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Theoretical Study of the Interactions between 1,3-Butanediol and Hydrogen Peroxide

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In this work, we report a theoretical study on the interactions between 1,3-butanediol and chiral hydrogen peroxide. The complexes formed between two isolated chiral hydrogen peroxide (*R* and *S*) and 1,3-butanediol molecules have been investigated by using B3LYP method at different basis set levels. Four pairs of equilibrium structures have been determined: one pair is a one hydrogen bonded structure and the others are cyclic double hydrogen bonded structures at the largest basis level. The optimized geometric parameters, interaction energies, and chirodiastatic energy for various isomers at different levels are estimated. The infrared spectrum frequencies and IR intensities for various complexes are reported.

Introduction

The structures of many compounds in nature, such as nonsuperimposable right- or left-handed mirror images, are enantimorphs. This character is defined as chirality. Chirality is one of the essential characters of nature. The biological functions of biomolecules, such as nucleic acids, proteins, and enzymes, are almost chiral. Intermolecular interactions between two isolated chiral molecules M and P (where each also can be *R* or *S*) are inherently asymmetric, leading to chirally discriminating molecular recognition and binding. Chiral discrimination forces and energies are very important for understanding and determining the mechanisms of chiral recognition, enantioselective reactions, and a multitude of chirally discriminating effects in chemistry and biology.[1−5] There is a large body of experimental work based on the existence of these so-called chirally discriminating interactions; the interaction energy ΔE between two molecules, both of which can exist in chiral *R* and *S* enantiomers, depends on their relative handedness. For an M$\cdots$M′ complex, the interaction energies for the interactions between these two homochiral partners are identical: $\Delta E_{\mathrm{hom}} \equiv \Delta E(R\cdots R') = \Delta E(S\cdots S')$. This is also true for the two possible heterochiral interactions: $\Delta E_{\mathrm{het}} \equiv \Delta E(R\cdots S') = \Delta E(S\cdots R')$. The difference of these energies $\Delta E_{\mathrm{chir}} \equiv \Delta E_{\mathrm{hom}} - \Delta E_{\mathrm{het}}$ is the energy term responsible for chiral discrimination.[6] In this work, we only discuss the complexes formed between 1,3-butanediol and chiral hydrogen peroxide, so the chirodiastatic energies motioned below are calculated as $\Delta E_{\mathrm{chir}} = \Delta E(R\cdots R') - \Delta E(R\cdots S')$.

Hydrogen peroxide is not only the smallest chiral O−H hydrogen donor molecule but also the smallest O-containing chiral proton acceptor. The equilibrium geometry of HOOH exhibits helical chirality, and the enantiomers are denoted M and P (see Figure 1). In fact, HOOH is not a protypical chiral molecule, since in the gas phase it interconverts between the M and P enantiomers. Hydrogen peroxide in low-temperature matrices has been studied by a few groups,[7−9] and the monomer spectrum has been published by Pettersson et al.[9] Goeble et al.[10] have studied the complex between hydrogen peroxide and dimethyl ether and shown that hydrogen peroxide forms a single, relatively strong hydrogen bond to the other oxygen. Engdahl et al. have studied the complex between water and hydrogen peroxide[11] and hydrogen peroxide dimer.[12] To the best of our knowledge, no study has reported on the interactions between 1,3-butanediol and chiral hydrogen peroxide. In this work, the chiral hydrogen bonds between 1,3-butanediol and chiral hydrogen peroxide have been studied. 1,3-Butanediol also has two O−H bonds. It is not only a proton acceptor but also a proton donor. Also, there exists an intermolecular hydrogen bond between the H1 atom and O2 atom. Therefore, this is a good model to study the chiral hydrogen bond.

Recently, density functional theory (DFT) has been accepted by the ab initio quantum chemistry community as a cost-effective approach for the computation of molecular structure, vibrational frequencies, and energies of chemical reactions. Many studies have shown that molecular structures and vibrational frequencies calculated by DFT methods are more reliable than MP2 methods.[13−15] We thus report geometry optimization, calculated binding energies, and chirodiastatic energies of these complexes for a variety of basis sets. The role of basis set size and basis set superposition error effects are analyzed in detail. In addition, the vibrational frequencies of the monomer and the stationary complexes are calculated; the intramolecular frequencies and their shifts due to the complex formation are analyzed.

Computational Methods

In the present paper, the popular hybrid density functional B3LYP method, namely Becke's three-parameter nonlocal exchange functional[16] with the nonlocal correlation functional of Lee, Yang, and Parr,[17] which had been shown to be effective at accurately predicting structure and energies, has been used throughout.

For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis sets; we thus analyze the separate influence of the diffuse and polarization functions. The geometry optimization of the hydrogen peroxide dimer has been carried out using B3LYP method with the 6-31G, 6-31G(d), 6-31+G(d), and 6-31++G(d,p) basis sets along with analytic vibrational frequency calculations.

