 0.29, 0.33, 0.25, and 0.25, respectively, and  $R_{HB} = 1.85 \text{ \AA}$ .

contributions shows that for all  $\chi_B$  values studied, the Coulomb term is the only significantly  $\theta$ -dependent term.<sup>23</sup> For  $\chi_B = 0.29$ , this is shown in Table II. It

Table II. Individual Energy Terms (kcal/mol) for FH...FH as a Function of the Acceptor Angle  $\theta^a$

$\theta$ , deg	-75.69	-45.69	-15.69	+14.31
$E_{\text{multipole}}$	-2.01	-2.90	-2.86	-2.86
$E_{\text{Coul}}$	-7.23	-8.09	-7.45	-7.43
$E_{\text{exch}}$	+15.05	+14.75	+14.66	+14.66
$E^1$	+7.82	+6.65	+7.21	+7.23
$E_{\text{ind}}$	-0.02	-0.00	-0.00	-0.00
$E_{\text{exch2}}$	+0.17	+0.02	+0.03	+0.03
$E_{\text{ct}}$	-2.42	-2.40	-2.35	-2.37
$E_{\text{disp}}$	-1.66	-1.66	-1.66	-1.66
$E^2$	-3.93	-4.04	-3.98	-4.00
$E_{\text{total}}$	+3.88	+2.62	+3.22	+3.23

<sup>a</sup>  $k = 0.65$ ,  $\chi_B = 0.29$ ,  $R_{HB} = 1.85 \text{ \AA}$ .

turns out that in addition to a dipole-dipole term (which favors  $\theta = 0^\circ$ ) the Coulomb energy also contains a dipole-quadrupole term (which favors  $\theta = 90^\circ$ ) whose relative importance increases with  $\chi_B$  (see also ref 20). As a result, the FH dimer is nonlinear for  $\chi_B$  values larger than about 0.26.

From the above it is clear that the H-bond energy and the observed  $\theta$  value provide criteria for choosing the  $\chi_B$  that we should employ for FH. For  $\chi_B = 0.32$  (the literature value quoted in Table I) the optimum  $\theta$  value is somewhat too large (about  $75^\circ$ ) and the calculated H-bond energy is much too small. A lower  $\chi_B$  value ( $\chi_B = 0.29$ ) was therefore adopted, and the remaining calculations were performed with the corresponding optimum acceptor angle  $\theta_{\text{opt}} = -45^\circ$ .<sup>24</sup> (The SCF re-

(23) This has previously been found in the case of (H<sub>2</sub>O)<sub>2</sub> also.<sup>20</sup>

(24) This value may not be the optimum value if other donor mole-

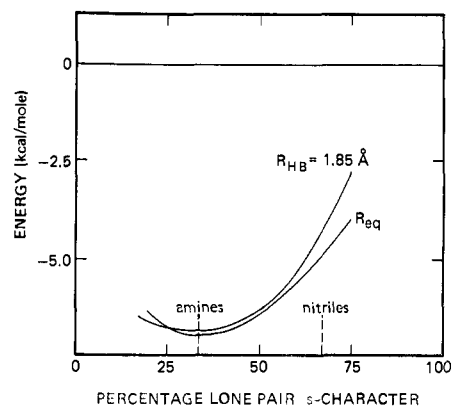


Figure 4. Dependence of the energy of OH...N hydrogen bonds ( $k = 0.75$ ) on the N lone-pair  $s$  character. The  $\chi_B$  values shown for amines and nitriles are assumed values.

sults of ref 4a were not yet available when these calculations were performed. It turns out that the  $\theta$  dependence in ref 4a closely resembles our curve for  $\chi_B = 0.28$ , except that the maximum near  $\theta = 0^\circ$  is almost missing.)

**OH<sub>2</sub> as Acceptor.** In a previous paper on (H<sub>2</sub>O)<sub>2</sub><sup>20</sup> we studied the optimum geometry for OH<sub>2</sub> as acceptor as a function of  $\chi_B$ . The optimum geometry found for  $\chi_B = 0.33$  is as shown in Figure 1 with the acceptor rotated about the  $x$  axis through an angle  $\theta_{\text{opt}} = 15^\circ$ , whereas  $\theta_{\text{opt}}$  obtained in SCF calculations varies from  $52^\circ$  to  $25^\circ$ , depending on the basis set employed.<sup>2,3</sup> Since the energy is not much affected by small departures from  $\theta_{\text{opt}}$  and since for different donors  $\theta_{\text{opt}}$  will not be  $15^\circ$  anyway, we have contented ourselves to use  $\theta = 0^\circ$  for all subsequent calculations where  $\theta$  is the acceptor atom.<sup>25</sup>

**NH<sub>3</sub> as Acceptor.** In this case the optimum geometry is near the one shown in Figure 1 for any donor and for any  $\chi_B$  value that we may choose. The H-bond energy, however, is quite sensitive to the  $\chi_B$  value employed, as may be seen from the results in Table III. This dependence of  $E$  on  $\chi_B$  is also shown in Figure 4 for the system OH...NH<sub>3</sub>, using a fixed H...B distance of

