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A COMPARATIVE THEORETICAL ANALYSIS OF THE HYDROGEN BOND IN DIMERS CONTAINING SUBSTITUTED CARBONYL COMPOUNDS

by

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ABSTRACT

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Francis T. Marchese

Master of Science

Youngstown State University, 1973

Ab-initio SCF calculations have been performed with a minimal STO-3G basis set to determine the structures and energies of the dimers H_2O-HFCO and H_2O-F_2CO, with H_2O as the proton donor. A comparison of the hydrogen bond energies of these dimers with the energy of the hydrogen bond in H_2O-H_2CO shows that the hydrogen bond strength decreases in order of decreasing sigma electron density at the oxygen. The equilibrium structures are well described by the general hybridization model for the hydrogen bond. The relative orientation of the dipole moments of proton donor and acceptor molecules is also found to be significant in the structures of these dimers. Configuration interaction (CI) calculations have also been performed to determine the excitation energies for the lowest vertical excited singlet states in the monomers and dimers. The vertical excitation energies in the dimers are greater than the $n \rightarrow \pi^*$ transition energies of the respective proton

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acceptors, and therefore the experimentally observed blue shift is reproduced. The blue shift is quantitatively attributed to the additional energy needed to break the hydrogen bond in the excited singlet states of these dimers.

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CHAPTER I

Introduction

It is generally agreed by chemists that hydrogen bonding contributes significantly to many and varied chemical phenomena. Formation of this type of bond has been known to alter numerous molecular properties. The most frequently encountered modifications are of boiling points, freezing points, and electrical conductivities. However, it is in the field of spectroscopy that the effects of the hydrogen bond are most dramatically demonstrated. The infrared and Raman spectra of hydrogen bonded species are characterized by a shift of the X-H stretching bands to lower frequencies, and an increase in the integrated intensity of the fundamental stretching band. Both bathochromic and hypsochromic shifts are observed in the ultraviolet spectrum of hydrogen bonded species. The $n \rightarrow \pi^*$ bands are generally displaced to shorter wavelengths (blue shift), and the $\pi \rightarrow \pi^*$ are commonly shifted to longer wavelengths. Lastly, in the nuclear magnetic resonance spectrum, the proton signal is generally transferred to lower fields.

An excellent review of hydrogen bonding is given by Pimentel and McClellan[1], in which the hydrogen bond is represented schematically by the formula X-H...Y. Of the two components of the hydrogen bond, X-H serves as a proton donor and Y as a proton acceptor. Quite commonly familiar groups which function as proton donors are: carbonyl, hydroxyl, amino, and amide. Common proton acceptors are oxygen in carbonyls, ethers, and hydroxyls; nitrogen in amines; and halogens in varied molecular enviroments, to name but a few. The hydrogen bond may exist within the same molecule (intramolecular), or between different molecules (intermolecular).

In order to gain an insight into the nature of the intermolecular hydrogen bond, it is necessary to ascertain the structures of hydrogen bonded systems, and to determine those factors which are important in stabilizing the hydrogen bonded dimer. The characterization of hydrogen bonding by experimental methods is limited to a description of the effects of such a bond. To understand this type of intermolecular interaction requires a theoretical analysis of this phenomenon.

Early theoretical approaches to the problem of hydrogen bonding were based on simple localized models. Coulson[2] analyzed the hydrogen bond energy into four components: the electrostatic interaction energy, charge transfer energy, polarization and dispersion energy, and exchange repulsion energy. Other studies of the hydrogen bond were based on simple localized dipole[3,4] or point-charge[5,6] models. However, the conclusions resulting from these investigations directly reflected the very assumptions made in the initial formulation of the models! Undoubtedly, a higher, less biased approach was needed.

Recently, semi-empirical molecular orbital (MO) studies of the hydrogen bond have been reported by several authors[7-15], but the results of these analyses have indicated that even this level of theory does not yield reliable and consistent results.

Within the past few years the development of computational techniques in molecular quantum mechanics, and the advent of high speed computers, have made it possible to apply ab-initio molecular orbital theory to simple hydrogen bonded systems. This level of theory makes no assumptions as to the types or magnitudes of interactions present in a hydrogen bonded system. Rather, it determines from first

principles the electronic distribution in any molecular system, and hence, it may be utilized to study the structures and energies of hydrogen bonded dimers without any a priori assumptions. It should therefore lead to a less biased, more realistic, and more reliable description of the hydrogen bond.

The first investigation employing this technique was reported by Clementi[16], and by Clementi and McClean[17], on the biflouride ion FHF^-. This was later followed by a rigorous analysis of NH_3-HCl[18]. Recently, studies of intermolecular hydrogen bonds have focused on the water dimer. The first inquiry into this dimer was undertaken by Morokuma and Pederson[19] employing a small Gaussian basis. Kollman and Allen[20] utilized a larger contracted Gaussian basis set to improve on their study. Meanwhile, Morokuma and Winick[21] showed that a minimal basis set of Slater type orbitals (STO's) could give a good representation of the hydrogen bonded water dimer. Hankins, Moskowitz, and Stillinger[22] studied water dimers and trimers using a very large basis which produced energies approaching the Hartree-Fock limit. Del Bene and Pople[23] investigated the stability of higher polymers with an STO-4G basis. It was determined that for trimers and higher polymers, a cyclic structure was preferred,

and that the hydrogen bond energies were nonadditive. Other studies of hydrogen bonded water molecules using different basis sets have also been reported[24-26]. Since these investigations were initiated, the hydrogen bond in various other systems has been explored. These include $(HF)_2$ [25,27,28]; $(HF)_n$ (n= 3,4,5,6)[28]; H_2O-NH_3 [25,29]; HF-NH_3 [25]; H_2O-HF[24]; $(NH_3)_2$ [25]; $(HCN)_2$ and $(HCN)_3$ [30]; HF-HCN[31,32]; H_2O-H_2CO[33]; ROH-H_2O and $(ROH)_2$, where R is H, CH_3, NH_2, OH, F[34-36]; and ROH-NH_3, with R varying as before[37].

Del Bene recently employed the SCF method to determine the ground state structures and energies of the hydrogen bonded dimers (ROH-H_2CO), where R is H, CH_3, NH_2, OH, F[38]. For these systems it was found that the order of increasing hydrogen bond strength parallels the order of increasing sigma electron withdrawing ability of the substituent, R. Hence the hydrogen bond energy increased in the series from the methyl substituted proton donor through the fluorine substituted proton donor. As a complement to this study, an inquiry was initiated in this work into the effects of substituents bonded to the proton acceptor H_2CO. Since fluorine is both a sigma electron withdrawing and also a pi electron donating substituent, its effects as a substituent on the hydrogen bond should be interesting.

Calculations were also performed by Del Bene, utilizing the SCF-CI technique, to study the lowest excited singlet states of the dimers ROH-H_2CO[39]. It was discovered that the vertical excitation energies in these dimers are greater than the vertical $n \rightarrow \pi^*$ transition energy for H_2CO. Thus, the experimentally observed blue shift for the $n \rightarrow \pi^*$ band upon hydrogen formation had been reproduced. In addition it was shown that the magnitude of the blue shift was equal to the hydrogen bond energy of the dimer in the ground state.

In the present study, a comparative analysis of the three dimers H_2O-H_2CO, H_2O-HFCO, H_2O-F_2CO has been undertaken. The purposes of this study are:

(1) To determine optimum ground state structures and energies for the dimers H_2O-HFCO and H_2O-F_2CO;

(2) To examine the dimer structures in light of the general hybridization model for the hydrogen bond[36,38];

(3) To examine substituent effects on hydrogen bond structures and energies; and

(4) To examine the effects of hydrogen bonding on the electronic transitions in these dimers.