After these optimized structures are obtained, the calculated binding energies obtained with all the above theoretical proce-

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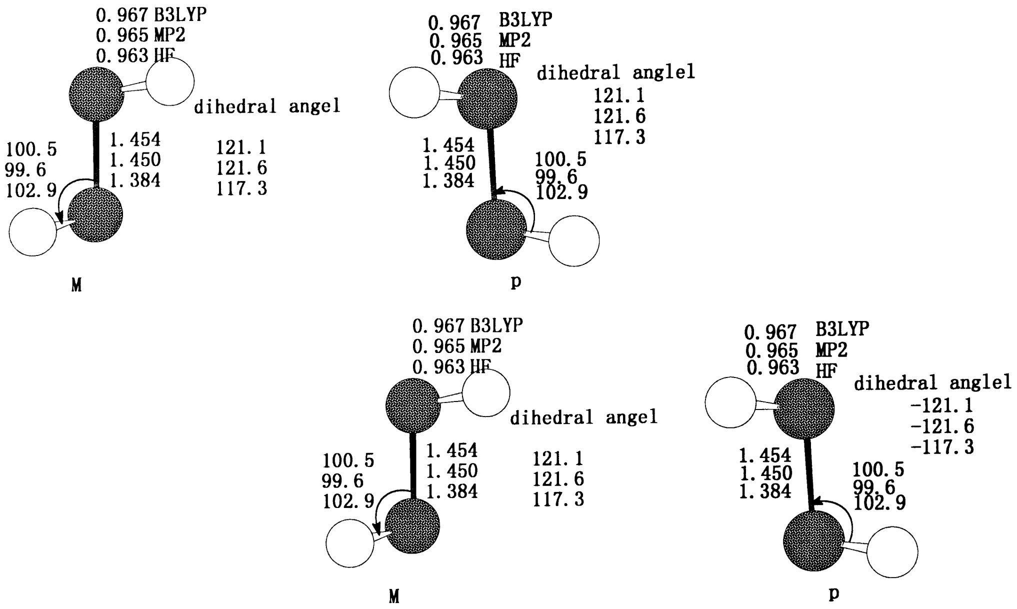
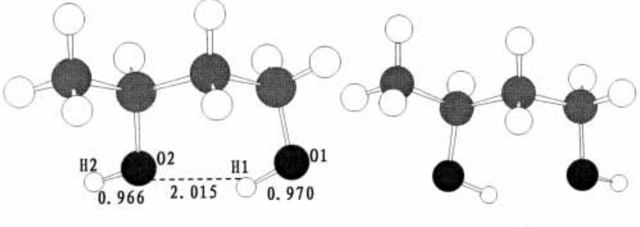


Figure 1. Optimized geometries of hydrogen peroxide at B3LYP, MP2, and HF/6-311++G(d,p) basis levels, respectively. Bond lengths are in angstroms and angles are in degrees.

TABLE 1: B3LYP Energies of the Two Conformers of 1,3-Butanediol at 6-31G(d), 6-31++G(d,P), 6-311++G(d,P), and 6-311++G(2d,2P) Levels[a]

	B3LYP/6-31G(d)	B3LYP/6-31++G(d,P)	B3LYP/6-311++G(d,P)	B3LYP/6-31++G(2d,2P)
configuration A	−810 955.2	−811 064.3	−811 255.7	−811 285.4
	(−810 579.9)	(−810 691.2)	(−810 883.4)	(−810 722.7)
configuration B	−810 953.8	−811 064.1	−811 255.3	−811 285.2
	(−810 578.6)	(−810 691.1)	(−810 883.1)	(−810 722.6)
ΔE	−1.460 041	−0.138 889	−0.367 045	−0.193 237
	(−1.260 24)	(−0.892 67)	(−0.338 69)	(−0.107 646)

[a] Values in parentheses are corrected for zero-point vibrational energy (kJ/mol).



configuration A configuration B

Figure 2. The two configurations of 1,3-butanediol optimized at B3LYP/6-31++G(d,p) basis level. Bond lengths are in angstroms.

dures are then corrected for the basis set superposition error (BSSE).[18] This is done using the counterpoise method.[19] All calculations are performed using the Gaussian 98 program.[20]