Table III. Individual Energy Terms (kcal/mol) for OH...N Hydrogen Bonds ( $k = 0.70$ ) as a Function of the N Lone-Pair  $s$  Character  $\chi_B$

$\chi_B$	0.33	0.67	0.33	0.67
$R_{HB}$ , $\text{\AA}$	1.85	1.85	2.12	2.12
$E_{\text{multipole}}$	-6.13	-5.56	-4.52	-4.13
$E_{\text{Coul}}$	-14.63	-13.24	-8.78	-7.98
$E_{\text{exch}}$	+11.39	+11.51	+4.29	+4.34
$E^1$	-3.24	-1.73	-4.49	-3.64
$E_{\text{ind}}$	-0.75	-0.56	-0.60	-0.48
$E_{\text{exch2}}$	-0.61	-0.48	-0.22	-0.18
$E_{\text{ct}}$	-2.02	-1.09	-0.62	-0.34
$E_{\text{disp}}$	-1.66	-1.66	-0.98	-0.98
$E^2$	-5.04	-3.79	-2.43	-1.98
$E_{\text{total}}$	-8.28	-5.52	-6.92	-5.62

cules are considered. That is, for NH<sub>3</sub> we expect that  $\theta_{\text{opt}} \approx -45^\circ$ , but H<sub>2</sub>O is likely to have  $\theta_{\text{opt}} \approx +45^\circ$ , with a secondary minimum at  $\theta \approx -45^\circ$ , so that our choice of a fixed  $\theta_{\text{opt}} = -45^\circ$  leads to low H-bond energies for HOH...FH. It is not clear what  $\theta_{\text{opt}}$  should be if CH<sub>4</sub> is the donor. If H is at the negative end of the C-H bond dipole, then  $|\theta_{\text{opt}}|$  may well be larger than  $45^\circ$ .

(25) This is in fact the correct  $\theta_{\text{opt}}$  for FH (and maybe CH<sub>4</sub>) as a donor, while for NH<sub>3</sub>,  $\theta_{\text{opt}} \approx -15^\circ$ .

Table IV. Parameters  $A$ ,  $B$ , and  $C$  Characterizing the Potential Energy Curves for Some H-Bonding Systems<sup>a,b</sup>

H donors		H acceptors					
		Ne	F (FH)	O (OH <sub>2</sub> )	N (HCN)	N (NH <sub>3</sub> )	F <sup>-</sup>
		Parameter values					
CH	$A$	10635	9249	7590	5046	6991	16629
$k = 0.95$	$B$	3.583	3.629	3.727	3.523	3.931	4.249
(H <sub>3</sub> CH)	$C$	4.332	11.164	21.289	32.710	28.696	121.28
CH	$A$	11450	9591	8010	5370	7615	17145
$k = 0.90$	$B$	3.674	3.689	3.803	3.599	4.029	4.256
	$C$	1.538	11.591	23.893	35.617	32.765	134.59
NH	$A$	11741	10157	8625	6000	8468	16461
$k = 0.85$	$B$	3.712	3.727	3.840	3.636	4.060	4.045
(H <sub>2</sub> NH)	$C$	1.008	20.231	36.474	50.457	48.941	197.10
NH	$A$	12273	10655	9208	6362	9448	16897
$k = 0.80$	$B$	3.788	3.803	3.931	3.712	4.181	4.052
	$C$	-0.382	20.936	39.658	54.174	53.649	212.32
OH	$A$	13229	11434	10147	7251	10930	17455
$k = 0.75$	$B$	3.878	3.893	4.007	3.780	4.264	3.939
(HOH)	$C$	-1.821	19.911	53.205	69.369	70.513	277.85
OH	$A$	14041	12184	11009	7799	12440	17848
$k = 0.70$	$B$	3.977	3.992	4.120	3.871	4.407	3.946
	$C$	-2.760	21.158	57.121	73.759	76.110	294.85
FH	$A$	15185	8553	11543	8685	17071	18326
$k = 0.65$	$B$	4.098	3.772	4.203	3.954	4.665	3.886
	$C$	-4.481	34.537	68.437	86.951	90.273	356.13

<sup>a</sup>  $A$  is in kcal/mol,  $B$  in Å<sup>-1</sup>,  $C$  in kcal/(mol Å<sup>3</sup>). <sup>b</sup> The deviations between the least-squares fits and the actual potential energy curves are usually about 0.3 kcal/mol at  $R_{HB} = 2.0$  au and less at longer distances.

1.85 Å, or using equilibrium distances. It is apparent that in both cases amines are predicted to be much better acceptors than nitriles (*cf.* ref 14). In view of our results on the  $\chi_B$  variation in (H<sub>2</sub>O)<sub>2</sub> and (HF)<sub>2</sub>, we may draw the conclusion that in general hydrogen bonds are destabilized by an increase in lone-pair  $s$  character.