CHAPTER II

METHOD OF CALCULATION

Determination Of The SCF Ground State Wavefunction

In order to describe the electron distribution in a molecular system, it is necessary to determine the wavefunction Ψ for the system. Ψ is a solution to the Schrödinger equation

$$H \Psi = E \Psi \tag{1}$$

where H is the nonrelativistic Hamiltonian operator

$$H = -\sum_{\mu} 1/2 \nabla_{\mu}^2 - \sum_{A\mu} \frac{Z_A}{r_{A\mu}} + \sum_{\mu<\nu} \frac{1}{r_{\mu\nu}} + \sum_{A<B} \frac{Z_A Z_B}{r_{AB}} \tag{2}$$

and is composed of kinetic energy, nuclear-electronic attraction, electronic repulsion, and nuclear repulsion terms. The energy is calculated as the expectation value,

$$E = \int \Psi^* H \Psi \, d\tau \tag{3}$$

where the integration is over all space and spin coordinates of all electrons. Since the nuclear motion is slow when compared to the electronic motion, the nuclear repulsion

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energy is essentially a constant for a set of nuclear coordinates, and independent of the electron distribution. Hence, the last term of equation (2) is calculated classically for a particular set of nuclear coordinates.

As is evident from equation (3), the calculation of E requires that Ψ be known. For a molecular system containing an even number of electrons, the wavefunction Ψ is generally written as a single Slater determinant

$$\Psi = 1/\sqrt{(2n)!}\,|\psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)| \qquad (4)$$

in which each molecular orbital (MO) ψ_i is occupied by two electrons of opposite spins. The MO's ψ_i are expressed parametrically as a linear combination of n atomic basis functions ϕ_μ (the LCAO approximation)

$$\psi_i = \sum_\mu c_{\mu i}\,\phi_\mu \qquad (5)$$

with the coefficients determined variationally. The method for obtaining the set of coefficients $c_{\mu i}$ was devised by Roothaan[40]. The Roothaan equations may be written in matrix form as

$$\underline{F}\,\underline{C} = \underline{S}\,\underline{C}\,\underline{E} \qquad (6)$$

or, in terms of the elements as

$$\Sigma_\nu (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0 \tag{7}$$

where $F_{\mu\nu}$ is

$$F_{\mu\nu} = H_{\mu\nu} + \Sigma_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - 1/2\ (\mu\lambda|\nu\sigma)], \tag{8}$$

with

$$H_{\mu\nu} = \int \phi_\mu \left[-1/2\ \nabla^2(1) - \Sigma_A \frac{Z_A}{r_{A1}}\right] \phi_\nu\, d\tau \tag{9}$$

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(1)\phi_\lambda(2) \frac{1}{r_{12}} \phi_\nu(1)\phi_\sigma(2)\, d\tau_1 d\tau_2 \tag{10}$$

$$S_{\mu\nu} = \int \phi_\mu(1)\, \phi_\nu(1)\, d\tau \tag{11}$$

$$P_{\lambda\sigma} = 2\Sigma_i^{occ} c_{\lambda i} c_{\sigma i} \tag{12}$$

and ε_i is an element of the diagonal matrix $\underline{E}$. If

$$\underline{F}' = \underline{S}^{-1/2}\ \underline{F}\ \underline{S}^{-1/2} \tag{13}$$

and

$$\underline{C}' = \underline{S}^{1/2}\ \underline{C} \tag{14}$$

where $\underline{S}^{1/2}$ is the square root of $\underline{S}$, then equation (6) may be transformed into the standard form for an eigenvalue problem

$$\underline{F}'\underline{C}' = \underline{C}'\underline{E}. \tag{15}$$

The elements ε_i of $\underline{E}$ are subsequently the roots of the determinental equation

$$| F'_{\mu\nu} - \varepsilon\delta_{\mu\nu} | = 0 \qquad (16)$$

$\underline{C}$ can thus be determined from $\underline{C}'$ as

$$\underline{C} = S^{-\frac{1}{2}}\underline{C}' \ . \qquad (17)$$

The Hartree-Fock matrix elements ($F_{\mu\nu}$) are dependent upon the orbitals ψ_i via the elements $P_{\lambda\sigma}$. The Roothaan equations are solved by first assuming an initial set of linear expansion coefficients $c_{\mu i}$, generating the elements $P_{\lambda\sigma}$, and computing the elements $F_{\mu\nu}$. The diagonalization procedure is carried out by standard matrix techniques, and a new coefficient matrix $\underline{C}$ is obtained. The process is repeated until the coefficient matrices obtained from two successive iterations are identical to within a specified tolerance. At this point the function Ψ is independent of the initial guess, and is comprised of a set of self-consistant molecular orbitals.

The set of Roothaan equations are common to both semiempirical and ab-initio molecular orbital methods. The calculations reported here have been performed within the framework of ab-initio MO theory. At this level, all one

and two-electron integrals associated with the elements in the Fock matrix are evaluated exactly in terms of the components of H, and the mathematical expressions for the basis functions ϕ_μ .

Basis Set

As noted above, the MO's ψ_i which comprise the Slater determinant are generally expressed as a linear combination of atomic basis functions ϕ_μ (the LCAO approximation)

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu \tag{18}$$

These basis functions are used to describe mathematically the atomic orbitals on the atoms. Either Slater type orbitals of the form

$$\phi = Ar^{n-1} e^{-\xi r} \tag{19}$$

or Gaussian orbitals

$$\phi = Br^{\ell} e^{-\alpha r^2} \tag{20}$$

are commonly employed.

For calculations on molecular systems, Slater type orbitals (STO's) are generally preferred from energetic considerations. However in this basis, the calculation of the two-electron integrals is prohibitive, since numerical integration must be employed. In contrast, these same integrals can be evaluated exactly with a Gaussian basis. Unfortunately, to obtain an energy comparable to that obtained with the STO's, it is necessary to use more Gaussian functions.

In order to incorporate the best characteristics of both types of functions, Pople and coworkers[41] replaced each Slater type orbital (STO) in a minimal basis set with a least squares fitted sum of N Gaussian functions. The new basis set, STO-NG, approaches at large N, the results which would have been obtained from a Slater basis. Studies performed on ground and excited states with the STO-NG basis, varied as a function of N, indicated that the STO-3G basis set represents the level at which computationally consistent results can be obtained with a minimal amount of computing time[23,34,41,42]. Therefore, all calculations reported here have been performed with the STO-3G basis. In this basis set, the orbitals of each atom (1s for H; 1s, 2s, $2p_x$, $2p_y$, $2p_z$, for C, O, F) are described by a set of

three Gaussian functions, fitted to the appropriate STO. The standard scale factors proposed by Pople have been used.[41]

Configuration Interaction

The solution of the Roothaan equations for a closed shell ground state yields a set of orbitals which are doubly occupied, and a set of unoccupied or virtual orbitals. The number of virtual orbitals is (n - N), where n is the total number of atomic basis functions and 2N is the number of electrons. The virtual orbitals are useful for describing molecular excited states. As a first approximation to an excited state, an electron may be promoted from an occupied MO ψ_i to an unoccupied one ψ_ℓ. This virtual orbital approximation gives rise to a singlet configuration, and to the three components of the triplet, which can be described by the functions

$$ {}^1\psi_i^\ell = \{ | 1\bar{1}\ldots i\bar{\ell}\ldots n\bar{n} | - |1\bar{1}\ldots\bar{i}\ell\ldots n\bar{n}| \}/\sqrt{2} \quad (21) $$

$$ {}^3\psi_i^\ell \begin{cases} = \{ | 1\bar{1}\ldots i\bar{\ell}\ldots n\bar{n} | + |1\bar{1}\ldots\bar{i}\ell\ldots n\bar{n}| \}/\sqrt{2} & (22) \\ = | 1\bar{1}\ldots i\ell\ldots n\bar{n} | & (23) \\ = | 1\bar{1}\ldots\bar{i}\bar{\ell}\ldots n\bar{n} | & (24) \end{cases} $$

Unfortunately, a single excited configuration does not take into account electron reorganization in the excited state, and hence is generally a poor approximation. However, a linear combination of single excitation functions (singlet or triplet) yields an improved wavefunction for the excited state, and an appropriate state energy which can be compared with experimental data. This configuration interaction (CI) function may be written as

$$\Phi = \sum_{i} \sum_{\ell} A_{i\ell} \Psi_i^{\ell} \qquad (25)$$

with the coefficients $A_{i\ell}$ determined variationally.