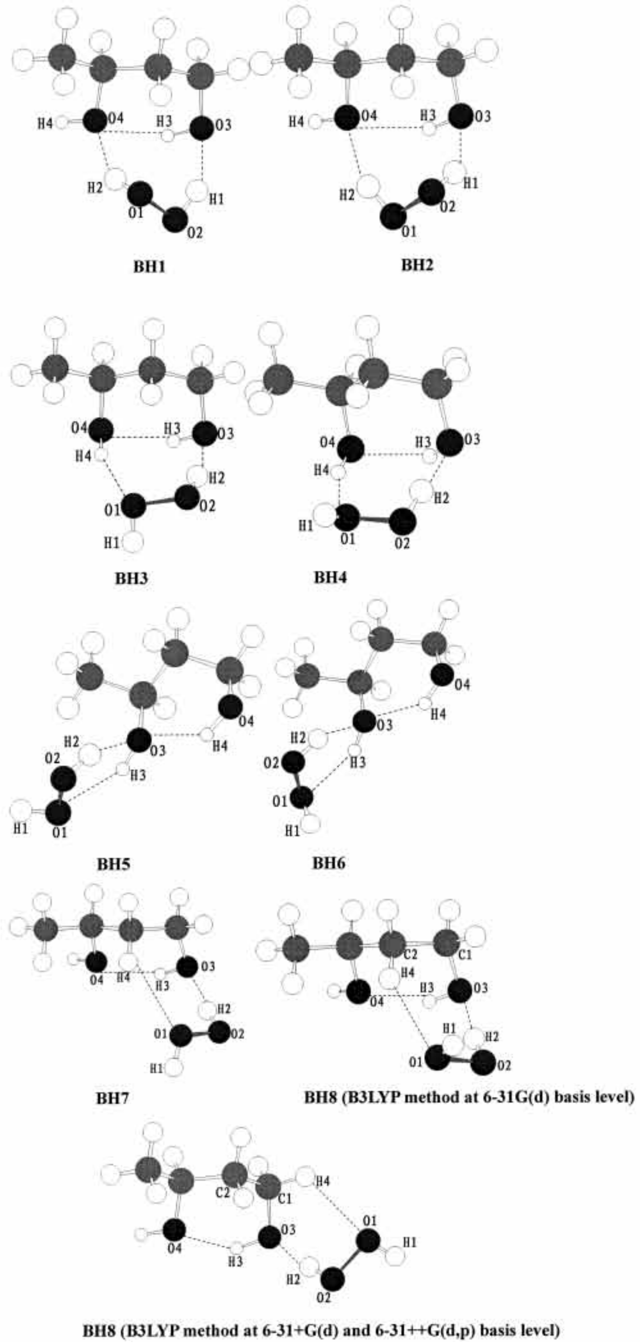
Results and Discussion

Structure of Hydrogen Peroxide Monomer. We optimized the H_2O_2 monomers by using B3LYP, MP2, and HF methods. The fully optimized geometries for the H_2O_2 monomers (M and P) are depicted in Figure 1. The two chiral structures are completely the same in bond lengths, angles, and molecular energy. The only difference between them is that the dihedral angle, $\angle$HOOH, in the M structure is 121.13°, 121.62°, and 117.36° whereas in the P structure it is −121.13°, −121.62°, and −117.36 for B3LYP, MP2, and HF/6-311++G(d,p) level, respectively. Thus the two structures are mirror images of each other.

Structure of 1,3-Butanediol Monomer. Ryderg electron transfer spectroscopy (RET) was used to determine the dipole-bound (DB) electron affinity (EA) of 1,3-butanediol by S. Carles.[21] In their work, a series of ab initio calculations was also carried out. They calculated the energies of four possible configurations, which differed in terms of thee orientation of the OH···OH hydrogen-bonded link with respect to the molecular axis and in terms of the shape of the C1−C2−C3−C4 backbone (linear or “L” shape). They found that the configurations with linear backbone are more stable than those with “L”-shape backbone. On the basis of their discussion, by using B3LYP method we calculated the two configurations with linear backbone, configurations A and B (Figure 2). Then these configurations were fully optimized by using B3LYP method at 6-31G(d), 6-31++G(d,p), 6-311++G(d,p), and 6-311++G-(2d,2p) levels. All these calculations show that configuration A is more stable than configuration B. All the calculated energies of the two configurations of 1,3-butanediol are presented in Table 1.

Structure of 1,3-Butanediol−Peroxide Complex. At all the levels of B3LYP method employed here, eight stable structures (four seven-membered-ring structures, two five-membered-ring structures, and two single hydrogen bond structures) were optimized. The structures of all the complexes are shown in Figure 3. All the complexes (from BH1 to BH8) have been positively identified for real minimum energy structures without imaginary frequency. The most interesting geometric parameters of these structures are listed in Tables 2, 3, 4, and 5, respectively.

Surveying the calculated results for the different methods at different basis set levels reveals that changes in the monomer geometries upon complexation are relatively minor. For the monomer peroxide, complex formation induces a small elonga-



BH1 BH2

BH3 BH4

BH5 BH6

BH7 BH8 (B3LYP method at 6-31G(d) basis level)

BH8 (B3LYP method at 6-31+G(d) and 6-31++G(d,p) basis level)

Figure 3. Configurations of 1,3-butanediol−peroxide optimized at B3LYP/6-31++G(d,p) basis level.

tion of the O−H bond and a very small contraction of the O−O bond. The maximum bond length change is less than 0.06 Å at 6-31++G(d,p) basis level. As for 1,3-butanediol, due to the formation of the hydrogen bonding, the O−H bond and the C−O bond are prolonged; of those, the O−H bond is elongated less than 0.03 Å and the other bond length change is less than 0.015 Å.

