J. Phys. Chem. A **2001,** *105,* 1163−1168

Long Range π-Type Hydrogen Bond in the Dimers $(HF)_2$, $(H_2O)_2$, and H_2O-HF

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Received: August 11, 2000; In Final Form: November 8, 2000

Based on ab initio calculations at MP2 and MP4 levels, a chemically intuitive π-type hydrogen-bond model is proposed to illustrate and interpret the small deviations from a strictly linear hydrogen bond X···H−Y in the dimers $(HF)_2$, $(H_2O)_2$, and H_2O-HF. The computational results show that π-type hydrogen-bond interaction is secondary and is an attraction between the H atom of the H−X bond and lone pair on Y. In particular, the orientations of lone pairs are detected, by the energy scan at the MP2/6-311+G (2df, 2p) level with a probing point charge of $q = -1$, which is important to show the existence of the π-type hydrogen bond. Furthermore, the interaction energy of π-type hydrogen bond, D_π, and stabilized energy of bent hydrogen bond, ΔE_{sb}, are also calculated and discussed.

I. Introduction

In recent years, many studies have contributed to the conceptual understanding of hydrogen bonding.[1−4] According to the concept of the donor−acceptor interaction, hydrogen bonds may exist as several forms, such as the neutral hydrogen bond between two neutral molecules, the ionic hydrogen bond between an ion and a molecule, and the π hydrogen bond between π electron donor and its acceptor (H−X bond).[2] For the neutral version, some hydrogen-bonding forms exist in the transition structures involved in interchange of hydrogen atoms within dimers, for example, the cyclic in $(HF)_2$ and $(H_2O)_2$, the bifurcated and the multiple in $(H_2O)_2$.[3,4] Those hydrogen bonds given by refs 1−4 are all first-order hydrogen bonds, and may not be used to explain the bends of hydrogen bond X···H−Y of the dimers. The question of the linearity or otherwise of hydrogen bonds is of interest in many areas of chemistry and biology, not least in connection with secondary structure in proteins and peptides. For a long time, the bend of hydrogen bond X···H−Y[18,19] has been paid much attention. Buckingham and Fowler predicted a number of the structures of hydrogen-bonded dimers by a simple model based on electrostatic interaction between the monomers,[5,6] and Klemperer's group has given a comment on this simple model.[7] According to experimental results of rotational spectroscopy, Legon discussed a nonlinearity of hydrogen bonds in terms of a secondary interaction in a series of hydrogen-bonded dimers.[8] The secondary interaction involving X is with the nearest H atoms carried by B in complex B···H−X. We establish here a long-range π-type hydrogen-bond model to embody the secondary interaction and to explain the nonlinearity of hydrogen bonds, which is based on a series of ab initio calculations.

In this paper, by using a probing point charge to detect the orientations of the lone pairs at the equilibrium structures of the dimers, we have discovered a long-range hydrogen-bond interaction (active at a distance beyond the normal hydrogen bond) of one and two pairs between a X−H and a lone pair on Y atom, *n*(Y). Because the X−H and the *n*(Y) are almost parallel, which is similar to two p-orbitals in a π bond of some molecules, the long-range hydrogen bond is named as π-type hydrogen bond. It accompanies the linear hydrogen bond X···H−Y (σ- type hydrogen bond) and leads to a bend of the primary hydrogen bond X···H−Y, which is stabilized in energy. It is a secondary hydrogen-bond interaction between the monomers in the dimers.

II. Computational Methods

Using the MP2/6-311+G (2df, 2p) method, the optimized equilibrium structures for the title dimers are obtained. Each also exhibits a bent hydrogen bond X···H−Y involving a small deviation from linearity. To obtain the stabilized energy of the bent hydrogen bond(s) at an optimized equilibrium geometry, the interaction energy of each dimer is calculated for the linear ($\angle X\cdots H-Y = 180°$) and for the bent (equilibrium structure with $\angle X\cdots H-Y = b$). Energy computations are performed using the basis set 6-311+G(2df,2p), and the full counterpoise (CP) procedure is used to correct the basis set superposition errors (BSSE),[9,10] and the bond functions (BF) {3s3p2d}[11] (the center is located at the middle point of X···H) are used to enlarge the efficiency of the basis set 6-311+G(2df, 2p) at the MP4 level.

The orientations of unbounded lone pairs (except primary hydrogen-bounded lone pairs) in optimized equilibrium structures is important for understanding the formation of π-type hydrogen bond. Using the probing point charge ($q = -1$), we scan the energies of the dimers in different planes and angles by the MP2/6-311+G (2df, 2p) method to find the extreme values and determine the orientations of the lone pairs. In the scans, the distance from the nucleus Y(or X) to the point charge is 0.9 Å (with this distance, we obtained 109.5° angle between two lone pairs of O^{2-}). In addition, the changes in interaction energy accompanying internal rotation are calculated by the MP4/6-311+G (2df, 2p) method with CP for estimating the interaction energies of π-type hydrogen bond.