The decrease in H-bond energy as the acceptor lone pair is rotated away from the donor H atom is depicted in curve d of Figure 3 for the system OH $\cdots$ NH<sub>3</sub>. The minimum occurs for  $\theta_{opt} = 5^\circ$ , and as before, this is governed by the Coulomb energy. The multipole terms in  $E_{Coul}$  by themselves would give  $\theta_{opt} \simeq 15^\circ$ , so it seems that in this case the overlap-dependent penetration part of  $E_{Coul}$  (which favors  $\theta = 0^\circ$ ) plays an important role in the angular energy dependence. In any case, the departure from linearity is small and we have used  $\theta = 0^\circ$  in all subsequent calculations where N is the acceptor atom. It should be emphasized that the steric requirements of N, O, and F acceptor atoms are basically different. N acceptors, such as amines, only give good H bonds for approach *along the lone-pair axis* (and slight departures from linearity result in a large loss in energy, *cf.* Figure 3d). O acceptors (ethers, water) give good H bonds for a variety of approaches in the *plane of high electron density* defined by the two lone pairs (*cf.* Figure 3b and 3c), while the three F lone pairs allow easy approach within a *hemisphere* around the F-H axis (*cf.* Figure 3a). Related observations have been made by Schuster,<sup>5c</sup> who also showed that the stereospecificity is decreased in cases where the acceptor forms part of a  $\pi$ -electron system.

#### IV. Potential Energy Curves and Equilibrium Energies for Some H-Bonding Systems

Using the parameters and optimum acceptor orientations described in sections II and III, we performed calculations at H $\cdots$ B distances from 2.0 to 4.0 au in steps of 0.5 au (1 au = 0.5292 Å) for a variety of H-bonding systems. It was found that the resulting energies ( $E =$

$E^1 + E^2$ ) can be well represented by curves of the form  $E = Ae^{-BR_{HB}} - CR_{HB}^{-3}$ .<sup>26</sup> The values of the parameters  $A$ ,  $B$ , and  $C$  were found by a least-squares procedure and are reported in Table IV. By differentiating these fitted curves, we determined equilibrium distances ( $R_{eq}$ ) and the corresponding H-bond energies. These are presented in Table V together with experimental and calculated values, where available. Except where noted, all values correspond to fixed monomer geometries. In practice, the A-H bond is known to stretch a little on H-bond formation, but SCF calculations show that this does not lower the H-bond energy significantly.<sup>4a</sup>

A number of comments can be made. (i) The SCF results in Table V cannot in all cases be regarded as definitive. In particular, most SCF results are from Kollman and Allen,<sup>3d,4</sup> who employed medium-sized basis sets without polarization functions, and they have shown that decontracting these sets may lead to large changes in the H-bond energy.<sup>4a,b</sup> Keeping these restrictions in mind, it appears that the present model produces energies of the right order of magnitude for a wide range of H-bonding systems, including strong H bonds such as F-H $\cdots$ F<sup>-</sup>. This may partly be due to a cancellation of errors because the assumptions in our model are less valid for strong H bonds than for weak ones. (ii) SCF and CNDO/2 calculations suggest that the equilibrium H $\cdots$ B distances for H bonds involving the same donor are about constant,<sup>4c,5a</sup> whereas we find a gradual shortening in the sequence A-H $\cdots$ F through A-H $\cdots$ N. Thus, the SCF results indicate that in our calculations H bonds where F is the acceptor are too long by about 0.5 Å, while those to N are about 0.3 Å too short. At first sight, this discrepancy might seem to be due to our use of a single orbital exponent ( $\zeta =$

(26) The exponent 3 in the second term has been chosen for convenience and in fact better fits can sometimes be obtained by varying this exponent as well (which leads to exponents in the range 1-3). The use of a fixed value was also preferred because it leads to a better representation of systematic changes going from one system to another.

**Table V.** Equilibrium H-Bond Energies  $-E$  (kcal/mol) and Equilibrium H...B Distances  $R_{eq}$  (Å) for Some H-Bonding Systems<sup>a,b</sup>