Since the number of possible configurations which arise in the CI expansion may be quite large, it is nearly impossible to obtain a full first-order CI function for the excited states of most molecules. Therefore, the number and combinations of excited configurations included in the CI calculation must be selected prudently[42]. The singly excited configurations included in the CI calculation are defined by the selection of a subset of M high energy occupied orbitals and M virtual orbitals, and allowing all possible excitations within the subset. For minimal basis calculations, M equals the number of virtual orbitals. Thus,

for HFCO and F_2CO, M equals 4, and 16 excited configurations are included in the CI wavefunction. For H_2O-HFCO and H_2O-F_2CO, M is 6, and 36 singly excited configurations have been included. A careful study of configuration selection has been made to ensure the adequate representation of the $n \rightarrow \pi^*$ states in both monomers and dimers. In dimers of C_s symmetry, configurations involving excitation from occupied orbitals of a" symmetry are not important in the dimer excited states[39]. Thus the set of M occupied orbitals from which excitation occurs has been limited to high energy MO's of a' symmetry.

Geometrical Optimization

Monomers

Geometrical optimization of each monomer was first performed using the minimal STO-3G basis set. Bond angles and lengths were varied until a minimum energy structure was achieved to within $\pm$ 0.1° and $\pm$ 0.001 Å, respectively.

For the water molecule, the STO-3G basis produces an O-H bond length of 0.990 Å and an intramolecular angle of 100.0° [43]. The calculated dipole moment of the structure is 1.71 D. The geometries of H_2CO[43], HFCO, and F_2CO are found

in Table 1. Both H_2CO and F_2CO, which posses C_{2v} symmetry, contain dipoles colinear with the C_2 axis with magnitudes of 1.54 D and 0.91 D, respectively. The calculated dipole moment of HFCO was found to be 1.52 D. This dipole vector makes an angle of 34° with the C-O bond, and is oriented such that if the positive end is place at the carbon, the negative end lies within the O-C-F angle, as shown in Figure 1. The monomer geometries have been held rigid for all dimer calculations.

Dimers

The description of the relative orientation of the monomers in a dimer requires that an intermolecular coordinate system be defined. In this system, the dimers can be readily described in terms of five intermolecular angles and an intermolecular distance, as illustrated in Figure 2. The use of the coordinate system requires the selection of a principal axis in each monomer. For F_2CO, H_2CO, and H_2O, this is the C_2 axis. Since HFCO has C_s symmetry, and thus no symmetry axis, it is most advantageous to select the principal axis as an axis colinear with the C-O bond. In the starting orientation from which the dimer coordinates are generated, the molecules are placed in the intermolecular

TABLE I

OPTIMIZED STO-3G MONOMER GEOMETRIES

	H_2O[a]	H_2CO[a]	HFCO	F_2CO
BOND LENGTHS (Å)				
C - O	–	1.217	1.210	1.209
C - H	–	1.101	1.108	–
C - F	–	–	1.351	1.347
O - H	0.990	–	–	–
BOND ANGLES (°)				
H - C - H	–	114.5	–	—
H - C - F	–	–	112.3[b]	—
F - C - F	–	–	–	110.0
H - O - H	100.0	–	–	—
DIPOLE MOMENT (D)	1.71	1.54	1.52	0.91

a) Data taken from Ref. 43.

b) Angle between the principal axis and the C-F bond is 57.9°.

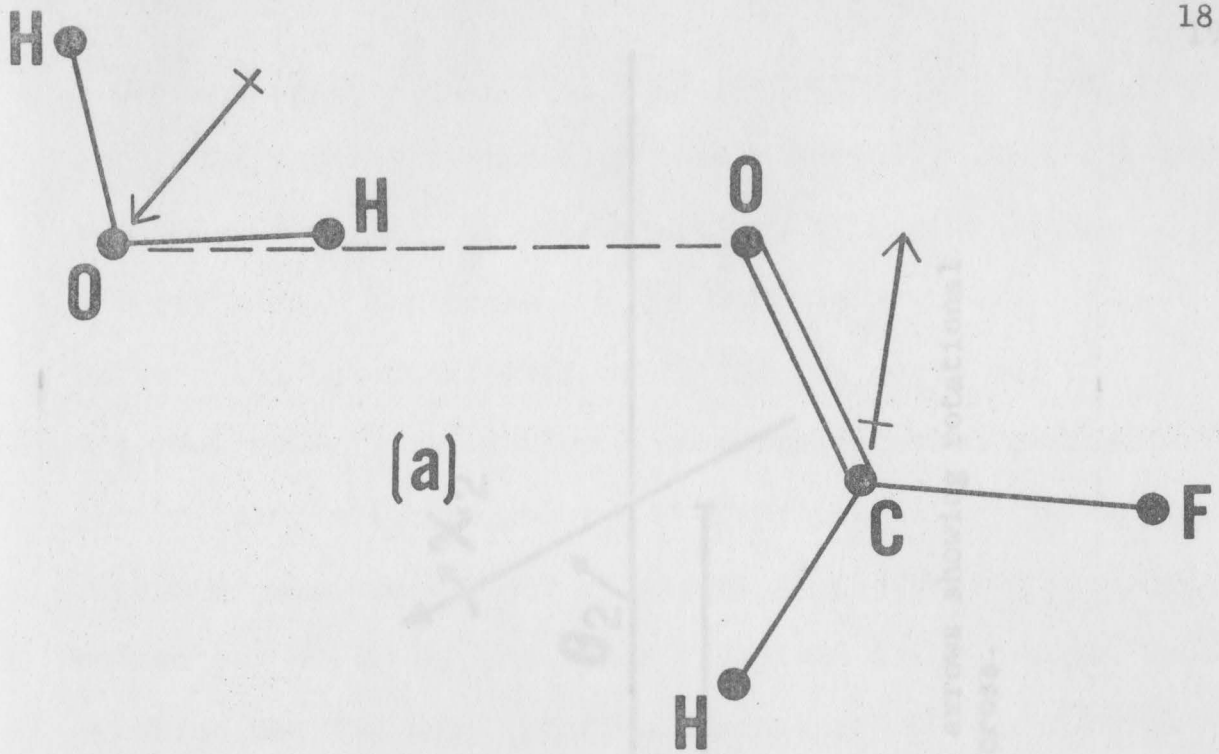
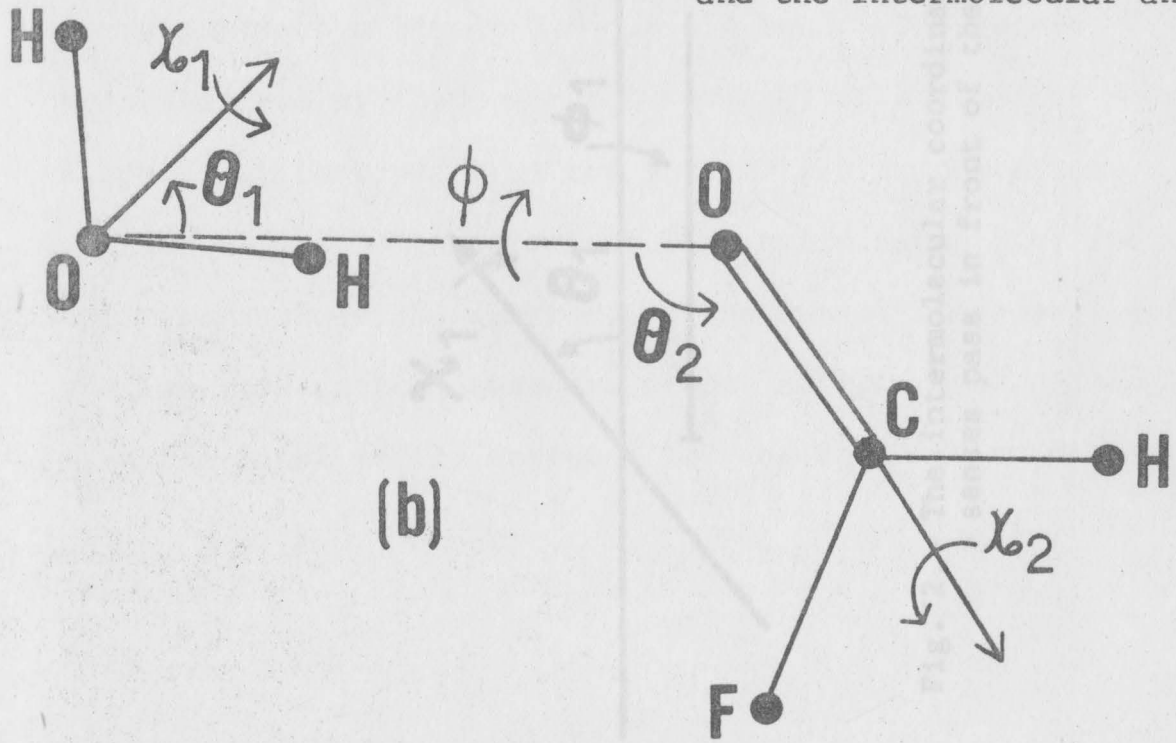


