Cooperativity between OH···O and CH···O Hydrogen Bonds Involving Dimethyl Sulfoxide−H₂O−H₂O Complex

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The cooperativity between the O−H···O and C−H···O hydrogen bonds has been studied by quantum chemical calculations at the MP2/6-311++G(d,p) level in gaseous phase and at the B3LYP/6-311++G(d,p) level in solution. The interaction energies of the O−H···O and C−H···O H-bonds are increased by 53 and 58%, respectively, demonstrating that there is a large cooperativity. Analysis of hydrogen-bonding lengths, OH bond lengths, and OH stretching frequencies also supports such a conclusion. By NBO analysis, it is found that orbital interaction plays a great role in enhancing their cooperativity. The strength increase of the C−H···O H-bond is larger than that of the O−H···O H-bond due to the cooperativity. The solvent has a weakening effect on the cooperativity.

1. Introduction

It is becoming increasingly apparent that cooperative interaction involving many molecules is an important component of intermolecular interactions, particularly those involving hydrogen bonds. When noncovalent binding interactions occur with positive cooperativity, then the observed binding energy is greater when the interactions occur together than when they occur in isolation from each other. Conversely, when the interactions occur with negative cooperativity, then the observed binding energy is less when the interactions occur together than when they occur in isolation.

The cooperativity of hydrogen bond plays an important role in controlling and regulating the processes occurring in living organisms. Many physical and chemical properties of materials are determined by hydrogen-bonding cooperativity. For example, the cooperativity of hydrogen bond can stabilize secondary and tertiary structures of biomolecules and related assemblies.[1−3] The cooperativity of hydrogen bonds has thus received intensive theoretical and experimental research.[4−7]

Hydrogen bonds (presented usually as X−H···Y) are classified into two types: a red-shifting one and blue-shifting one according to the shift of the X−H stretching vibration in infrared spectroscopy, The cooperativity of a red-shifting hydrogen bond has been investigated thoroughly with many methods;[8,9] however, the cooperativity involving a C−H···O blue-shifting hydrogen bond was studied only recently with experimental methods[10−13] and quantum chemical calculations.[14−16] Kar and Scheiner[15] compared the cooperativity in C−H···O and O−H···O hydrogen bonds with quantum chemical calculations, and they also studied the solvent effect on the cooperativity of conventional and unconventional hydrogen involving imidazole with the conductor polarized continuum model.[16] Their results showed that C−H···O hydrogen bonds are much less coopera-

tive than O−H···O hydrogen bonds and two types of H-bonds are weakened as the dielectric constant of the solvent grows when placed in a polarizable medium.

Although C−H···O interaction has been accepted as a true hydrogen bond,[17] the exact origin of the improper blue-shifting behavior has not been conformably understood. One prevailing point is that electrostatic repulsion is responsible for this blue-shifting phenomenon. That is to say, the present understanding of both conventional and unconventional hydrogen bonds is that they are electrostatic in nature, and the red-shifted H-bond is governed mainly by electrostatic attraction and the blue-shifted H-bond by electrostatic repulsion.[18,19] Additionally, hyperconjugation interaction is also of importance in both types of hydrogen bond.[19] If so, the cooperativity would be found between conventional and unconventional hydrogen bonds. In this paper, this question will be answered with quantum chemical calculations based on a DMSO−H₂O−H₂O (DMSO = dimethyl sulfoxide) model.

2. Computational Details

The structures of complexes were first optimized in the gas phase using B3LYP/6-311++G(d,p) and MP2(FC)/6-311++G-(d,p) methods. Then the geometry of each species in heptane was calculated at the B3LYP/6-311++G(d,p) level with polarized continuum model (PCM).[20−22] This model has successfully been applied to describe solvent effect on structures and properties of hydrogen bond complexes.[23−25] In geometry optimizations, the tight convergence criteria were used to ensure the significance of small bond length differences. The optimized geometries were confirmed by frequency calculation to be a real minimum on the potential energy surface without any imaginary frequency.