H donors	H acceptors										
	F (FH)		O (OH <sub>2</sub> )		N (HCN)		N (NH <sub>3</sub> )		F <sup>-</sup>		
	$-E$	$R_{eq}$	$-E$	$R_{eq}$	$-E$	$R_{eq}$	$-E$	$R_{eq}$	$-E$	$R_{eq}$	
CH $k = 0.95$ (H <sub>3</sub> CH)											
	Exptl										
	SCF										
	CNDO										
	Present	0.26	3.18	0.76	2.70	1.34	2.53	1.53	2.33	12.86	1.79
CH $k = 0.90$	Exptl			2-3		2-3		2-5			
	SCF										
	CNDO										
	Present	0.28	3.11	0.95	2.59	1.63	2.43	2.00	2.22	15.12	1.74
NH $k = 0.85$ (H <sub>2</sub> NH)	Exptl										
	SCF	1.4	2.3	2.28	2.41			2.71	2.49		
	CNDO	1.50	1.74	1.26	1.82			3.69	1.81		
	Present	0.63	2.85	1.78	2.40	2.75	2.27	3.62	2.05	23.12	1.68
NH $k = 0.80$	Exptl			2-3		1-2		3-5			
	SCF										
	CNDO										
	Present	0.70	2.78	2.17	2.30	3.28	2.18	4.51	1.96	26.15	1.65
OH $k = 0.75$ (HOH)	Exptl			2-4		1-2		3-6			
	SCF	3.00	2.12	4.84 <sup>c</sup>	2.04			5.80	2.16	24.07 <sup>d</sup>	1.55
	CNDO	3.38	1.59	5.94	1.57	4.4 <sup>e</sup>	1.64	10.51	1.68		
	Present	0.70	2.73	3.51	2.14	4.92	2.05	7.03	1.83	35.81	1.59
OH $k = 0.70$	Exptl			4-5		3-4		6-9			
	SCF			8.1 <sup>f</sup>							
	CNDO			17 <sup>g</sup>	1.4						
	Present	0.83	2.63	4.26	2.05	5.84	1.97	8.63	1.75	39.78	1.56
FH $k = 0.65$	Exptl									37 <sup>i</sup>	
	SCF	4.58 <sup>h</sup>	1.96	9.29	1.80			12-16	1.75	40, <sup>j</sup> 52 <sup>k</sup>	1.13 <sup>l</sup>
	CNDO	6.58	1.50	10.70	1.49			13.08	1.55	30.0 <sup>m</sup>	1.10 <sup>l</sup>
	Present	1.52	2.49	6.05	1.92	7.95	1.86	12.33	1.65	51.56	1.49

<sup>a</sup> Experimental values are taken from ref 6. The CNDO and SCF results are taken from the work by Kollman and Allen,<sup>3d,4,5</sup> except where noted otherwise. <sup>b</sup> The CNDO results are for experimental monomer geometries. If CNDO-calculated geometries are used, one finds H-bond energies some 50% larger.<sup>5a,c</sup> <sup>c</sup> From ref 2a. <sup>d</sup> From ref 2c. <sup>e</sup> For methanol-acetonitrile, ref 5d. <sup>f</sup> Formic acid cyclic dimer, ref 4f. <sup>g</sup> Formic acid cyclic dimer, ref 5c. <sup>h</sup> Reference 4a also reports a value of 6.4 kcal/mol. <sup>i</sup> S. A. Harrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, **86**, 4497 (1964). <sup>j</sup> From ref 2d. <sup>k</sup> From ref 4d. <sup>l</sup> Results for a symmetrical H bond. <sup>m</sup> From ref 5d.

2.0) for all acceptor atoms considered, for this implies that all atoms have the same radius. However, the error involved is probably small: if Slater exponents had been used, the radius of the N atom would have been about 0.2 Å larger than that of the F atom, and the respective van der Waals radii are also about 0.2 Å different. The calculated differences in  $R_{eq}$  are much larger than this.

The H bonds to F are not only too long, but also too weak, and this points to a second deficiency in our model, namely that net charges on the acceptor atoms are not allowed for. This omission probably accounts for the fact that the H-bond energies for H bonds to FH and OH<sub>2</sub> are underestimated by some 60 and 30%, respectively, as well as for the erroneous variation in  $R_{eq}$ . It should be added that our results for H bonds to Ne, N, and F<sup>-</sup> are probably little affected by our neglect of net charges, but their radii are, of course, not well represented.

(iii) Even though the above discussion shows that our results for F as acceptor (and to some extent for O also) are less accurate than the other results in Table V, the prediction that O is a better acceptor than F and that N (at least NH<sub>3</sub>) is better than both seems to be correct, since it is also obtained in the SCF calculations.<sup>4</sup> The experimental evidence, though less conclusive, points in the same direction (e.g., see ref 27, p 464).