Fig. 1 Equilibrium H_2O-HFCO "trans" dimers A and B. A shows orientations of dipole moment vectors while B illustrates orientations of principal axes, and the intermolecular angles.



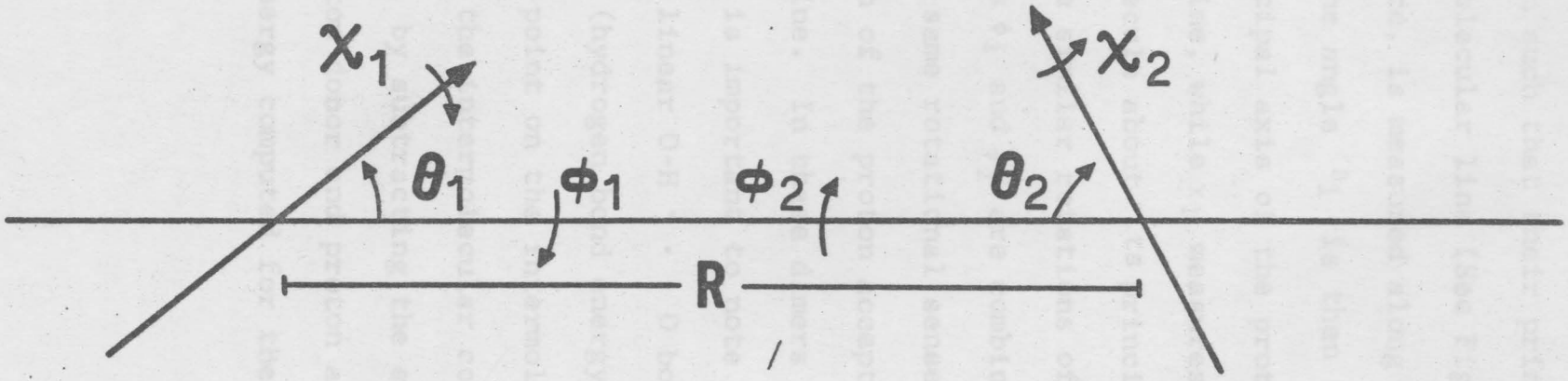


Fig. 2. The intermolecular coordinates. Curved arrows showing rotational senses pass in front of the lines they cross.

coordinate system such that their principal axes point inward along the intermolecular line (See Figure 1). R, the intermolecular distance, is measured along this line as the O-O distance. The angle θ_1 is then the angle between the principal axis of the proton donor and the intermolecular line, while χ_1 measures rotation of the proton donor molecule about its principal axis. The angles θ_2 and χ_2 measure similar rotations of the proton acceptor molecule. Angles ϕ_1 and ϕ_2 are combined into a single angle ϕ which has the same rotational sense as ϕ_2, and which measures rotation of the proton acceptor molecule about the intermolecular line. In these dimers having H_2O as the proton donor, it is important to note that $\theta_1 = 50°$, $x_1 = 0°$ corresponds to a linear O-H · · · O bond. The intermolecular energy (hydrogen bond energy) of a dimer is computed at that point on the intermolecular potential surface at which the intermolecular coordinates have their optimized values, by subtracting the sum of the energies of the isolated proton donor and proton acceptor molecules from the total energy computed for the equilibrium dimer.

CHAPTER III

RESULTS AND CONCLUSIONS

Ab-initio SCF calculations have been performed on the dimers H_2O-HFCO and H_2O-F_2CO (in double precision on an IBM 360/50 computer) until a minimum energy structure was obtained for each dimer with respect to a $\pm$ 0.01 Å change in the intermolecular distance R, and a $\pm$ 1° change in each of the intermolecular angles. The coordinates which describe the optimized dimers and their hydrogen bond energies are provided in Table 2. The plane defined by the principal axis of the proton donor and the intermolecular line is a symmetry plane for each dimer. This plane contains both the proton donor and acceptor molecules.

In order to discuss the structural features of each hydrogen bonded dimer, the "General Hybridization Model" (GHM) for the hydrogen bond will be employed. GHM is based on the concepts that a directed lone pair of electrons on the proton acceptor molecule participates in the formation of a linear or nearly linear hydrogen bond. The name of this model emphasizes the relationship between the hybridization (arrangement of bonds and lone pairs) of the proton acceptor

TABLE 2

DIMER STRUCTURES

AND ENERGIES

DIMER	R(Å)	θ_1(°)[a]	χ_1(°)	θ_2(°)	χ_2(°)	ϕ(°)	ΔE(a.u.)[b]
H_2O-H_2CO[c]	2.88	51	0	119	0	180	-0.00530
H_2O-HFCO							
Dimer A	2.89	53	0	117	0	180	-0.00502
B	2.91	47	0	125	180	180	-0.00458
C[d]	2.95	42	0	125	180	0	-0.00386
D[d]	2.97	42	0	138	0	0	-0.00338
H_2O-F_2CO	2.94	50	0	125	0	180	-0.00418

a) $\theta_1 = 50°$ corresponds to a linear O-H· · ·O bond.

b) ΔE is the hydrogen bond energy. 1 a.u. = 627.49 kcal.

c) Data taken from Ref. 38.

d) Not an equilibrium structure with respect to ϕ.