III. Results and Discussion

The optimized geometry from the calculations at the MP2/6-311+G (2df, 2p) level for each dimer is shown by Figure 1,

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10.1021/jp0029313 CCC: \$20.00

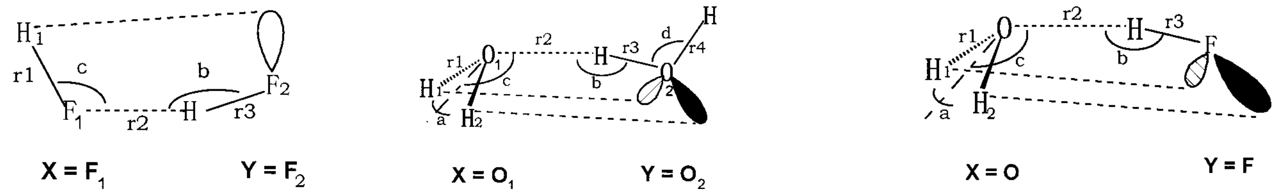
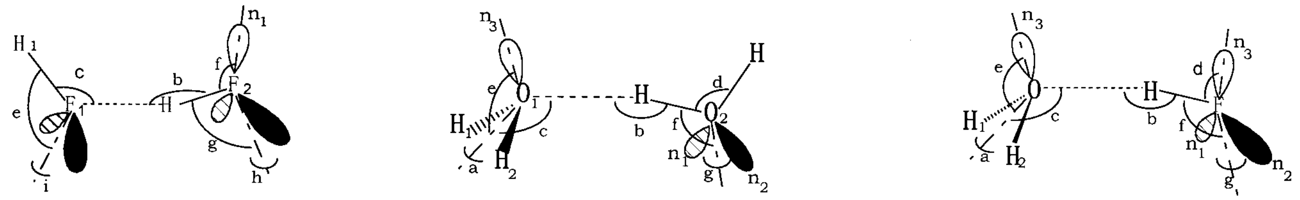


Figure 1. Equilibrium structures with π-type hydrogen bond for dimers.

TABLE 1: Optimized Parameters for Equilibrium Structures from MP2/6-311+G(2df,2p)[a]

dimer	*r*1	*r*2	*r*3	*r*4	A	b	c	d	Δ*b*	reference
$(HF)_2$	0.919	1.870	0.921			171.3	124.5		8.7	[12]
	0.919	1.850	0.921			171.0	120.1		9.0	[9, 10]
	0.921	1.840	0.923			173.1	116.2		6.9	this work
									7.0	[32, 33, 34]
									7.0	expt [35]
						169.4			10.6	expt [14, 15]
$(H_2O)_2$	0.964	1.941	0.969	0.962	105.7	175.6	135.6	105.6	4.4	[3]
	0.960	1.952	0.965	0.958	104.8	173.0	126.4	104.6	7.0	this work
H_2O-HF	0.959	1.729	0.934		105.2	177.9	130.5		2.1	[16]
	0.960	1.732	0.934		105.2	177.9	131.7		2.1	this work

[a] Distances in Å, angles in deg.



b	173.08°
c	116.16°
e	115.0°
f	116.0°
g	140.0°
i	120.0°
h	120.0°

a	104.78°
b	173.02°
c	126.4°
d	104.59°
e	133.0°
f	130.0°
g	108.0°

a	105.24°
b	177.95°
c	131.67°
d	116.0°
e	130.0°
f	116.0°
g	120.0°

Figure 2. Orientations of lone pairs in equilibrium structures.

and the geometrical parameters are shown by Table 1. Our calculated results are in agreement with others' theoretical calculations and experiments.[3,9,10,12,14–16,32–35]