At first sight this is unexpected because H bonds are usually thought to become stronger with increasing elec-

tronegativity of the acceptor atom. In fact, such an increase will increase the net negative charge on the acceptor atom, and from the results for F<sup>-</sup> as acceptor it is clear that this charge increase by itself would strengthen the H bonds involved. There are at least two factors, however, which may oppose this trend. First, an F atom is more compact than an O or N atom, which implies that the H...B distances where overlap-dependent terms become important are shorter, as well as that the relative magnitude of these terms may change. Thus, for a fixed H...B distance the attractive penetration part of the Coulomb energy, the repulsive exchange energy, and the attractive charge-transfer energy should decrease going from NH<sub>3</sub> to FH. It is not obvious, however, whether this will stabilize or destabilize H bonds to FH. In any case, our model does not allow for such

**Table VI.** Individual Energy Terms (kcal/mol) for H Bonds in which OH ( $k = 0.70$ ) is the Donor<sup>a</sup>

H acceptor	Ne	F (FH)	O (OH <sub>2</sub> )	N (HCN)	N (NH <sub>3</sub> )	F <sup>-</sup>
$E_{multipole}$	0	-1.56	-4.78	-5.56	-6.13	<sup>b</sup>
$E_{Coul}$	-4.45	-7.26	-11.81	-13.24	-14.63	-29.68
$E_{exch}$	+17.37	+15.27	+13.07	+11.51	+11.39	+10.44
$E^1$	+12.91	+8.00	+1.26	-1.73	-3.24	-19.24
$E_{ind}$	-0.31	-0.00	-0.26	-0.56	-0.75	-8.20
$E_{exch2}$	+0.75	+0.07	-0.44	-0.48	-0.61	-1.65
$E_{ct}$	-2.14	-1.97	-2.22	-1.09	-2.02	-2.82
$E_{disp}$	-1.66	-1.66	-1.66	-1.66	-1.66	-1.66
$E^2$	-3.35	-3.57	-4.59	-3.79	-5.04	-14.32
$E_{total}$	+9.56	+4.44	-3.32	-5.52	-8.28	-33.56

<sup>a</sup>  $R_{HB} = 1.85$  Å. <sup>b</sup> Not evaluated.

(27) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 12.

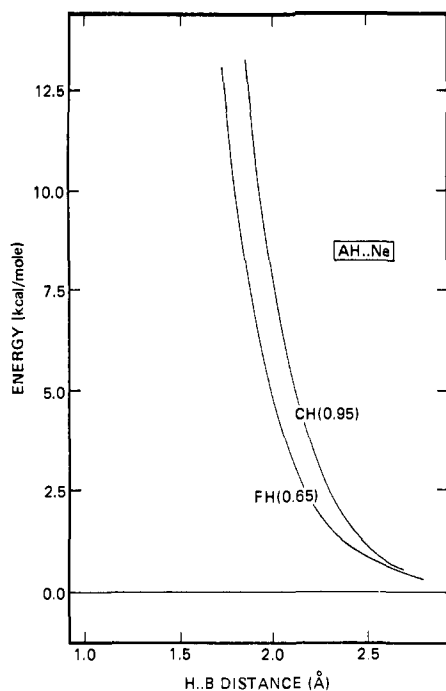


Figure 5. Variation of H-bond energy with distance for A—H...Ne.

changes in the size of the acceptor atom. Secondly, the charge distribution of the acceptor atom in the region of the approaching A—H group is very asymmetrical in  $\text{NH}_3$ , but nearly spherical in FH (this is apparent, for example, from the results in section III). It was shown in ref 14 that in the case of N as acceptor, the exchange energy becomes more repulsive and the penetration part of  $E_{\text{Coul}}$  less attractive as the acceptor lone pair becomes more nearly spherically symmetric. From the present results it appears that this rule also applies when the overall lone pair region of the acceptor atom becomes

Table VII. Individual Energy Terms (kcal/mol) for H Bonds in Which  $\text{NH}_3$  ( $\chi_B = 0.33$ ) Is the Acceptor

H donor	$\text{H}_2\text{NH}$	$\text{H}_3\text{NH}$	HOH	FH	FH
$k$ value	0.85	0.85	0.75	0.65	0.65
$R_{\text{HB}}, \text{Å}$	2.12	1.85	1.85	1.85	1.59
$E_{\text{multipole}}$	-1.63	-2.08	-5.20	-8.28	-11.73
$E_{\text{Coul}}$	-6.33	-11.65	-14.11	-16.43	-29.36
$E_{\text{exch}}$	+4.99	+13.12	+12.14	+11.04	+28.66
$E^1$	-1.34	+1.46	-1.97	-5.39	-0.70
$E_{\text{ind}}$	-0.59	-0.71	-0.75	-0.85	-0.66
$E_{\text{excl}2}$	-0.23	-0.63	-0.62	-0.62	-1.32
$E_{\text{ct}}$	-0.44	-1.48	-1.89	-2.41	-6.54
$E_{\text{disp}}$	-0.98	-1.66	-1.66	-1.66	-2.94
$E^2$	-2.25	-4.48	-4.92	-5.54	-11.46
$E_{\text{total}}$	-3.59	-3.02	-6.89	-10.93	-12.17

more nearly symmetrical. Thus, in Table VI, both  $E_{\text{exch}}$  and  $E_{\text{Coul}}$  become less attractive going from  $\text{NH}_3$  to Ne,<sup>28</sup> and in our model these changes in the first-order energy are responsible for nearly all of the predicted changes in stability in this series (cf. Table VI).