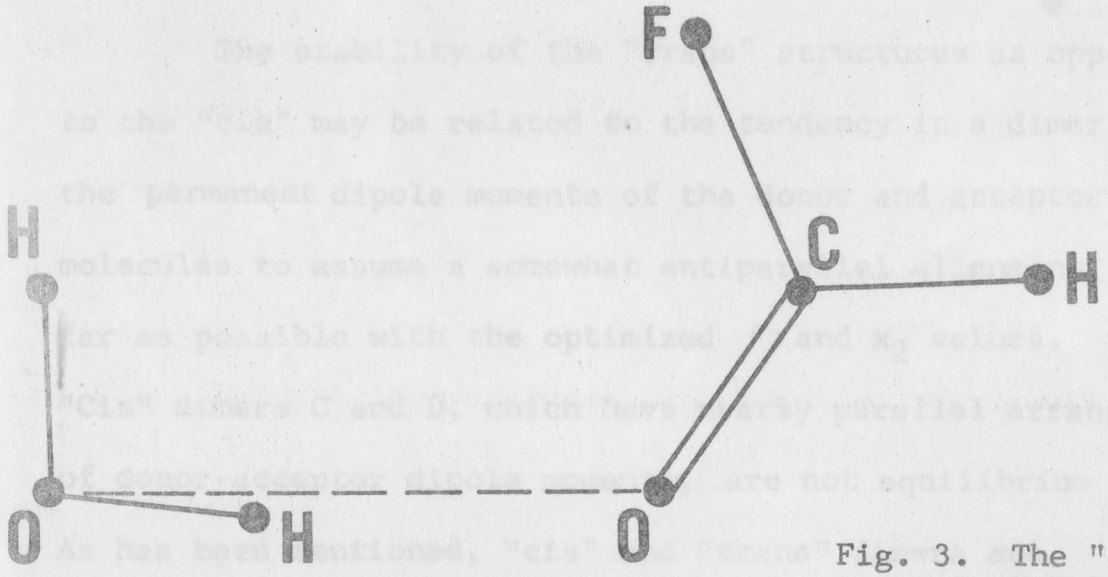
atom and the direction with respect to this atom in which the hydrogen bond forms. Based on GHM, dimer structures for H_2O-HFCO and H_2O-F_2CO would have θ_1 values near 50° and x_1 values of 0° to provide for the linear O-H· · ·O bond. From this model, directed lone pairs for hydrogen bond formation would be provided when θ_2 approaches 120°, and x_2 equals 0° or 180°. The computed structures of H_2O-HFCO and H_2O-F_2CO will now be examined in terms of GHM.

Even a cursory examination of the dimer H_2O-HFCO suggests that there are several plausible structures. Yet, if the structure of this hydrogen bonded dimer is to be consistent with the structure anticipated from GHM, only four orientations should be favorable. These structures are realized for certain combinations of x_2 and θ_2. When x_2 has values of either 0° or 180°, the lone pairs of electrons on the proton acceptor lie in the dimer symmetry plane, and with θ_2 approximately 120°, one of these pairs is directed toward the proton donor. These values of x_2 and θ_2 can be realized with two values of the ϕ coordinate which preserve the dimer symmetry plane, namely ϕ equals 0° or 180°. Dimers A and B (Figure 2) are the "trans" forms of these dimers, where trans indicates that the principal axes of the proton donor and proton acceptor

molecules are trans to each other with respect to the intermolecular line. Dimers C and D (Figure 3) in turn, are seen to have "cis" structures.

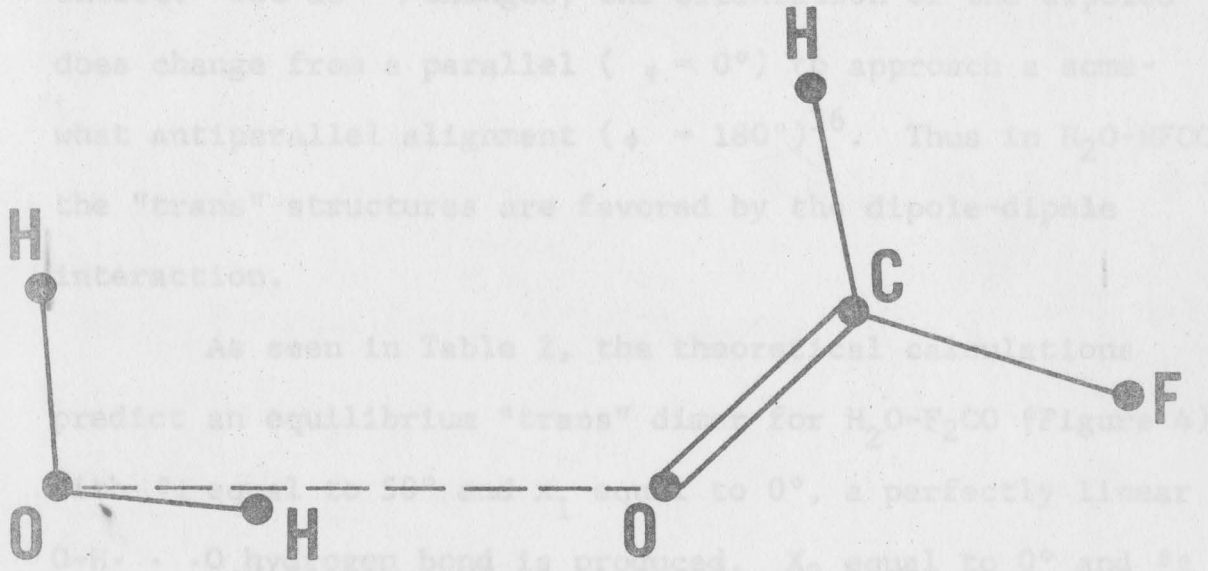
Optimization of the dimer structures produced an equilibrium dimer A, with a hydrogen bond energy of -0.00502 a.u. Dimer B was also found to be an equilibrium dimer, with a slightly weaker hydrogen bond of -0.00458 a.u. However, neither of the "cis" forms of these dimers, namely dimer C with an intermolecular energy of -0.00386 a.u. or dimer D with an energy of -0.00338 a.u., were found to be equilibrium structures on the intermolecular surface with respect to the ϕ coordinate. Upon rotation by ϕ they are converted to dimers B and A, respectively, without any energy barrier to the conversion.

A detailed examination of dimer A reveals that its structure is well described by GHM. The value of 0° for x_2 places the oxygen lone pairs of electrons in the dimer symmetry plane, and a θ_2 value of 117° directs one of these lone pairs toward the proton donor. With x_1 equal to 0° the O-H bond lies in the dimer symmetry plane, and makes a three degree angle with the intermolecular line (θ_1= 53°). Hence, the O-H· · ·O bond is nearly linear. In dimer B, x_2 is 180° and θ_2 is 125° to provide the directed lone pair. Again, a x_1 value of 0° and a θ_1 value of 47° produces a nearly linear hydrogen bond.



(c)

Fig. 3. The "cis" dimers C and D of H_2O-HFCO



(d)

The stability of the "trans" structures as opposed to the "cis" may be related to the tendency in a dimer for the permanent dipole moments of the donor and acceptor molecules to assume a somewhat antiparallel alignment, in so far as possible with the optimized θ_2 and x_2 values. "Cis" dimers C and D, which have nearly parallel arrangements of donor-acceptor dipole moments, are not equilibrium structures. As has been mentioned, "cis" and "trans" dimers are identified by their ϕ values. It has been shown that a change in the ϕ coordinates generally does not weaken the hydrogen bond to a large extent, since rotation by ϕ does not remove the directed lone pair of electrons from the intermolecular line. Hence, the hydrogen bond remains intact. Yet as ϕ changes, the orientation of the dipoles does change from a parallel ($\phi = 0°$) to approach a somewhat antiparallel alignment ($\phi = 180°$)[36]. Thus in H_2O-HFCO, the "trans" structures are favored by the dipole-dipole interaction.