BH1 (formed by peroxide (P) and 1,3-butanediol) and BH2 (formed by peroxide (M) and 1,3-butanediol) are seven-membered rings made up of two hydrogens of peroxide and two oxygens of 1,3-butanediol. In BH1 the O4−H3 bond (the intramolecular hydrogen bond distance of 1,3-butanediol) is shortened, while in BH2 it is elongated. The length of this bond is 1.938, 1.997, 2.055, and 2.067 Å, respectively, in BH1 and 2.029, 2.052, 2.099, and 2.114 Å, respectively, in BH2 for B3LYP method at different levels. At 6-31G level the difference of the length is about 0.091 Å, but it is only about 0.047 Å at 6-31++G(d,p) level. Table 2 shows that, compared with the lengths of other intermolecular hydrogen bonds, in BH2 this intramolecular hydrogen bond is relatively weak. In BH1 the length of the O4−H2 bond is 1.956, 2.014, 2.047, and 2.085 Å, respectively, at different levels but the length of the corresponding bond in BH2 (O3−H1 bond) is 1.910, 1.993, 2.032, and 2.051 Å, respectively, which shows that this hydrogen bond of BH2 is stronger than that of BH1. However, the variation of the length of the hydrogen bond at different basis sets is less than the intramolecular hydrogen bond: at 6-31G level the difference of the length is about 0.046 Å, and it is 0.054 Å at 6-31++G(d,p) level. In BH1, R_{O3-H1} is 1.853, 1.942, 1.977, and 1.990 Å, respectively, but it is 1.867, 1.929, 1.962, and 1.986 Å, respectively in BH2 at different levels, which means that this hydrogen bond in BH2 is stronger than that in BH1, too. Furthermore, the cyclic arrangement results in more bent hydrogen bonds: for A1 the deformation from linearity is 30.2° (28.8°), while the deformation of A2 is 33.5° and 31.9° for BH1 and BH2, respectively, at the largest basis level. The values of A1 in the two structures are similar to each other, and the maximum difference at different levels is less than 1.6°. It can be seen from Table 3 that for A1 there is little difference caused by using diffuse functions and polar functions in the two structures. As to A2 and A3, high basis levels may get a comparatively low value. It is very interesting to see that for A2 and A3 in the two structures at 6-31+G(d) and 6-31++G(d,p) level we almost get the same value. The dihedral angle of HOOH is 79.7° for BH1 and −80.7° for BH2 at the largest level. Compared with the parameters of hydrogen peroxide monomer, the distortions are obvious, which should be attributed to the cyclic arrangement. It seems that when the diffuse functions and polarization functions are used, the dihedral angle of HOOH does not vary significantly.

As to BH3 (formed by peroxide (P) and 1,3-butanediol) and BH4 (formed by peroxide (M) and 1,3-butanediol), they are also cyclic conformers, in which hydrogen peroxide accepted a proton from the 1,3-butanediol group and donated a proton to the 1,3-butanediol group. There are two hydrogen bonds, O1−H4 bond and O3−H2 bond, in the two structures. R_{O1-H4} is 2.032 Å and R_{O3-H2} is 1.767 Å for BH3 at the largest basis level, while in BH4 the two bonds are 2.063 and 1.769 Å, respectively, which is a little longer than those of BH3. Therefore, the interaction energy of this structure will be higher than that of BH3. The cyclic arrangement also results in more bent hydrogen bonds, the deformation from linearity being 24.2° (24.4°) for A1, while the deformation of A2 is 33.5° and 31.9° for BH3 and BH4 at the largest basis level, respectively. At B3LYP/6-31++G(d,p) level Table 2 shows that the differences of the hydrogen bonds caused by the by different basis set levels are more significant than those of the angles. The B3LYP/6-31++G(d, p) calculations which yield A1 of 155.8° and A2 of 169.7° are in good agreement with the B3LYP/6-31+G(d) values of 155.6° and 170.1°. The intramolecular hydrogen bond is strengthened in the two structures, and from Table 2 it can be seen that the hydrogen bond in BH3 is stronger than that in BH4. However, from 6-31G to 6-31++G(d, p) level, R_{O4-H3} and R_{O1-H4} are increased by 0.147 and 0.188 Å, respectively. We cannot find a steady conformer of the BH4 at 6-31G level, which shows that the polarization functions are very important in getting the accurate conformer of complexes formed by chiral hydrogen peroxide and other molecules. The dihedral angle of HOOH is 113.8° for BH3 and −128.2° for BH4 at the largest

TABLE 2: Optimized Geometric Parameters of BH1 and BH2 Using B3LYP Method at Different Basis Set Levels[a]

		B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31++G(d,p)
BH1	R_{O4-H2}	1.956	2.014	2.047	2.085
	R_{O4-H3}	1.938	1.997	1.055	2.067
	R_{O3-H1}	1.853	1.942	1.977	1.990
	A1[b]	148.5	149.2	151.4	149.8
	A2[c]	134.7	135.1	130.9	130.9
	A3[d]	144.7	145.6	146.1	146.5
	ψ[e]	81.7	82.7	79.1	79.7
BH2	R_{O4-H2}	1.910	1.993	2.032	2.051
	R_{O4-H3}	2.029	2.052	2.099	2.114
	R_{O3-H1}	1.867	1.929	1.962	1.986
	A1	150.1	147.7	150.7	151.2
	A2	131.6	133.3	129.5	129.2
	A3	144.3	147.5	148.9	148.1
	ψ[e]	−85.7	−85.8	−80.5	−80.9

[a] Distance in angstroms, angles in degrees. [b] A1 is O4H2O1. [c] A2 is O4H3O3. [d] A3 is O3H1O2. [e] ψ is the dihedral angle of HOOH.