The interaction energies ΔE were corrected with zero-point vibrational energies (ZVPE) and basis set superposition errors (BSSE). BSSE correction for both interactions was estimated using the counterpoise method of Boys and Bernardi[26] through the following equation:

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$$BSSE = [E_a - E_{a(b)}] + [E_b - E_{(a)b}]$$

where $E_{a(b)}$ (or $E_{(a)b}$) is the energy of fragment a (or b), based on the geometry extracted from the optimized structure, with its own basis set augmented by the basis set of b (or a). E_a or E_b is the energy of the isolated fragment a (or b), with just its own basis set. The optimized geometries in the gas phase were used to perform NBO analysis.[27] All calculations were carried out using the GAUSSIAN 98 program package.[28]

3. Results and Discussion

3.1. Cooperativity in the Gas Phase. It is generally accepted that C−H···O hydrogen bond is a weak interaction and its energy is dependent on the basis sets used in quantum chemical calculations. The larger basis sets and corrections for BSSE are required in describing such weak interactions. The issue of the sensitivity of H-bond cooperativity to basis sets has been discussed in refs 15 and 29. There is by and large a consensus that this sensitivity is surprisingly low. The 6-311++G(d,p) basis set is adopted in this study because it has successfully described many properties of such weak hydrogen bonds.[30−32] Figure 1 shows the optimized structures of DMSO−H$_2$O (**A**), DMSO−H$_2$O−H$_2$O (**B**), and H$_2$O−H$_2$O (**C**) complexes at the MP2/6-311++G(d,p) level. To the best of our knowledge, there are no reports on structure **B**. There are two C−H···O hydrogen bonds and one O−H···O hydrogen bond in structure **B**; thus, it can be used to investigate the cooperativity between the C−H···O and O−H···O hydrogen bonds. For convenience of analysis and comparison, structure **B** is divided into three parts: DMSO (1), middle H$_2$O (2), and terminal H$_2$O (3).

Table 1 lists the interaction energies of the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds in three complexes at the MP2/6-311++G(d,p) level. The interaction energies, corrected with ZPVE and BSSE, of the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds in structure **B**, were calculated with the formula $\Delta E(C(1)-H(1)\cdots O(2)) = E_{123} - E_1 - E_{23}$ and $\Delta E(O(2)-H(2)\cdots O(3)) = E_{123} - E_{12} - E_3$, respectively. $\Delta E(C(1)-H(1)\cdots O(2)) = -7.86$ kJ/mol in structure **A**, where there are two C(1)−H(1)···O(2) H-bonds; thus, the mean interaction energy of the C(1)−H(1)···O(2) H-bond is −3.93 kJ/mol. The mean interaction energy of the C(1)−H(1)···O(2) H-bond is changed to −6.22 kJ/mol in structure **B**, increased by 58%. $\Delta E(O(2)-H(2)\cdots O(3))$ in structure **B** is increased by 53% more than that in complex **C** (−8.72 kJ/mol). The sum of $\Delta E(C(1)-H(1)\cdots O(2))$ and $\Delta E(O(2)-H(2)\cdots O(3))$ in structure **B** (19.54 kJ/mol) is larger than that of $\Delta E(C(1)-H(1)\cdots O(2))$ in structure **A** and $\Delta E(O(2)-H(2)\cdots O(3))$ in structure **C** (−12.65 kJ/mol), indicating that there is a larger cooperativity between the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds.