As seen in Table 2, the theoretical calculations predict an equilibrium "trans" dimer for H_2O-F_2CO (Figure 4). With θ_1 equal to 50° and x_1 equal to 0°, a perfectly linear O-H· · ·O hydrogen bond is produced. X_2 equal to 0° and θ_2 equal to 125° provide for the directed lone pair. The

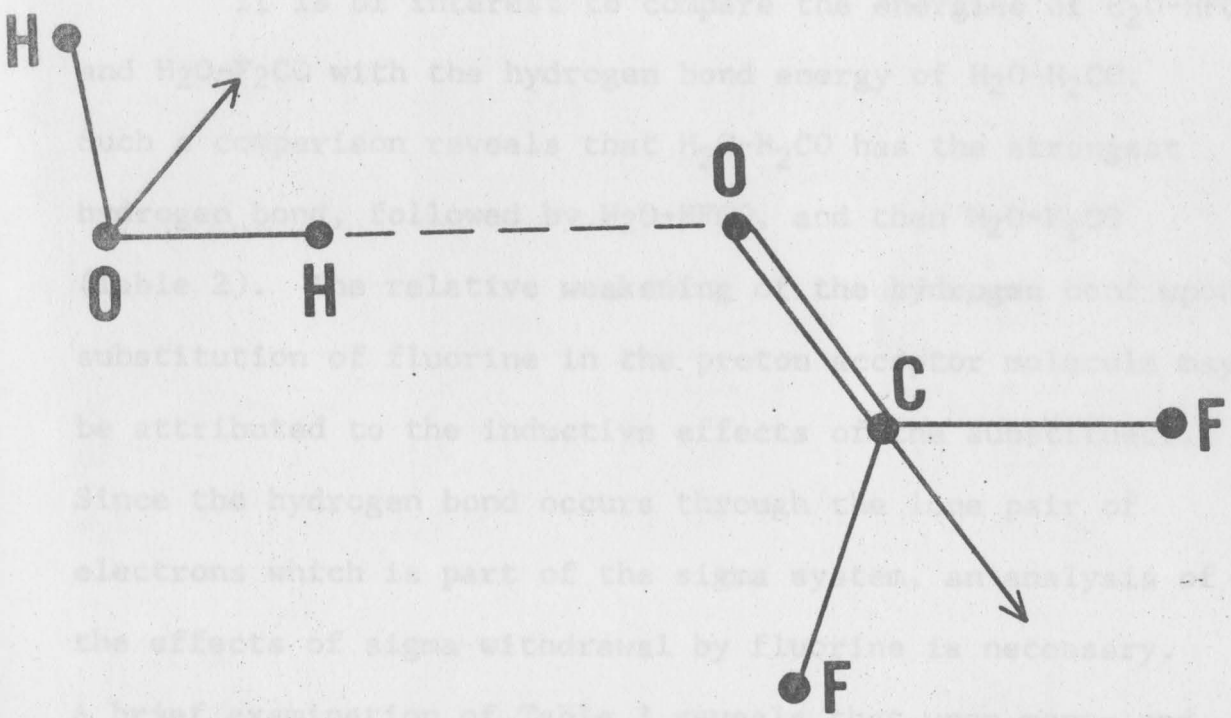


Fig. 4. The equilibrium H_2O-F_2CO dimer.

"trans" structure (ϕ = 180°) is seen once again to be favored by a more favorable dipole alignment. The "cis" conformation (ϕ = 0°) of this dimer was also investigated, but did not correspond to a potential energy minimum with respect to the ϕ coordinate. It converted to the trans dimer upon ϕ rotation by 180°.

It is of interest to compare the energies of H_2O-HFCO and H_2O-F_2CO with the hydrogen bond energy of H_2O-H_2CO. Such a comparison reveals that H_2O-H_2CO has the strongest hydrogen bond, followed by H_2O-HFCO, and then H_2O-F_2CO (Table 2). The relative weakening of the hydrogen bond upon substitution of fluorine in the proton acceptor molecule may be attributed to the inductive effects of the substituent. Since the hydrogen bond occurs through the lone pair of electrons which is part of the sigma system, an analysis of the effects of sigma withdrawal by fluorine is necessary. A brief examination of Table 3 reveals that upon mono- and then di-fluoro substitution in H_2CO, the sigma electron population on the carbonyl oxygen decreases. This reduction of sigma electron density on the carbonyl oxygen parallels the diminishing stability of the hydrogen bond in the respective dimers H_2O-H_2CO, H_2O-HFCO, and H_2O-F_2CO. As a result of sigma withdrawal, the calculated lone pair

TABLE 3

OXYGEN ELECTRON DENSITIES AND
LONE PAIR ORBITAL ENERGIES

	TOTAL	SIGMA	LONE PAIR ORBITAL ENERGY (eV)
H_2CO	8.188	7.103	-9.64
HFCO	8.217	7.042	-10.45
F_2CO	8.236	6.980	-11.18

ionization potentials increase, indicating that the oxygen lone pairs are more tightly bound to the oxygen in the order H_2CO, HFCO, F_2CO. They are therefore less available for hydrogen bond formation.

It is also interesting to note that the total charge on the oxygen (Table 3) increases in going from H_2CO to HFCO to F_2CO. In as much as the total electronic population of oxygen in H_2CO is the smallest of the three proton acceptors, one might have anticipated that H_2CO would form the weakest hydrogen bond. It is important to note that while fluorine has a sigma electron withdrawing effect, it also has a pi donating inductive effect (Table 4). There is an increase in the density of the pi orbital on oxygen which parallels the increase in the total oxygen populations in the series of proton acceptors. Hence, as fluorine withdraws electrons from the sigma system, it donates electrons to the carbonyl oxygen through the pi system. Therefore, the increase in electron density on oxygen is a result of the pi donating ability of fluorine. However, the pi electrons have no direct involvement in the formation of the hydrogen bond. No direct correlation between total or pi electron densities and hydrogen bond strengths in the series is found, or even expected.

TABLE 4

PI ORBITAL

POPULATIONS IN

MONOMERS AND DIMERS

	OXYGEN π	CARBON π	TOTAL π (C = O)
H_2CO			
Monomer	1.085	0.915	2.000
Dimer	1.115	0.885	2.000
HFCO			
Monomer	1.175	0.920	2.095
Dimer A	1.202	0.897	2.099
B	1.201	0.898	2.099
F_2CO			
Monomer	1.256	0.926	2.182
Dimer	1.279	0.909	2.188

A further comparison of the intermolecular energies of these systems shows that the hydrogen bond strength decreases by 3×10^{-4} a.u. in going from H_2O-H_2CO to H_2O-HFCO, and by 8×10^{-4} a.u. in going from H_2O-HFCO to H_2O-F_2CO. As can be seen, the weakening is more than doubled with the addition of the second fluorine.

It should be noted that variation in the intermolecular distance R is related to the strength of the hydrogen bond. Hence, H_2O-F_2CO, with the weakest hydrogen bond, has the largest intermolecular distance, while H_2O-H_2CO with the strongest hydrogen bond, has the shortest intermolecular distance. These results are quite consistent with the findings of earlier studies[35-39], which also found the parameter R to be related to the hydrogen bond strength.