TABLE 3: Optimized Geometric Parameters of BH3 and BH4 Using B3LYP Method at Different Basis Set Levels[a]

		B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31++G(d,p)
BH3	R_{O1-H4}	1.844	1.927	2.004	2.032
	R_{O3-H2}	1.634	1.764	1.771	1.767
	R_{O4-H3}	1.814	1.864	1.941	1.961
	A1[b]	154.8	159.3	156.5	155.8
	A2[c]	167.8	169.8	170.1	169.7
	A3[d]	137.1	139.6	135.4	134.7
	ψ[e]	137.6	106.6	113.3	113.8
BH4	R_{O1-H4}		1.927	2.0354	2.063
	R_{O3-H2}		1.763	1.774	1.769
	R_{O4-H3}		1.887	1.955	1.980
	A1		159.4	156.3	155.6
	A2		169.4	169.9	170.1
	A3		137.9	134.1	133.1
	ψ[e]		−151.9	−127.4	−128.2

[a] Distance in angstroms, angles in degrees. [b] A1 is O4H4O1. [c] A2 is O2H2O3. [d] A3 is O4H3O3. [e] ψ is the dihedral angle of HOOH.

TABLE 4: Optimized Geometric Parameters of BH5 and BH6 Using B3LYP Method at Different Basis Set Levels[a]

		B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31++G(d,p)
BH5	R_{O1-H3}		2.057	2.250	2.256
	R_{O3-H2}		1.919	2.049	2.063
	R_{O3-H4}		1.992	2.049	2.063
	A1[b]		128.4	118.5	118.9
	A2[c]		143.9	147.1	146.6
	A3[d]		137.2	135.1	134.9
	ψ[e]		−121.3	−124.6	−124.9
BH6	R_{O1-H3}	2.005	2.023	2.219	2.221
	R_{O3-H2}	1.833	1.920	1.908	1.929
	R_{O3-H4}	1.922	1.978	2.027	2.041
	A1	125.4	129.9	119.7	120.5
	A2	143.9	142.9	146.3	145.9
	A3	139.1	138.3	136.2	136.2
	ψ[e]	144.2	115.1	118.9	119.3

[a] Distance in angstroms, angles in degrees. [b] A1 is O1H3O3. [c] A2 is O2H2O3. [d] A3 is O3H4O4. [e] ψ is the dihedral angle of HOOH.

level. Compared with the parameters of hydrogen peroxide monomer, the dihedral angle of HOOH has been increased, which should be attributed to the intermolecular repulsion of other parts of 1,3-butanediol. It has been shown in Table 2 that at low basis level the values of the dihedral angle of HOOH are inaccurate, but when one diffuse function and one polarization function are used, the values are very close to those at 6-31++G(d,p) level.

BH5 (formed by peroxide (M) and 1,3-butanediol) and BH6 (formed by peroxide (P) and 1,3-butanediol) are five-membered rings, in which the peroxide accepts one proton from the 1,3-butanediol group and donates a proton to it. We cannot get the configuration of BH5 at 6-31G basis level, which is due to the lack of the polarization function in the basis set. In BH5 and BH6, the O3−H2 bond is 2.063 and 1.929 Å at the largest basis level, while the O1−H3 bond is 2.256 and 2.221 Å, respectively, which means that in the two structures the O3−H2 bond is much stronger than the O1−H3 bond and the intermolecular hydrogen bonds in BH5 are relatively weak. From Table 4 it can be found that in both structures the intramolecular bonds are elongated and the bonds in BH5 are weaker than those in BH6. For A1 the deformation from linearity is 81.1° (79.5°), while the deformation of A2 is 33.4° and 34.1° for BH5 and BH6 at the largest basis level, respectively. Also, the dihedral angle of HOOH is 116.4° for BH5 and −112.3° for BH6 at the largest level. Compared with the parameters of hydrogen peroxide monomer, the distortions of A1, A2, and the dihedral angle of HOOH are not obvious; they are due to that the peroxide formed hydrogen bonds with only one of the O−H bonds of 1,3-butanediol and there is no cyclic arrangement as in other

TABLE 5: Optimized Geometric Parameters of BH7 and BH8 Using B3LYP Method at Different Basis Set Levels[a]