The bond lengths of the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds were also given in Table 1. $r(H(1)\cdots O(2))$ in structure **A** is 2.5618 Å, while $r(H(1)\cdots O(2))$ in structure **B** is 2.4911 Å, decreased by 0.0707 Å. $r(H(2)\cdots O(3))$ is 1.9502 and 1.9158 Å in structures **C** and **B**, respectively, and $r(H(2)\cdots O(3))$ is shorter by 0.0344 Å due to the cooperativity. These geometrical changes show that both types of interactions are enhanced when the cooperativity happens. Interestingly, the strength increase of the C(1)−H(1)···O(2) interaction is greater than that of the O(2)−H(2)···O(3) hydrogen bond, as shown in changes of the interaction energies and bond lengths. This may be attributed to the difference in strength of both types of hydrogen bonds. The strong O(2)−H(2)···O(3) hydrogen bond has a big influence on the weak C(1)−H(1)···O(2) interaction. Although the
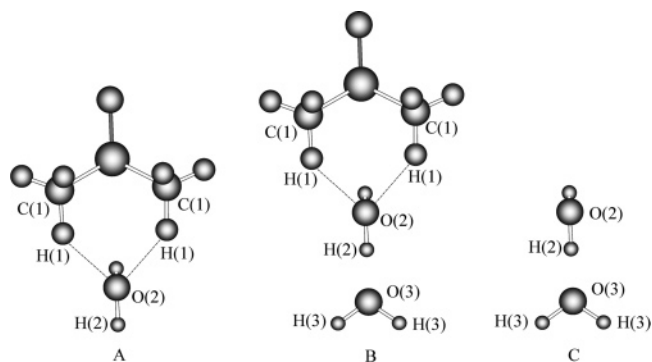
Figure 1. Optimized structures of three complexes at the MP2/6-311++G(d,p) level. Part atoms are labeled with letter and number.

TABLE 1: Interaction Energies (ΔE/(kJ·mol^{-1})) of Two Hydrogen Bonds, Binding Distances (r/Å) of Two Hydrogen Bonds, Bond Lengths (R/Å) of O(2)−H(2), and OH Asymmetric Stretching Frequencies (v/cm^{-1}) of H$_2$O (2) in Three Complexes Calculated at the MP2/6-311++G(d,p) Level

parameter	A	B	C
$\Delta E(C(1)\text{-}H(1)\cdots O(2))^a$	−3.93	−6.22	
$\Delta E(O(2)\text{-}H(2)\cdots O(3))$		−13.32	−8.72
$r(H(1)\cdots O(2))^a$	2.5618	2.4911	
$r(H(2)\cdots O(3))$		1.9158	1.9502
$R(O(2)\text{-}H(2))$		0.9677	0.9653
$v(O(2)\text{-}H(2))^b$	3983	3948	3976

^{a} The means are given because there are two C−H···O hydrogen bonds in **A** and **B**. ^{b} No scale was performed.

TABLE 2: Atom Charges (q/e) and Charge Transfers (CT/e) at the MP2/6-311++G(d,p) Level and Stabilization Energies (E/(kJ·mol^{-1})) at the HF/6-311++G(d,p) Level of Two Hydrogen Bonds in Three Complexes

parameter	A	B	C
$q(H(1))$	+0.223	+0.231	
$q(C(1))$	−0.756	−0.761	
$q(O(2))$	−0.914	−0.945	−0.927
$q(H(2))$	+0.456	+0.484	+0.473
$q(O(3))$		−0.917	−0.913
$q(H(3))$		+0.466	+0.463
$E(n(O(2))\rightarrow\sigma^*(C(1)-H(1)))$	5.25	8.23	
$E(n(O(3))\rightarrow\sigma^*(O(2)-H(2)))$		33.43	29.90
$CT(C(1)-H(1)\cdots O(2))$	0.004	0.003	
$CT(O(2)-H(2)\cdots O(3))$		0.013	0.012

C(1)−H(1)···O(2) hydrogen bond is weaker than the O(2)−H(2)···O(3) hydrogen bond, the former has a considerable influence on the latter as shown in Table 1.