The Bend of Hydrogen Bond X···H−Y. Now we focus on a small bend of the hydrogen bond in the dimers. From Table 1 we can easily see that the bend of F···H−F in $(HF)_2$, which is characterized by $\Delta b = 180°$, is $\Delta b = 6.9°$ in this work, $\Delta b = 7°$, 8.7°, 9.0° in other works, and $\Delta b = 7°$, 10.6° from experiment.[14,15,35] For $(H_2O)_2$, our result $\Delta b = 7.0°$ is larger than $\Delta b = 4.4°$[3] and the bend of O···H−F in H_2O-HF, $\Delta b = 2.1°$ is the same as that from ref 16. By examining the equilibrium structures and considering lone pair directions in the dimers, it is found in Figure 1 that there is a long range (the distance is more than a sum of r_2 and r_3 instead of r_2) hydrogen bonding. This hydrogen bond is an interaction between the X−H bond(s) of one monomer and the lone pair(s) on the Y atom in the other monomer. We refer to it as π-type hydrogen bond in this paper, because the X−H and the n(Y) are almost parallel and in a plane. It is a chemically intuitive model of the secondary interaction as Legon's explanation of his experimental results.[8] In B···H−X, the secondary interaction involving X is with the nearest H atom carried by B. The primary hydrogen bond is bent in the equilibrium structure, which results from an attraction of the π-type hydrogen bond in the dimers. We can image that if the attraction between X−H(s) and the lone pair(s) on Y is non existent, all of the equilibrium conformers of the dimmers will be staggered. In fact, the results from Figure 2 show that the conformers are eclipsed. It is noted that an X−H bond and a lone pair n(Y) are nearly parallel and almost in the same plane. And the bend of hydrogen bonds and the attractions between the X−H(s) and the lone pair(s) are the same orientations. It shows a existence of π-type hydrogen bond(s) in each dimer.

Long-Range π-Type Hydrogen Bond. The orientations of some lone pairs play an important role in the forming the long range π-type hydrogen bond. Through a large number of energy scan calculations in different planes and angles using the probing point charge, the orientations of the lone pairs are detected at the equilibrium structures of the dimers, as shown by Figure 2.

From Figure 2, we can see that in $(HF)_2$, the F_1-H_1 bond and lone pair $n_1(F_2)$ are in the same plane. If we take $\angle c = \angle f = 90°$ as parallel direction, the deviation is about 40°(i.e., $\angle c = 116.2°$, $\angle f = 116°$). The bend of the primary hydrogen bond is $\Delta b = 7°$ and comes from the attraction (a single π-type hydrogen bond) between F_1-H_1 and the lone pair $n_1(F_2)$. For $(H_2O)_2$, $\angle a = 104.8°$ and $\angle g = 108.0°$ are almost the same, as O_1-H_1 and $n_1(O_2)$ almost are parallel and in a plane, while O_1-H_2 and $n_2(O_2)$ are almost parallel and in a plane. The bend $\Delta b = 7°$ shows the forming of a double π-type hydrogen bond. In H_2O-HF, the $O-H_1$ bond corresponds to the lone pair on

TABLE 2: Total Energies and Interaction Energies for Two Structures[a]

dimer		E (E_h) SCF	E (E_h) MP2	E (E_h) MP4	D_e (CP) (mE_h) HF	D_e (CP) (mE_h) MP2	D_e (CP) (mE_h) MP4
$(HF)_2$	bent[b]	−200.1205755	−200.6660856	−200.6865447	−6.064	−6.8262	−6.8533
		(−200.117559)	(−200.6567887)	(−200.6765475)	(−5.9227)	(−6.267)	(−6.1759)
	linear	−200.1204248	−200.6659828	−200.6864416	−5.9004	−6.7104	−6.7407
		(−200.1173871)	(−200.65669)	(−200.6764547)	(−5.7433)	(−6.1371)	(−6.0504)
$(H_2O)_2$	bent [c]	−152.1215058	−152.6461924	−152.6753531	−5.8432	−7.6762	−7.6598
		(−152.119556)	(−152.6382159)	(−152.6669922)	(−5.7835)	(−7.2344)	(−7.1241)
	linear	−152.1214183	−152.6461269	−152.6752974	−5.7654	−7.5790	−7.5678
		(−152.1194886)	(−152.6381422)	(−152.6669247)	(−5.7072)	(−7.1381)	(−7.0222)
$H_2O{-}HF$	bent[d]	−176.1265519	−176.6627438	−176.6873353	−12.2352	−13.554	−13.4359
		(−176.1239307)	(−176.6537392)	(−176.6778806)	(−11.8682)	(−12.7276)	(−12.474)
	linear	−176.1265175	−176.6627294	−176.6873204	−12.2005	−13.5353	−13.4165
		(−176.1238928)	(−176.6537203)	(−176.6778619)	(−11.8323)	(−12.7072)	(−12.4537)

[a] The values with the 6-311+G(2d,2p) basis set and bond function [sp(0.9,0.3,0.1),d(0.6,0.2)], the values in bracket come from using 6-311+G(2df,2p) without BF. [b] −7.0166 mE_h [22], 7.203 mE_h[25] − 7.3927mE_h[26], −8.750mE_h[27], and experimental De = −6.9529 mE_h [28]. [c] −7.52179 mE_h from MP2/aug-cc-pvtz but the best estimate of D_e is −7.9680 mE_h from model potential. [29], −7.606 mE_h estimated at full-CI level [30]. [d] −12.55 mE_h from MP2/6-311++g(2df,2p) but −13.07 mE_h is experiment value [31]. (1 E_h = 1 a.u. = 27.2107 eV= 6.275×10^2 kcal/mol.)