(iv) Let us now consider the case of H bonds involving the same acceptor. SCF and CNDO/2 calculations<sup>4,5</sup> show that in this case a change in donor that leads to

(28) About one-half of the change in  $E_{\text{Coul}}$  is due to the decrease in the multipolar part, which vanishes for Ne.

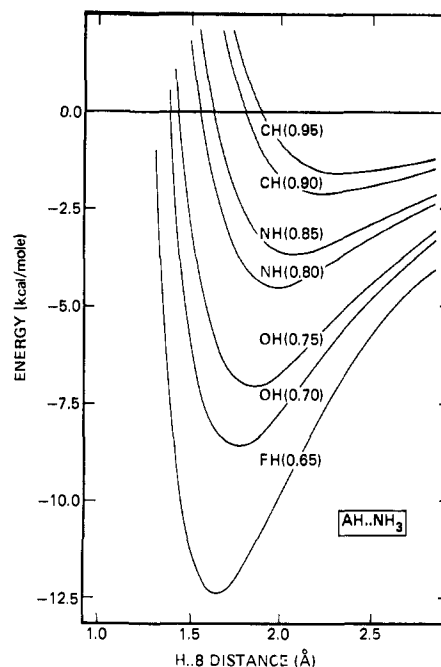


Figure 6. Variation of H-bond energy with distance for A—H... $\text{NH}_3$  ( $\chi_B = 0.33$ ).

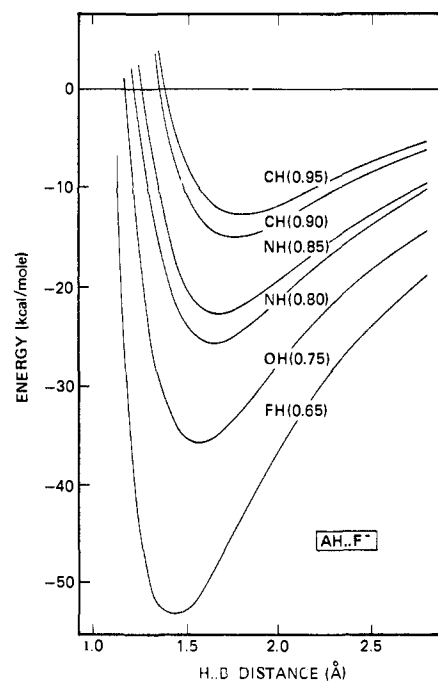


Figure 7. Variation of H-bond energy with distance for A—H... $\text{F}^-$  (note the change of scale).

larger H-bond energies will also result in shorter equilibrium distances. The present results show a similar correlation, as may be seen from Table V and from Figures 5–7, in which the common acceptors are Ne,  $\text{NH}_3$ , and  $\text{F}^-$ , respectively.

Individual energy terms for H bonds in which  $\text{NH}_3$  is the acceptor are collected in Table VII (see also Figure 8). If  $R_{\text{HB}}$  is kept fixed (cf. columns 2–4), then the variation in the H-bond energy arises mainly from a change in the first-order energy  $E^1$ . In fact, the overall change in energy can be predicted quite well by considering the multipolar terms in the Coulomb energy alone. The



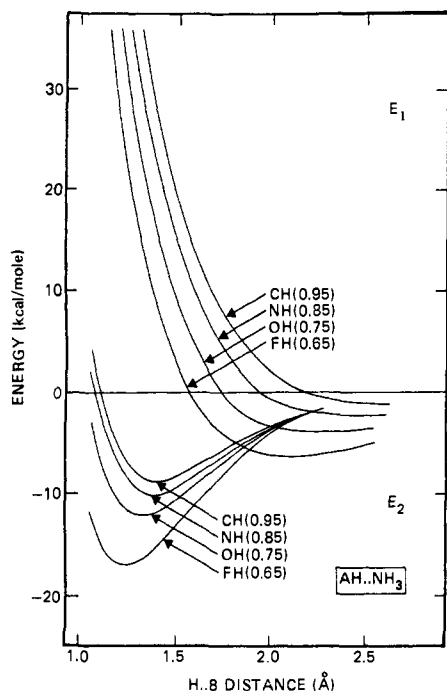


Figure 8. Variation of the first- and second-order energies with distance for A-H...NH<sub>3</sub>.

reason for this is that the decrease in the repulsive exchange energy as the A-H bond becomes more polar (*i.e.*, as  $k$  decreases) is largely canceled by a corresponding decrease in the attractive penetration part of  $E_{\text{Coul}}$ . From these arguments it follows that in the case of Ne as acceptor, where the multipolar terms vanish, the total energy should depend little on the donor system employed. This expectation is borne out by the results shown in Figure 5.

A somewhat different interpretation of the change in H-bond energy if obtained if one compares the various systems at their equilibrium distance (*cf.* columns 1, 3, 5 in Table VII and Figure 8). The overall change in energy is about the same as for a fixed  $R_{\text{HB}}$  and still correlates well with the change in the multipolar terms alone, but there are now several other terms in the H-bond energy which change considerably. Consequently, no single energy term can be held responsible for the changes in equilibrium energy and distance observed in H bonds involving a common acceptor.