		B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31++G(d,p)
BH7	$R_{\mathrm{O4-H3}}$	1.784	1.886	1.934	1.945
	$R_{\mathrm{O3-H2}}$	1.627	1.773	1.771	1.759
	$R_{\mathrm{O1-H4}}$	2.495	2.537	2.779	2.762
	A1[b]	141.8	142.4	139.2	138.9
	A2[c]	169.5	172.8	173.6	172.8
	ψ[d]	154.68	110.4	116.4	116.4
BH8	$R_{\mathrm{O4-H3}}$		1.878	1.942	1.942
	$R_{\mathrm{O3-H2}}$		1.781	1.782	1.773
	$R_{\mathrm{O1-H4}}$		2.543	2.840	2.778
	A1		141.8	138.4	138.9
	A2		174.3	172.7	171.9
	ψ[d]		−121.3	−113.1	−112.3

[a] Distance in angstroms, angles in degrees. [b] A1 is O4H3O3. [c] A2 is O3H2O2. [d] ψ is the dihedral angle of HOOH.

TABLE 6: Interaction Energies of 1,3-Butanediol−Peroxide Complex (kJ/mol)[a]

	B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31++G(d,p)
BH1	−58.4 (−49.6) (−46.1)	−57.1 (−34.8) (−41.0)	−34.7 (−31.1) (−25.3)	−30.9 (−28.8) (−25.2)
BH2	−59.3 (−47.7) (−47.6)	−52.9 (−34.2) (−42.4)	−35.7 (−32.2) (−26.0)	−33.2 (−30.9) (−24.1)
BH3	−86.2 (−73.4) (−73.2)	−71.8 (−53.9) (−59.7)	−51.6 (−48.9) (−40.3)	−48.1 (−45.9) (−37.7)
BH4		−67.6 (−49.9) (−56.2)	−46.4 (−44.6) (−36.2)	−43.2 (−41.1) (−33.8)
BH5		−40.7 (−23.7) (−32.1)	−28.6 (−24.8) (−21.7)	−26.6 (−24.3) (−20.1)
BH6	−50.9 (−36.3) (−41.1)	−42.9 (−27.6) (−34.0)	−31.3 (−27.1) (−23.8)	−29.1 (−26.5) (−22.1)
BH7	−64.2 (−54.6) (−55.6)	−47.7 (−36.0) (−40.0)	−39.4 (−35.5) (−32.4)	−37.9 (−35.7) (−31.0)
BH8		−46.5 (−36.9) (−39.1)	−39.4 (−35.1) (−31.9)	−37.5 (−35.3) (−30.7)

[a] Values in the first set of parentheses are results with correction for basis set superposition error, and those in the second set of parentheses are corrected for zero-point vibrational energy.

complexes. From Table 4 it is not difficult to find that, if we ignore the result at 6-31G level for BH6, there is little difference among the results calculated at different basis set levels for A1, A2, and the dihedral angle of HOOH.

BH7 (formed by peroxide (P) and 1,3-butanediol) and BH8 (formed by peroxide (M) and 1,3-butanediol) are also cyclic structures. There is only one classical hydrogen bond in BH7 and BH8, namely the O3−H2 bond. There also exists a weakly intermolecular hydrogen bond, O1−H4, in the two structures. In Figure 3, we also line out the O1−H4 bond in BH7 and BH8, respectively, because this bond plays a very important role in determining the configurations of BH8 at different basis set levels. At 6-31G level, we cannot find a steady configuration for BH8, which is due to the lack of the polarization function at this basis level. When it is optimized at the same initial structure, at 6-31G(d) and other basis levels, two different configurations of BH8 have been found. In the two structures there exists one hydrogen bond between the H2 atom and the O3 atom, but in the structure calculated at 6-31+G(d) level the O1 atom formed one hydrogen bond with the H4 atom, while in the structure calculated at 6-31++G(d,p) level the O1 atom formed one hydrogen bond with the H5 atom. Maybe the two weak hydrogen bonds are the biggest determinant for forming the different configurations. The diffuse functions and the polarization functions play an important role again, and in this case without the proper basis set the right configuration cannot even be achieved. The length of the O4−H3 bond is 1.945 and 1.942 Å at 6-31++G(d,p) level for BH7 and BH8, respectively. Compared with other intermolecular hydrogen bonds in other structures, there is little difference between the two bonds; at 6-31G(d) level, the difference between the length of the O1−H4 bond for the two structures is negligible, which should be attributed to the fact that the peroxide formed hydrogen bonds with only one of the O−H bonds of the 1,3-butanediol and there is no circularity in them. The O4−H3 bond is 1.945 and 1.942 Å for the two structures at 6-31++G(d,p) level, which shows that the intramolecular bonds in them are strengthened. Because there is no cyclic arrangement, the A2 at different basis levels are almost linear. Similar to BH5 and BH6, there is little distortion on the dihedral angle of HOOH.