The Mulliken gross atomic populations for the monomers and dimers in these systems (Table 5) indicate there is minimal charge transfer associated with hydrogen bond formation. The amount of electron transfer increases as the hydrogen bond becomes stronger, but varies only from 0.021 electrons for H_2O-F_2CO, 0.026 electrons for H_2O-HFCO (Dimer A), to 0.027 electrons for H_2O-H_2CO. Electron transfer always results in a loss of electron density by the proton acceptor. As a result of hydrogen bond formation,

TABLE 5

MULLIKEN GROSS ATOMIC

POPULATIONS

FOR MONOMERS AND DIMERS

	H	O	H*				
H_2O	0.835	8.330	0.835				
				O	C	H	H
H_2CO				8.188	5.925	0.943	0.943
H_2O-H_2CO	0.850	8.363	0.814	8.197	5.911	0.934	0.931
				O	C	H	F
HFCO				8.217	5.720	0.927	9.135
H_2O-HFCO Dimer A	0.848	8.362	0.816	8.227	5.706	0.915	9.127
B	0.849	8.359	0.816	8.227	5.706	0.918	9.125
				O	C	F	F
F_2CO				8.236	5.523	9.121	9.121
H_2O-F_2CO	0.847	8.357	0.818	8.245	5.509	9.111	9.113

*H-Bonded Proton

the electron densities of the oxygen atoms increase, and the electron densities of the carbon, fluorine, and hydrogen atoms in the proton acceptors decrease. Since the total electron density in the pi systems of the proton acceptors remains constant, electron transfer occurs through the sigma electron system. However, the pi orbital becomes more polarized toward oxygen in the dimer than it is in each respective monomer.

Some estimates of the rigidity of these hydrogen bonded systems have been obtained by calculating the second derivatives of the dimer energies with respect to the intermolecular coordinates. These derivatives are approximated by changing the intermolecular distance by 0.1 Å (Δ = $\pm$ 0.1 Å) and each of the intermolecular angles by 20° ($\Delta = \pm 20°$), and using the formula

$$\frac{\partial^2 \varepsilon}{\partial x^2} \simeq [\varepsilon(x + \Delta) + \varepsilon(x - \Delta) - 2\varepsilon(x)] / \Delta^2$$

where $\varepsilon(x + \Delta)$ is the intermolecular energy computed at that point on the potential surface at which one of the optimized corrdinates (x) is varied by the amount Δ . These derivatives are reported in Table 6. The force constants with respect to R increase in the order H_2O-H_2CO, H_2O-HFCO, and H_2O-F_2CO, paralleling the increase in the hydrogen bond

TABLE 6

VALUES OF SECOND DERIVATIVES

OF

INTERMOLECULAR ENERGIES[a]

		DIMER A	DIMER B	
$\frac{\partial^2 \varepsilon}{\partial x^2}$	H_2O-H_2CO	H_2O-HFCO	H_2O-HFCO	H_2O-F_2CO
$x = -R$	0.01330	0.01291	0.01210	0.01028
θ_1	0.02222	0.02063	0.01686	0.01527
x_1	0.01275	0.01123	0.01065	0.00929
θ_2	0.01600	0.01499	0.01129	0.00995
x_2	0.00515	0.00422	0.00333	0.00222
ϕ	0.00082	0.00108	0.00062	0.00076

a) In atomic units with angles in radians.

strength. Similarly, the force constants with respect to θ_2 and x_2 increase with increasing stability of these dimers. This is also true of derivatives taken with respect to θ_1 and x_1. Since rotation about the intermolecular axis does not remove the directed lone pair of electrons from the hydrogen bond, the derivatives with respect to ϕ are as expected, quite small.

The virtual and CI excitation energies for the lowest vertical excited states, the lone pair orbital energies, and the hydrogen bond energies in the dimers H_2O-H_2CO, H_2O-HFCO, and H_2O-F_2CO are given in Table 7. For each dimer, the calculated CI transition energy for the lowest singlet state is larger than the $n \rightarrow \pi^*$ transition energy for the respective proton acceptor molecule. Hence, the "blue shift" of the $n \rightarrow \pi^*$ band associated with hydrogen bond formation is reproduced by theory. It is quite obvious from Table 7 that a correlation exists between the hydrogen bond strength in the dimer and the magnitude of the blue shift. If the vertical excitation energy in H_2CO, HFCO, and F_2CO is added to the hydrogen bond energy in the corresponding dimer, the vertical excitation energy in the dimer may be approximated to within 0.02 eV. Consequently, these results suggest that the increment in the $n \rightarrow \pi^*$

TABLE 7

VIRTUAL, CI, AND LONE PAIR
ORBITAL ENERGIES OF IMPORTANCE
IN THE LOWEST SINGLET
EXCITED STATES OF DIMERS
H_2O-H_2CO, H_2O-HFCO, H_2O-F_2CO

	LONE PAIR (eV)	EXCITATION ENERGY VIRTUAL (eV)	CI (eV)	HYDROGEN BOND ENERGY (eV)
H_2CO	-9.64	4.56	4.21	———
H_2O-H_2CO	-10.01	5.21	4.35	0.14
HFCO	-10.45	5.57	5.23	———
H_2O-HFCO A	-10.71	6.74	5.36	0.14
B	-10.69	7.01	5.36	0.13
F_2CO	-11.18	6.27	6.03	———
H_2O-F_2CO	-11.26	9.00	6.16	0.11

transition energy on dimer formation is essentially contingent on the additional energy necessary to break the hydrogen bond on excitation to the $n \rightarrow \pi^*$ state in the dimer. This phenomenon has been observed previously in the series of dimers ROH-H_2CO[37]. However, this work represents the first case in which the calculation has been extended to a substituted proton acceptor molecule. Considering the differences between the amount of configuration interaction in the lowest excited states of monomers and dimers, it is significant that these results quantitatively reproduce the blue shift. This implies that theoretical studies of the blue shift in even larger systems may be approached with a certain degree of confidence.

It is also important to note that although the energy of the n orbital in the dimer is lower than it is in the respective monomer, and the single configuration excitation energy in the dimer is greater than in the monomer, there is no quantitative relationship between the stabilization of the n orbital or the single configuration excitation energy and the CI excitation energies. Obviously, no correlation between orbital energies or virtual excitation energies and hydrogen bond strengths can occur either. This again indicates that such one-electron properties are

inadequate in terms of quantitive descriptions of molecular excited states.

Electron excitation associated with the formation of an excited state produces a rearrangement of all electrons in the system. In order to understand the electronic changes which occur, it is first necessary to discern the shifts of population upon excitation to the monomer $n \rightarrow \pi^*$ states, and then contrast these densities with those found in the dimers. Moreover, it is also of interest to make a comparison of the ground and excited state electron densities in the proton donor molecule to determine to what extent electron population rearrangement occurs when an excited state associated with the proton acceptor molecule is formed.