(v) The case of H bonds where Ne or F<sup>-</sup> is the common acceptor deserve special mention. In our model the electron distribution in these two acceptors is identical and only their nuclear charge is different. From Figures 5 and 7 this is seen to have a profound effect on the stability of H bonds to these acceptors. Ne does not give stable H bonds even with the strongest proton donor considered (FH) and, in fact, the choice of proton donor is of little significance. On the other hand, H bonds to F<sup>-</sup> display the largest variation in H-bond energies of all acceptors considered. Our results suggest that all such H bonds are strong. Comparison with the SCF values suggests that our energies are somewhat too large<sup>29</sup> and it may therefore be that

(29) The SCF result for (FHF)<sup>-</sup> in ref 2d is more accurate than that in ref 4d. Our own result was obtained with constant F-H bond length. This is probably not serious because the energy of (FHF)<sup>-</sup> is insensitive to the precise location of the proton along the molecular axis.<sup>30</sup>

C-H...F<sup>-</sup> bonds, which we find to be strong, are in fact rather weak.

(vi) Whether C-H bonds form H bonds to neutral molecules is an open question. Our results suggest that even normal C-H bonds (such as in alkanes) show a distinct attraction for most acceptors (*cf.* Table V). However, the equilibrium distances that we obtain are near the limit where one normally concludes the absence of an H bond (*viz.*,  $R_{\text{HB}}(\text{limit}) = 2.3, 2.4, \text{ and } 2.5 \text{ \AA}$  for C-H...F, C-H...O, and C-H...N, respectively<sup>31</sup>). In view of the inaccuracies in our model, we cannot therefore draw any final conclusions on this point.<sup>32</sup>

(vii) Finally, we wish to emphasize that although a comparison of energy terms for different systems may be meaningful, our results for the absolute magnitude of the individual energy terms for one particular H-bonding system are likely to be in error by several kilocalories per mole, for we constrain the total energies of some selected systems to agree with experiment, and in doing so the relative magnitudes of first- and second-order energies, for example, may be misrepresented. Let us therefore compare our findings with some SCF results for the individual energy terms  $E^1$  and  $E^2$  that have been obtained very recently using the technique mentioned in the introduction. Pullman and Dreyfus<sup>4e</sup> studied the N-H...O bond in formamide dimer. At  $R_{\text{HO}} = 2.0 \text{ \AA}$  their results for  $E_{\text{Coul}}$ ,  $E_{\text{exch}} (\equiv E^1 - E_{\text{Coul}})$ , and  $E^2$  are (kcal/mol) -8, +3, and -3, whereas we find values of -6, +6, and -2 at  $R_{\text{HO}} = 2.12 \text{ \AA}$  ( $k = 0.8$ ). Similarly, Kollman and Allen<sup>4b</sup> report  $E^1$  and  $E^2$  values of -4.5 and -3.1 for HOH...OH<sub>2</sub> at  $R_{\text{OH}} = 1.84 \text{ \AA}$ , whereas we find +2.4 and -4.4, respectively, at that distance ( $k = 0.75$ ). Finally, Clementi and van Duijneveldt<sup>32</sup> (in a calculation in which all polarization functions were deleted) found  $E^1$  and  $E^2$  values of 1.7 and -0.8 for H<sub>3</sub>C-H...FH at  $R_{\text{HF}} = 2.12 \text{ \AA}$ , whereas we find +4.5 and -1.4 at that distance ( $k = 0.95$ ).

The largest differences are seen to occur for  $E^1$ . This is to be expected, since our expression for  $E^1$  is different from that in ref 4b, 4e, and 32, and in the introduction it was noted that this leads to different results when minimal basis sets are employed. Moreover, the approximations in our model may further cause the agreement to deteriorate. It would be of interest to see how the two expressions for  $E^1$  compare if near-Hartree-Fock molecular wave functions are employed.

## V. Conclusions

(i) The semiempirical perturbation calculations in this paper yield H-bond energies of the right order of magnitude both for weak and strong H bonds. (ii) Comparison with SCF results shows that the energies obtained here are roughly of the same accuracy as those obtained in recent CNDO/2 calculations. The equilibrium distances obtained are sometimes too short and sometimes too long, whereas in CNDO/2 calculations they are invariably too short. (iii) H bonds to a

(30) A. D. McLean and M. Yoshimine, *IBM J. Res. Develop.*, **12**, 206 (1968), and supplement.

(31) W. C. Hamilton in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1967, p 466.