From the discussion above it can be found that in the structures with cyclic arrangements the distortions of the bond angle and dihedral angle of HOOH are obvious. However, for the structures with one hydrogen bond, the influence is negligible. With the diffuse functions and polarization functions considered the bond angle is decreased, but the length of the hydrogen bond is increased. In some cases, without polarization functions we cannot even get a steady configuration. For BH8, at different levels two different configurations have been achieved, which means that in further calculation work on larger systems, if accurate calculations are to be performed, at least the 6-31G(d,p) basis level should be used.

Interaction Energies. Interaction energies are calculated for the hydrogen peroxide−1,3-butanediol hydrogen bond by taking the energy difference between the fragments and the complex. To correct the basis set superposition error (BSSE), the counterpoise (CP) method[20] is employed. The zero-point vibrational energy (ZPVE) corrections are also applied in the present case.

To analyze in more detail the role of basis set size effects on the binding energy between hydrogen peroxide and 1,3-butanediol, we show all the results in Table 6, which gives a detailed analysis of the binding energy obtained with B3LYP method at several basis sets. The numbers in the first set of parentheses are corrected for zero-point vibrational energy, and those in the second set of parentheses are results with correction for basis set superposition error using the counterpoise method of Boys and Bernadi.[20] As expected, basis set sensitivity exists. The interaction energy computed with B3LYP using the minimal basis set 6-31G is much higher. As the basis set is enlarged, the computed values decrease and converge smoothly. All the ZPVE-corrected energies are smaller than the uncorrected ones, and all of the ZPVE-corrected energies calculated at 6-31+G(d) and 6-31++G(d,p) levels are smaller than the BSSE-corrected ones at the same basis levels. Moreover, at 6-31+G(d) and 6-31++G(d,p) levels the correction is not sensitive to the

TABLE 7: Chirodiastatic Energies of 1,3-Butanediol−Peroxide Complex (kJ/mol)[a]

	B3LYP/6-31G	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31++G(d,p)
BH1−BH2	0.87 (−1.82) (1.51)	0.86 (−0.51) (1.44)	0.97 (1.11) (0.72)	2.23 (2.10) (−1.1)
BH3−BH4		−4.23 (−3.99) (−3.51)	−5.22 (−4.28) (−4.08)	−4.91 (−4.88) (−3.93)
BH5−BH6		2.21 (3.86) (1.89)	2.74 (2.25) (2.14)	2.56 (2.23) (2.03)
BH7−BH8		−1.11 (0.90) (−0.94)	0.03 (−0.49) (−0.48)	−0.33 (−0.36) (−0.07)

[a] Values in the first set of parentheses are results with correction for basis set superposition error, and those in the second set of parentheses are corrected for zero-point vibrational energy.

TABLE 8: Vibrational Frequencies (ν, in cm^{-1}) and IR Intensities (I, in km/mol) of Monomers and Complexes at B3LYP/6-31++G(d,p) Level

expt	ν (I)	assignment	BH1 ν (I)	BH2 ν (I)	BH3 ν (I)	BH4 ν (I)	BH5 ν (I)	BH6 ν (I)	BH7 ν (I)	BH8 ν (I)
hydrogen peroxide										
371	371 (221)	HOOH bend out of plane	734 (138)	710 (169)						
877	945 (1)	OO stretch	944 (0.5)	943 (0.1)	943 (6)	942 (6)	940 (25)	940 (2)	944 (3)	942 (3)
1266	1301 (96)	HOOH rock in plane					1320 (70)	1327 (70)	1331 (68)	1338 (58)
1402	1445 (0.1)	HOOH bend in plane	1448 (35)	1431 (52)	1571 (13)	1562 (11)	1528 (13)	1522 (11)	1527 (8)	1560 (19)
3599	3767 (60)	HOOH asym stretch	3594 (185)	3587 (185)						
3608	3768 (11)	HOOH sym stretch	3671 (171)	3662 (211)						
			BH1 ν (I)	BH2 ν (I)	BH3 ν (I)	BH4 ν (I)	BH5 ν (I)	BH6 ν (I)	BH7 ν (I)	BH8 ν (I)
1,3-butanediol		assignment								
3756 (127)		O3−H3 stretch	3751 (112)	3764 (95)	3648 (180)	3655 (172)	3760 (179)	3754 (193)	3703 (181)	3704 (183)
3827 (22)		O4−H4 stretch	3817 (27)	3818 (28)	3680 (256)	3690 (230)	3773 (43)	3769 (50)	3830 (27)	3830 (27)

basis sets. The general importance of including BSSE corrections in calculated binding energies has been well documented in the literature. From Table 6 we can see the magnitude of the BSSE is decreasing with the basis set enlarging, when the diffusion and polarization functions are considered; especially for the 6-31++G(d,p) basis set using B3LYP method, the inclusion of BSSE correction has minor importance to the binding energy.