atom F, $n_1(F)$, and the $O{-}H_2$ correspondes to $n_2(F)$, each pair is almost parallel and approximately in a plane, and the bend, $\Delta b = 2°$ is produced by the attraction of a double π-type hydrogen bond. Because the difference between $\angle a$ and $\angle g$ in $H_2O{-}HF$ ($\angle a = \angle HOH = 105.2°$, $\angle g = \angle n_1Fn_2 = 120°$) is bigger than that in $(H_2O)_2$, the double π-type hydrogen bond is weaker than that in the dimer $(H_2O)_2$ (see stabilized energy of the bent hydrogen bond $X{\cdots}H{-}Y$).

The magnitude of the bending of the hydrogen bond $X{\cdots}H{-}Y$, described by Δb, reflects the strength of the π-type hydrogen bond. When $\angle c$ reduces and the length of bond $X{\cdots}H$ increases, Δb increases.

From the discussion mentioned above, we know that the π-type hydrogen bond is related to $\angle c$ and the length of bond $X{\cdots}H$, r_2, as shown by Figure 1. We can define the conditions for forming π-type hydrogen bonds in a dimer as follows:

1. No less than one π-type interaction of an $X{-}H$ and a lone pair on Y, $n(Y)$, exist in a hydrogen-bonded dimer.

2. The $X{-}H$ bond and the lone pair on Y should be almost parallel and in the same plane.

The three dimers mentioned above satisfy the conditions, and there are π-type hydrogen bonds in the three dimers.

We note the relationship between bent hydrogen bond $X{\cdots}H{-}Y$ and π-type hydrogen bond. It is as follows:

1. When there are no π-type hydrogen bonds, the hydrogen bond is not bent, for example, and FHF^- and so on. In HF_2^-, on the $F{\cdots}H{-}F$, only lone pairs on atom Y exist but a bond $X{-}H$ corresponding to a $n(Y)$ does not exist, so that no π-type hydrogen bond is formed and then the hydrogen bond $F{\cdots}H{-}F$ is not bent. Our result is that the angle $\angle F{\cdots}H{-}F$ is 180.0° and two H−F bond lengths are 1.141 Å from the MP4/6-311+G (2df, 2p) calculation. It is in agreement with the results given by ref 18.

2. The existence of single or double π-type hydrogen bonds makes the hydrogen bond $X{\cdots}H{-}Y$ bent. In addition to the above three dimers, for the hydrogen bond $Cl{\cdots}H{-}Cl$ of $(HCl)_2$ with single π-type hydrogen bond and hydrogen bond $O{\cdots}H{-}F$ of $H_2O{-}CH_2F_2$ with double π-type hydrogen bond (between two lone pairs on atom O and two H−C combined with atom F, very strong), the hydrogen bonds are bent by12°[23]and 45°,[24] respectively.

3. The equivalent triple π-type hydrogen bond does not make the hydrogen bond $X{\cdots}H{-}Y$ bent because of the dynamic balance coming from the symmetry. For example, for $NH_3{-}HF$ with a equivalent triple π-type hydrogen bond, the hydrogen bond $X{\cdots}H{-}Y$ is on a straight line. This is agreement with the result of the experiments.[1]

TABLE 3: Stabilized Energy of Bending Hydrogen Bond Comes from π-Type Hydrogen Bond[a]

dimer	ΔE_{sb} (mE_h) SCF	ΔE_{sb} (mE_h) MP2	ΔE_{sb} (mE_h) MP4
$(HF)_2$	−0.164 (−0.179)	−0.116 (−0.130)	−0.113 (−0.125)
$(H_2O)_2$	−0.078 (−0.077)	−0.097 (−0.096)	−0.092 (−0.102)
$H_2O{-}HF$	−0.035 (−0.036)	−0.019 (−0.021)	−0.019 (−0.020)

[a] The values in brackets are with 6-311+G(2df,2p), without BF.

We can conclude that the π-type hydrogen bond causes the bend of the hydrogen bond $X{\cdots}H{-}Y$ in the dimers. The existence of a single or double π-type hydrogen bond is a criterion for the bend of hydrogen bond $X{\cdots}H{-}Y$.

Stabilized Energy of Bending Hydrogen Bond $X{\cdots}H{-}Y$. Total energies and interaction energies of the bent (equilibrium) and linear structures are shown in Table 2. For the three systems $(HF)_2$, $(H_2O)_2$, and $H_2O{-}HF$, many satisfactory calculations have been made[22,25−31] that consider the interaction energies for equilibrium structures.