(32) Some near-Hartree-Fock calculations on H<sub>3</sub>C-H...F-H (linear) have recently been performed by E. Clementi and F. B. van Duijneveldt (manuscript in preparation). A minimum was found at  $R_{\text{HB}} \approx 3.0 \text{ \AA}$ , the energy of formation being 0.16 kcal/mol, in good agreement with the C-H...F result in Table V.

common acceptor are predicted to become shorter as they get stronger, in agreement with available data. C-H donors show some attraction for most neutral acceptors, but it is not clear whether these interactions should be classified as H bonds. (iv) H bonds to a common donor are predicted to become stronger in the acceptor order  $\text{Ne} < \text{FH} < \text{OH}_2 \lesssim \text{N} (\text{HCN}) < \text{N} (\text{NH}_3) < \text{F}^-$ . They are also predicted to become shorter in the same order, which (except for  $\text{F}^-$ ) is not observed in recent SCF calculations. In addition to the electronegativity of the acceptor atoms, the size of the acceptor atom and the local asymmetry of its lone-pair electron distribution are found to be of importance in determining the acceptor strength. (v) "H bonds" to Ne are little affected by varying the donor, and in all cases the potential curve is repulsive. (vi) H bonds to an atom B are predicted to become weaker and longer as the lone-pair s character of B increases. Thus

amines are better acceptors than nitriles, and ethers should be better acceptors than ketones. (vii) Steric requirements for H bonding to N, O, and F are found to differ considerably, N in amines giving good H bonds only for an approach along the N lone-pair axis. For O and F acceptors, the optimum direction of approach depends sensitively on the lone-pair s character. (viii) Many of the trends in stability discussed above can be rationalized by considering changes in the electrostatic energy alone. This is also true for the optimum orientations adopted by the acceptor in linear  $\text{A}-\text{H}\cdots\text{B}$  bonds, providing that one goes beyond the usual dipole-dipole approximation.

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## Extended Woodward-Hoffmann Rules for Sigmatropic Rearrangement of Stereochemically Nonrigid Organometallic Compounds with Carbon-Metal $\sigma$ Bonds

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**Abstract:** A combination of energy level correlation diagrams and a simple perturbation method indicates that the rearrangement pathways (under thermal conditions) of fluxional organometallics with carbon-metal  $\sigma$  bonds are governed by the highest occupied molecular orbital of the organic portion of the transition state. This conclusion is in accord with the Woodward-Hoffmann rules for sigmatropic rearrangements. With additional consideration of the metal moieties, guidelines are established which correlate specific pathways involved in fluxional behavior.

Cotton and coworkers<sup>1,2</sup> have examined the dynamic processes of some fluxional organometallic compounds. Fluxional behavior is a set of concerted displacements of the metal from one carbon to another. This paper attempts to relate the fluxional behavior of some organometallics, which contain one metal group  $\sigma$  bonded to a  $\pi$ -conjugated organic portion, to the Woodward-Hoffmann rules<sup>3,4</sup> for sigmatropic rearrangements of organic compounds.<sup>5</sup>

Two steps are necessary. First, energy correlation diagrams<sup>6a</sup> are constructed. Then the detailed rear-

range pathway is treated by a simple perturbation method.<sup>6b</sup>

### Correlation Diagrams

Consider, for example,  $(h^1\text{-C}_5\text{H}_5)\text{M}$ , in which M is the migrating moiety. The symmetry planes of the molecule and the transition state are shown in Figure 1.

In the rearrangement, six orbitals of  $(h^1\text{-C}_5\text{H}_5)\text{M}$  change, namely,  $\sigma$ ,  $\sigma^*$ ,  $\psi_1'$ ,  $\psi_2'$ ,  $\psi_3'$ , and  $\psi_4'$ . Here  $\sigma$  and  $\sigma^*$  are the bonding and antibonding orbitals of the carbon-metal  $\sigma$  bond and the latter four orbitals are the conjugated diene molecular orbitals. The corresponding six orbitals in the transition state are  $\text{M}_s$ ,  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ ,  $\psi_4$ , and  $\psi_5$ . Here  $\text{M}_s$  is the orbital of the migrating metal and the latter five orbitals are those of the cyclopentadienyl group. Table I gives the symmetries of the orbitals. Charts I-VI give the correlation diagrams of the orbitals as the  $\text{M}_s$  energy level varies.

In these diagrams, the  $\text{M}_s$  orbital is an  $\text{A}'$  orbital (*i.e.*, it is symmetric with respect to the symmetry plane); examples are s,  $p_x$ ,  $p_y$ , and certain hybrid orbitals of the M atom, depending upon its valence shell.

(1) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968), and references therein.

(2) M. T. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(3) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

(4) R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(5) For additional applications of the Woodward-Hoffmann rules to the reactions of transition metal complexes, see, for example, (a) D. R. Eaton, *J. Amer. Chem. Soc.*, **90**, 4272 (1968); (b) T. H. Whitesides, *ibid.*, **91**, 2395 (1969); (c) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970). None of these treatments applies to reversible sigmatropic arrangements.

(6) (a) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (b) H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).