From Table 6, we can see that the relative stability order of the eight structures is BH3 > BH4 > BH7 > BH8 > BH2 > BH1 > BH6 > BH5. It is easy to understand that the stability of BH3 derives from the formation of a pair of hydrogen bonds between hydrogen peroxide and 1,3-butanediol due to the strongest interaction (the shortest hydrogen bond distance). The reason BH3 is more stable than BH4 is that in BH4 the distance between the H1 atom and of 1,3-butanediol is shorter than that in BH3. At the same time, the instability of BH5 is because of the weakest interaction, though it is also a cyclic structure. In BH7 and BH8 the H1 atom is distant from 1,3-butanediol, so there is little stability caused by the chirality of hydrogen peroxide. For the other structures, we can also estimate the stability by the interaction energy and the lengths of the intermolecular hydrogen bonds.

To analyze the difference caused by the chiral structures of hydrogen peroxide, we show the chirodiastatic energy for four pairs of complexes at different levels in Table 7. When diffuse functions and polarization functions are added, most of the chirodiastatic energies calculated by using ZPVE data are smaller than the uncorrected ones and most of the ZPVE-corrected energies are smaller than the BSSE-corrected ones at the same basis level. We also find that in BH7 and BH8 when the BSSE data are considered we even get the opposite conclusions, mainly because at different levels there is a different configuration of BH8.

Infrared Spectrum. Vibrational spectroscopy is one of the most useful experimental tools for study of H-bonded clusters, so the information on calculated harmonic vibrational frequencies can be useful. The values for both vibrational frequencies and IR intensities of the monomers and the eight complexes are listed in Table 8 at the B3LYP/6-31++G(d, p) level. Since there are little shifts at other frequencies for 1,3-butanediol, we have only discussed the frequencies involved in the intermolecular hydrogen bond. Since the frequency shifts are relatively stable with respect to variation of basis set, one can estimate the IR spectrum for the complex by combining the observed fundamental vibrational frequency of its moieties and the frequency shift in Table 8.

The HOOH frequency of the bend in-plane mode is found to reduce for all structures considered here (1448, 1431, 1571, 1562, 1528, 1522, 1527, and 1560 cm^{-1}, respectively). Expect in BH1 and BH2, the frequencies of the stretch mode in other complexes are all blue shifted. The frequency of the O−O stretching mode shows a very slight change for all of the structures, which shows that the forming of the complexes has little effect on this vibrational mode. The HOOH frequencies of the bend out-of-plane mode have disappeared from other complexes (it has been found in only BH1 and BH2) mainly because hydrogen peroxide forms an intermolecular hydrogen bond with only one OH bond of 1,3-butanediol. The HOOH asymmetric stretch mode and HOOH symmetric stretch mode only appear in BH1 and BH2, maybe also because the vibration of H atom in hydrogen peroxide is restricted to the forming of the intermolecular hydrogen bond. The HOOH rock in-plane mode vanishes from the four eight-membered-ring structure mainly because of the forming of two intermolecular hydrogen bonds in them. For the vibrational modes of 1,3-butanediol in the complex, like that of H_2O_2, most of the stretching frequencies associated with the hydrogen bond undergo red shift compared to the free monomer. The reason is that the formation of the hydrogen bond weakens the O−H bond.

With respect to IR intensities, they are all IR active and most of them have large intensities. These predicted IR spectral characteristics might be of great interest in the analysis of the experimental spectral features. It is more difficult to predict accurate shifts in absorption intensities. For this system, there is an extremely large increase in the intensity of the stretching vibrational modes of the hydrogen donor. From the results presented in Table 8, it can be seen that the hydrogen bonded OH stretching mode intensities are enhanced largely in every hydrogen bond complex. For example, the HOOH bend in-plane mode intensities varied from 8 to 52 km/mol for the eight structures, and it is notable that the largest change of this mode intensity occurs in BH2 (to 53 km/mol, approximately 500 times larger than that of the mode in the monomer), which is due to the strongest interaction. For the O−O stretch mode, the intensities have decreased in BH1 and BH2, which should be due to the forms of hydrogen bond restricted the vibration of O−O bond. In other structures it has increased, mainly because there is no restriction on the O−O bond. In a word, owing to the formation of the hydrogen bond, the force constants of the bond involved in the hydrogen bonding reduce and the frequencies are red shifted. At the same time, the increasing of the change of the vibrational dipole moments results in the enhancement of the IR intensities.

Conclusions

The hydrogen bond interaction of 1:1 complex between hydrogen peroxide and 1,3-butanediol has been analyzed by B3LYP method employing different basis set levels. Eight structures are considered, one of which are one hydrogen bonded structure and the others are cyclic double hydrogen bonded structures at the largest basis level. Of the eight structures, BH3 is the most stable at all levels and BH5 is the most unstable, due to the weakest interaction. For other complexes, their stabilities depend on the values of the interactions between hydrogen peroxide and 1,3-butanediol. Moreover, the infrared spectrum frequencies, IR intensities, and vibrational frequency shifts are reported. It can be found that the configurations of the complexes play an important role in determining the IR intensities and the vibrational frequency shifts. The stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the free monomer, and there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor.

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