Table 2 shows that the values of total energy E reduces with the increasing of the level of computational method. The calculated values of E with BF are lower than that without BF. For the bent and linear structures of each dimer, mentioned above, the E value for the bent structure is the lower, because a double π-type hydrogen bond is formed for $(H_2O)_2$ and for $H_2O{-}HF$ while a single π-type hydrogen bond is formed for $(HF)_2$. The higher value of E comes from the linear structure, because of the absence of the attraction of the π-type hydrogen bond. It may be assumed that without the effect of the π-type hydrogen bond, the linear structure would be an equilibrium structure.

From Table 2, we can also see that the bent structures have the lower interaction energy D_e at each level (SCF, MP2, and MP4). They are −6.1759 mE_h for $(HF)_2$, −7.1241 mE_h for $(H_2O)_2$, and −12.474 mE_h for $H_2O{-}HF$ at MP4 level without BF, using the counterpoise procedure. With the addition of BF in the basis set and by using counterpoise procedure, the MP4 values are lowered greatly. They are −6.8533 mE_h for $(HF)_2$, −7.6598 mE_h for $(H_2O)_2$, and −13.4359 mE_h for $H_2O{-}HF$, which are in agreement with the known results.[25−31]

To show the part of the interaction energy contributed by the π-type hydrogen bond in a dimer, we define the stabilized

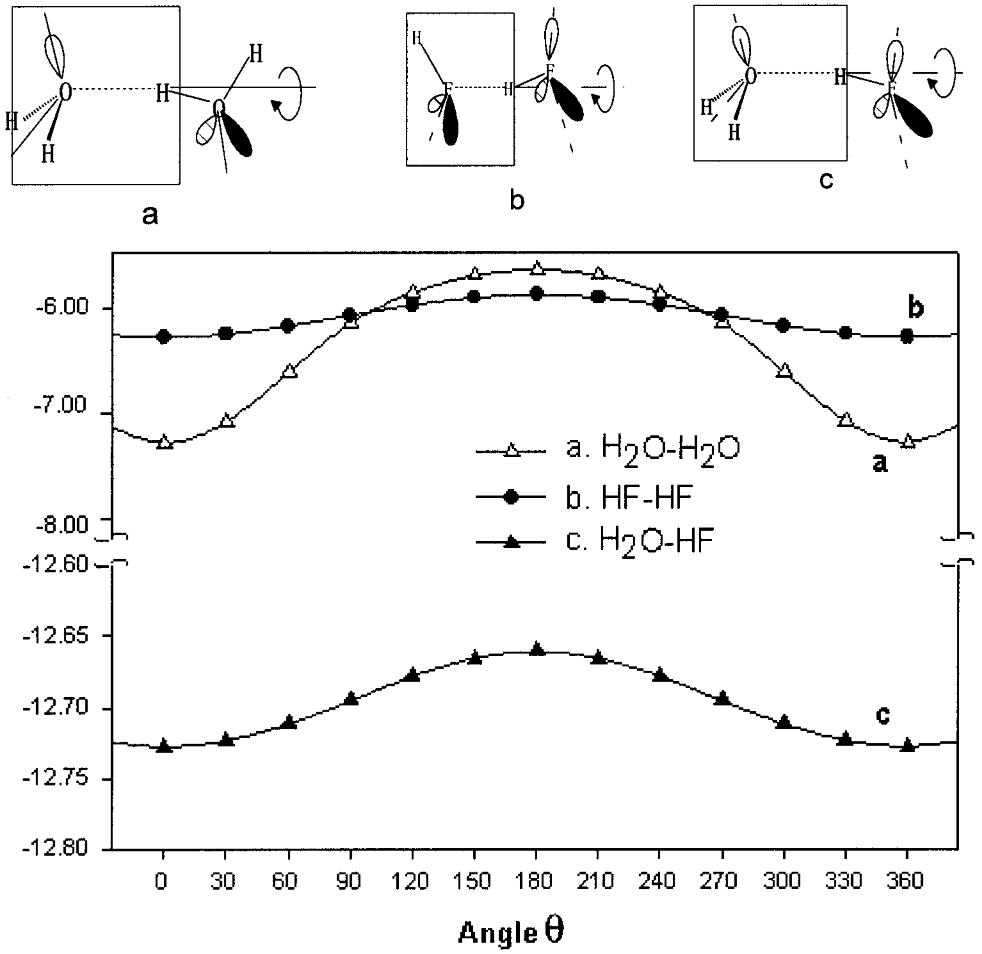


Figure 3. Curves of internal rotations.