A comparison of Tables 5 and 8 reveals that upon excitation in the monomer there is a substantial change in the electron density of the carbonyl group. The oxygen, which is negatively charged in the ground state, becomes positively charged in the excited state. Conversely, the carbon atom, which bears a small positive charge in the ground state, acquires a relatively large negative charge upon excitation. The hydrogens in H_2CO and HFCO also become more positively charged in the excited state than in the ground state. The fluorines in HFCO and F_2CO also lose

TABLE 8

MULLIKEN GROSS ATOMIC POPULATIONS FOR MONOMERS AND DIMERS IN EXCITED STATES

	H	O	H*	O	C	H	H
H_2CO				7.795	6.460	0.872	0.872
H_2O-H_2CO	0.850	8.351	0.813	7.811	6.458	0.860	0.857
				O	C	H	F
HFCO				7.775	6.256	0.860	9.109
H_2O-HFCO							
Dimer A	0.848	8.350	0.815	7.787	6.253	0.846	9.101
B	0.849	8.347	0.816	7.788	6.252	0.849	9.099
				O	C	F	F
F_2CO				7.739	6.054	9.104	9.104
H_2O-F_2CO	0.847	8.346	0.818	7.750	6.049	9.094	9.096

*H-Bonded proton

electron density. It has already been shown that the stability of the hydrogen bond between a proton and a lone pair of electrons is related to the negative charge on the proton acceptor atom[36-37]. Consequently, it would seem unlikely that a hydrogen bond would exist through the sigma system in any of the excited dimers H_2O-H_2CO, H_2O-HFCO, H_2O-F_2CO, due to the positive charge on oxygen. This observation is consistent with the calculated dimer excitation energies which also imply that the bond formed in the ground state is essentially broken in the vertical excited $n \rightarrow \pi^*$ states of the dimers.

Table 8 also lists the gross atomic populations for the excited states of the dimers. The electron distributions in H_2CO, HFCO, and F_2CO in the dimer excited states are similar to those found in the monomers. However, it should be noted that the carbonyl oxygen is slightly less positively charged in the dimer excited states than in the monomer. The hydrogens and fluorines attached to the carbonyl group experience a decrease in excited state electron density in the dimers. In the proton donor, it is interesting to note that there is essentially no change in charge on the hydrogens in the excited states, yet the oxygen on the proton donor molecule becomes more positively charged. This loss results

from electron transfer from H_2O to the proton acceptors. It was noted earlier that on formation of a hydrogen bond, the pi orbital of the carbonyl becomes more polarized toward oxygen in order to compensate for electron transfer from the oxygen of the carbonyl through the sigma system. In the excited state of each dimer, electron transfer also occurs in the sigma framework, but only in the reverse direction.

Conclusions

From the ab-initio calculations that have been performed on the dimers H_2O-HFCO and H_2O-F_2CO, the following conclusions may be drawn.

1. The structures of these dimers can be described by the general hybridization model for the hydrogen bond, in which a linear or nearly linear bond is formed between a proton and a directed lone pair of electrons.

2. Since the hydrogen bond is primarily an electrostatic interaction, the strength of this bond appears to be directly related to the sigma electron density on the carbonyl oxygen.

3. Even though the principal interaction which stabilizes the hydrogen bond is electrostatic, the dipole-dipole term is also quite important. These dimers have trans structures which allow the permanent dipole moments of the proton donor and acceptor molecule to approach a somewhat antiparallel alignment in so far as possible within the orientational requirement for the directed lone pair.

4. The small amount of electron transfer from acceptor to donor molecule upon dimer formation occurs through the sigma system, and is accompanied by a further polarization of the pi orbital toward the carbonyl oxygen. Hence, although the proton acceptor loses electron density, the carbonyl oxygen acquires a larger negative charge in the dimer than in the monomer.

5. The vertical $n \rightarrow \pi^*$ excitation energies are greater in these dimers than in the respective proton acceptor molecules. Hence, the experimentally observed blue shift of the $n \rightarrow \pi^*$ band upon hydrogen bond formation is reproduced by the theory. The calculations also show that the magnitude of the blue shift is essentially determined by the hydrogen bond strength.

REFERENCES

[1]G. C. Pimentel and A. D. McClellan, The Hydrogen Bond, W. A. Freeman & Co., San Francisco, (1960).

[2]C. A. Coulson, Research (London) 10, 149 (1957).

[3]G. Briezleb, Z. Physik. Chem. (Leipzig) B51, 9 (1941).

[4]J. S. Rowlinson, Trans. Faraday Soc. 47, 120 (1951).

[5]J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. A205, 115 (1951).

[6]W. G. Schneider, J. Chem. Phys. 23, 26 (1955).

[7]P. A. Kollman, J. Amer. Chem. Soc. 94, 1839 (1972).

[8]A. Ocvirk, A. Azman, D. Hadzi, Theoret. Chim. Acta. (Berl.) 10, 187 (1968).

[9]A. Pullman, H. Berthod, Theoret. Chim. Acta. (Berl.) 10, 461 (1968).

[10]A. S. N. Murthy, C. N. R. Rao, Chem. Phys. Letters 2, 123 (1968).

[11]P. Schuster, Th. Funck, Chem. Phys. Letters 2, 587 (1968).

[12]A. S. N. Murthy, R. E. Davis, C. N. R. Rao, Theoret. Chim. Acta. (Berl.) 13, 81 (1969).

[13]L. Pederson, Chem. Phys. Letters 4, 280 (1969).

[14]P. A. Kollman, L. C. Allen, J. Amer. Chem. Soc. 92, 753 (1973).

[15]A. Azman, J. Koller, D. Hadzi, Chem. Phys. Letters 5, 159 (1970).

[16]E. Clementi, J. Chem. Phys. 34, 1468 (1961).

[17]_____, A. D. McClean, J. Chem. Phys. 36, 745 (1962).

[18]E. Clementi, J. Chem. Phys. 46, 3851 (1967); 47, 2323, 3837 (1967).

[19]K. Morokuma, L. Pederson, J. Chem. Phys. 48, 3275 (1968).

[20]P. A. Kollman, L. C. Allen, J. Chem. Phys. 51, 3285 (1969).

[21]K. Morokuma, J. R. Winick, J. Chem. Phys. 52, 1301 (1970).

[22]D. Hankins, J. W. Moskowitz, F. H. Stillinger, J. Chem. Phys. 53, 4544 (1970).

[23]J. E. Del Bene, J. A. Pople, J. Chem. Phys. 52, 4858 (1970).

[24]P. A. Kollman, L. C. Allen, J. Chem. Phys. 52, 5085 (1970).

[25]_____, J. Amer. Chem. Soc. 93, 4991 (1971).

[26]G. H. F. Diercksen, Theoret. Chim. Acta. (Berl.) 21, 335 (1971).

[27]_____, W. P. Kraemer, Chem. Phys. Letters 6, 419 (1970).

[28]J. E. Del Bene, J. A. Pople, J. Chem. Phys. 55, 2296 (1971).

[29]Lucjan Piela, Chem. Phys. Letters 15, 199 (1972).

[30]A. Johansson, P. Kollman, S. Rothenberg, Theoret. Chim. Acta. 26, 97 (1972).

[31]J. E. Del Bene, F. T. Marchese, J. Chem. Phys. 58, 926 (1973).

[32]A. Johansson, P. Kollman, S. Rothenberg, Chem. Phys. Letters 16, 123 (1972).

[33]K. Morokuma, J. Chem. Phys. 55, 1236 (1971).

[34]J. E. Del Bene, J. Chem. Phys. 55, 4633 (1971).

[35]_____, J. Chem. Phys. 56, 4923 (1972).

[36]_____, J. Chem. Phys. 57, 1899 (1972).

[37]_____, J. Amer. Chem. Soc. paper VII (in press).

[38]J. E. Del Bene, J. Chem. Phys. 58, 3139 (1973).

[39]_____, J. Amer. Chem. Soc. paper VI (in press).

[40]C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[41]W. J. Hehre, R. F. Stewart, J. A. Pople, J. Chem. Phys. 51, 2657 (1969).

[42]J. E. Del Bene, R. Ditchfield, J. A. Pople, J. Chem. Phys. 55, 2236 (1971).

[43]M. D. Newton, W. A. Lathan, W. J. Hehre, J. A. Pople, J. Chem. Phys. 52, 4064 (1970).