energy of bent hydrogen bond X···H−Y, ΔE_{sb}, as

$$\Delta E_{sb} = \Delta E_b - \Delta E_1 = D_\pi + R_b \tag{1}$$

where, ΔE_b and ΔE_1 are interaction energies of a dimer for the bent (equilibrium) and the linear structure, respectively, D_π is the interaction energy produced by π-type hydrogen bond, and R_b the repulsion energy produced by bent hydrogen bond X···H−Y as the effect of π-type hydrogen bond at the equilibrium structure. The values of ΔE_{sb} are listed in Table 3. The contribution of BF for the stabilized energy at the SCF and MP4 level changes with the difference of the dimer. About −0.01 mE$_h$ comes from the contribution of BF for $(HF)_2$. But for $(H_2O)_2$ and H_2O−HF, the contribution of BF is very small. The ΔE_{sb} at the MP4 level using BF are −0.113 mE$_h$ for $(HF)_2$, −0.092 mE$_h$ for $(H_2O)_2$, and −0.019 mE$_h$ for H_2O−HF. Although $(HF)_2$ has only single π-type hydrogen bond, the R_b value of $(HF)_2$ is smaller than one-fifth of that of $(H_2O)_2$, and the ΔE_{sb} value for $(HF)_2$ is the lowest. In $(H_2O)_2$ and H_2O−HF, double π-type hydrogen bonds are formed. Despite the R_b for H_2O−HF being the smallest, the double π-type hydrogen bond is very weak, and the stabilized energy of H_2O−HF is still smaller than that of $(H_2O)_2$. It is noted that the values of R_b used above, are the approximate values, R'_b, defined by eq 4. To obtain the exact value of R_b is very difficult. The approximate repulsion energies of bent hydrogen bond, R'_b values, are 0.043 mE$_h$ for H_2O−HF, 0.2371 mE$_h$ for $(HF)_2$, and 1.232 mE$_h$ for $(H_2O)_2$. These values depend on the angle of the bent hydrogen bond and the size of the dimer.

Interaction Energy D_p of π-Type Hydrogen Bond. We calculated the change in the interaction energy with internal rotation about the primary hydrogen bond X···H and show that the minima correspond to positions consistent with the π-type hydrogen-bond interaction. It is noted that each equilibrium structure with π-type hydrogen bond is just a conformer in the broad sense but is different from the conformer between C−H σ-bond pair in different methyl groups for C_2H_6 molecule. The conformer of a dimer is formed between σ-bond X−H and lone pair n(Y) or between lone pairs in different monomers. This is shown as Figure 2. It is interesting that the conformer is eclipsed in each hydrogen-bonded dimer owing top-type hydrogen-bond interaction but it is staggered for CH_3−CH_3. In the eclipsed form of $(HF)_2$, X−H$_1$ corresponds to n_1(Y), and n_2(X), n_3(X) correspond to n_2(Y), n_3(Y), respectively. For $(H_2O)_2$, X−H$_i$ corresponds to n_i(Y) (i = 1,2) and Y−H$_3$ corresponds to n_3(X). For H_2O−HF, X−H$_i$ corresponds to n_i(Y) (i = 1,2) and n_3(X) corresponds to n_3(Y). We pay attention to the expression between the interaction energy of a dimer and rotation angle about hydrogen bond

$$V(\theta) = D_\pi(\theta) + R_b(\theta) + \Delta E_1 \tag{2}$$

where the $D_\pi(\theta)$ and $R_b(\theta)$ are functions of the rotation angle θ and the ΔE_1 is the interaction energy of the hydrogen bond of the linear structure.

The interaction energy at zero degree (θ = 0°) is

$$V(0) = D_\pi + R_b + \Delta E_1 = \Delta E_b \tag{3}$$

where $R_b(0)$ and $D_\pi(0) = D_\pi$.

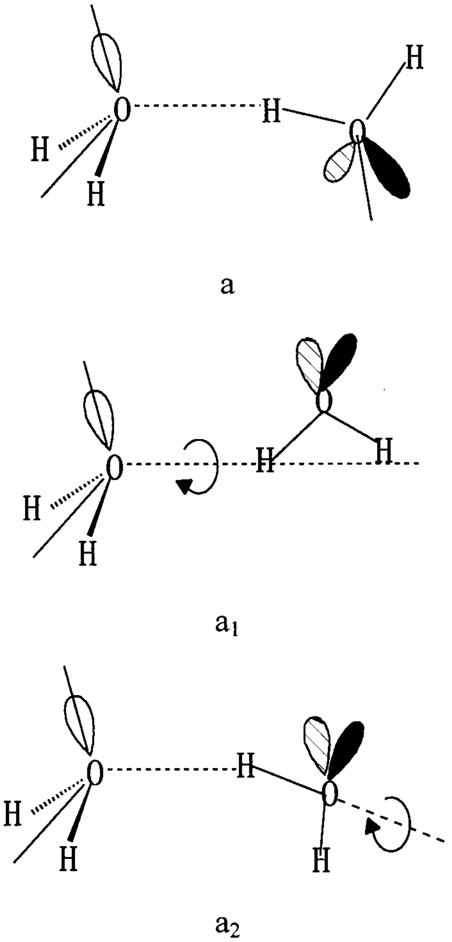


Figure 4. Conformers of $(H_2O)_2$ about two different axes.

But when rotation angle at 180°, π-type hydrogen bond does not exist ($D_\pi = 0$), then

$$V(180) = R'_b + \Delta E_1 \tag{4}$$

where $R'_b = R_b(180)$ is the repulsion energy between two monomers yielded by bending hydrogen bond X···H−Y and fixed the angle X···H−Y in the rotation. An internal rotation barrier (ΔV) about the X···H bond is

$$\Delta V = V(180) - V(0) = D_\pi + R_b - R'_b \tag{5}$$

To illustrate whether the value of R'_b is equal to the value of R_b approximately, we made a possible calculation of $R''_b(180)$ at MP4 level, using the structure rotated by angle 180° about the H−O in the hydrogen bond O···H−O for $(H_2O)_2$ (see Figure 4 a2) and obtained computational result, $R''_b(180)/R'_b = 1.05$. By means of analysis of rotation models (Figure 4), we found that $R''_b(180)$ (structure a2) > R_b (structure a) and R'_b (structure a1) < R_b for $(H_2O)_2$. So It is reasonable to take $R_b \approx R'_b$ for $(H_2O)_2$, $(HF)_2$, and H_2O-HF. Finally, we obtained an expression of D_π from eqs 1 and 5:

$$D_\pi = \Delta E_{sb} - R_b \approx -\Delta V \tag{6}$$

We calculated the interaction energy of π-type hydrogen bond, D_π, that is given in Table 4 by using eq 6.

$(H_2O)_2$ and $(HF)_2$ have the same angle (7°) of bent hydrogen bond, the former with strong double π-type hydrogen bond has $D_\pi = -1.324$ and the latter with single π-type hydrogen bond has the intermediate value $D_\pi = -0.350$ mE$_h$. Although H_2O-HF has double π-type hydrogen bond, it is the weakest, ($\Delta b = 2$, the smallest), with D_π for H_2O-HF only -0.067 mE$_h$.

TABLE 4: Interaction Energy of π-Type Hydrogen Bond[a]

dimer	π-type hydrogen bond	D_p(mE$_h$) MP2	D_p(mE$_h$) MP4
$(HF)_2$	single	−0.360 (−0.384)	−0.350 (−0.373)
$(H_2O)_2$	double	−1.359 (−1.465)	−1.324 (−1.439)
H_2O-HF	double	−0.062 (−0.067)	−0.062 (−0.067)

[a] The values in brackets come from basis set without BF.

On the other hand, this internal rotation of the dimers is different from the interchange hydrogen atoms within a dimer (degenerate rearrangement).[3] From Figure 3 we know that at the maximum value point for the former, The bent hydrogen bond is maintained and the π-type hydrogen bond is broken. But at the maximum value point for the latter, the transition structure is formed: the bifurcated hydrogen-bond structure for $(H_2O)_2$ and for $HF-H_2O$, but the cyclic structure for $(HF)_2$. In the rearrangement processes, the barrier is a little higher than that of the internal rotation around hydrogen bond. They are 2.05037 mE$_h$ (450 cm^{-1}) for $(H_2O)_2$,[3] 1.10263 mE$_h$ (242 cm^{-1}) for $(HF)_2$,[22] and 0.57409 mE$_h$ (126 cm^{-1}) for H_2O-HF,[21] which is comparable with the value of the barrier ($\approx D_\pi$) of the internal rotation.

IV. Conclusion

With a probing point charge to scan the energy of the equilibrium structures in different orientations for the dimers ($(HF)_2$, $(H_2O)_2$, H_2O-HF), we have detected the orientations of lone pairs. We further found that a long-range π-type hydrogen-bond model is an embodiment of the secondary interaction and explains the nonlinearity of hydrogen bonds. The existence of single or double π-type hydrogen bond is a useful criterion to confirm bent hydrogen bond X···H−Y in the dimers. The interaction energy of π-type hydrogen bond and the stabilized energy of bent hydrogen bond as the effect of the π-type hydrogen bond are obtained, on the basis of the calculations of internal rotation process, the linear and bent structures for the tree title dimers.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (29873016, 29892168), Visiting Scholar Foundation of State Key Lab of Theoretical and Computational Chemistry of Jilin University. F.-M. Tao acknowledges the support from the Petroleum Research Fund of American Chemical Society (PRF No. 30399-GB6). The authors thank Prof. Y. K. Pan for helpful discussion.

References and Notes

(1) Hobza, P.; Zahradnik, R. *Chem. Rev.* **1988**, *88*, 871.
(2) Kollman, P.; Mckelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975**, *97*, 955.
(3) Smith, B. J.; Swanton, D. J.; Pople, J. A.; Schaefer, H. F., III. *J. Chem. Phys.* **1990**, *92*, 1240.
(4) Scheirner, S. *Annu. Rev. Phys. Chem.* **1994**, *45*, 23−56.
(5) Buckingham, A. D.; Fowler, P. W. *J. Chem. Phys.* **1983**, *79*, 6426.
(6) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 2018.
(7) Baiocchi, F. A.; Reiher, W.; Klemperer, W. *J. Chem. Phys.* **1983**, *79*, 6428.
(8) Legon, A. C. *Faraday Discuss. Chem. Soc.* **1994**, *97*, 19.
(9) Li, Z.-R.; Tao, F.-M.; Pan, Y.-K. *Int. J. Quantum Chem.* **1996**, *57*, 202.
(10) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(11) Tao, F.-M.; Li, Z.-R.; Pan, Y.-K. *Chem. Phys. Lett.* **1996**, *255*, 179.
(12) Racine, S. C; Davidson, E. R. *J. Phys. Chem.* **1993**, *97*, 6367.
(13) Michael, D. W.; Dystra, C. E.; Lisy, J. M. *J. Chem. Phys.* **1984**, *81*, 5998.

(14) Gufowsky, H. S.; Chuang, C.; Keen, J. D.; Klots, T. D.; Emilsson, T. *J. Chem. Phys.* **1985**, *83*, 2070.

(15) Bohac, E. J.; Marshall, M. D.; Miller, R. E. *J. Chem. Phys*. **1992**, *96*, 6681.

(16) Novoa, J. J.; Planas, M.; Whangbo, M.-H.; Williams, J. M. *Chem. Phys.* **1994**, *186*, 175.

(17) Bene, J. D.; Pople, J. A. *J. Chem. Phys.* **1970**, *12*, 4858; **1971**, *55*, 2296.

(18) Schaefer, H. F., III. *Applications of Electronic Structure Theory*; Plenum Press: New York, 1974, 1977.

(19) Novoa, J. J.; Planas, M.; Rovira, M. C. *Chem. Phys. Lett.* **1996**, *251*, 33.

(20) Sweiss, S.; Leroi, G. *J. Chem. Phys.* **1968**, *48*, 962.

(21) Legon, A. C.; Millen, D. J. *Farady Discuss. Chem. Soc*. **1982**, *73*, 71.

(22) Necoechea, W. C.; Truhlar, D. G. *Chem. Phys. Lett*. **1996**, *248*, 1820.

(23) Tao, F.-M.; Klemperer, W. *J. Chem. Phys.* **1995**, *103*, 950.

(24) Caminati, W.; Melandri, S.; Rossi, I.; Favero, P. G. *J. Am. Chem. Soc*. **1999**, *121*, 10098.

(25) Quack, M.; Suhm, M. A. *Theor. Chim. Acta* **1996**, *93*, 61.

(26) Hodgens, M. P.; Stone, A. J.; Lago, E. C. *J. Phys. Chem*. **1998**, *102*, 2455.

(27) Lukes, V.; Laurinc, V.; Biskupic, S. *Int. J. Quantum Chem*. **1999**, *75*, 81.

(28) Bohac, E. J.; Marshall, M. D.; Miller, R. E. *J. Chem. Phys.* **1992**, *96*, 6681.

(29) Feyereisen, M. W.; Feller, D.; Dixon, D. A. *J. Phys. Chem*. **1996**, *100*, 2993.

(30) Van Duijneveldt-van de Rijdt, J. G. C. M.; Van Duijneveldt, F. B. *J. Chem. Phys*. **1992**, *97*, 5019.

(31) Legon, A. C.; Millen, D. J.; North, H. M. *Chem. Phys. Lett*. **1987**, *135*, 303.

(32) Mele, F.; Mineva, T.; Russo, N.; Toscano, M. *Theor. Chim. Acta.* **1995**, *91*, 169.

(33) Petersson, K. A.; Dunning, T. H., Jr. *Chem. Phys*. **1995**, *102*, 2032.

(34) Collins, C. L.; K. Morihashi, C. L.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys*., in press.

(35) Howard, B. J.; Dyke, T. R.; Klemperer, W. *J. Chem. Phys*. **1984**, *81*, 5417.