Compared with those in structure **A**, the CH$_3$ stretching frequencies in structure **B** only have very a little red shift (about 1 cm^{-1}), and the bond length of C(1)−H(1) is almost not changed (results are not given). Thus, Table 1 only lists the O(2)−H(2) bond length and its asymmetrical stretching frequency. The bond length of O(2)−H(2) in structure **C** is 0.9653 Å, while it is 0.9677 Å in structure **B**. Elongation of $R(O(2)-H(2))$ (0.0024 Å) is seen due to the cooperativity. The elongation leads to a 28 cm^{-1} red shift of the OH stretching vibration from structure **C** to **B**, resulting from addition of the C(1)−H(1)···O(2) hydrogen bond. The red shift of 35 cm^{-1} is found from structure **A** to **B**, which results from the presence of the O(2)−H(2)···O(3) hydrogen bond. This again shows that the contribution of the O(2)−H(2)···O(3) hydrogen bond on the cooperativity is larger than that of the C(1)−H(1)···O(2) hydrogen bond.

To evaluate contribution from orbital interaction to the cooperativity of both hydrogen bonds, the NBO second-order

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TABLE 3: Direct Interaction Energies (DE/(kJ·mol⁻¹)), Binding Distances (r/Å), and Stabilization Energies (E/(kJ·mol⁻¹)) of Two Hydrogen Bonds in Three Complexes Calculated at the B3LYP/6-311++G(d,p) Level in Vacuum and at the PCM/B3LYP/6-311++G(d,p) Level in Heptane

parameter	vacuum ($\epsilon = 1$)			heptane ($\epsilon = 2$)		
	A	**B**	**C**	**A**	**B**	**C**
DE(C(1)-H(1)···O(2))^{a,b}	−2.81	−5.53		−7.56	−9.85	
DE(O(2)−H(2)···O(3))^{b}		−16.50	−11.35		−29.21	−24.63
r(H(1)···O(2))^{a}	2.5915	2.4738		2.4928	2.4293	
r(H(2)···O(3))		1.8973	1.9331		1.8723	1.8985
E(n(O(2))→σ*(C(1)−H(1)))	6.01	11.84		11.21	15.16	
E(n(O(3))→σ*(O(2)−H(2)))		35.03	32.05		39.73	37.88

^{a} The means are given because there are two C−H···O hydrogen bonds in **A** and **B**. ^{b} Data are given in interaction energies (ΔE/(kJ·mol⁻¹)) for the gas phase.

perturbation analysis was applied for three complexes at the HF/6-311++G(d,p) level. The obtained stabilization energies due to the $n(O(2))$→$\sigma^*(C(1)−H(1))$ and $n(O(3))$→$\sigma^*(O(2)−H(2))$ orbital interactions were listed in Table 2. The $E(n(O(2))$→$\sigma^*(C(1)−H(1)))$ value is increased by 57% from structure **A** to **B**, while the $E(n(O(3))$→$\sigma^*(O(2)−H(2)))$ value is also increased by 12% from structure **C** to **B**. In other words, the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds cooperatively enhance each other in complex **B**. Through comparison of the stabilization energy and interaction energy changes in both types of hydrogen bonds, it is found that the contribution from the orbital interaction to the cooperativity of C(1)−H(1)···O(2) hydrogen bond is much larger.

The origin of the cooperativity can be traced by examining charges from natural population analysis and bond polarizations within the complexes. Upon formation of hydrogen bond, it is generally found that negative charge flows from the proton acceptor to the proton donor. The bonded oxygen O(2) has more negative charge in structure **C** (−0.927 e) than that in isolated water (−0.894 e). The negative charge increase on the O(2) atom makes this site more susceptible to the C(1)−H(1)···O(2) hydrogen bonding as occurs in structure **B**. Similarly, the hydrogen H(2) in structure **A** has more positive charge (+0.456 e) than that in isolated water (+0.447 e), making it easy to form O(2)−H(2)···O(3) hydrogen bonding as occurs in complex **B**. The increase of O(2) negative charge (0.033 e) is larger than that of H(2) positive charge (0.009 e). These charge changes are in good agreement with the cooperativity changes in both types of hydrogen bonds. The positive charge of H(1) atom (+0.231 e) and negative charge of C(1) atom (−0.761 e) in structure **B** are larger than those in structure **A** (H(1), +0.223 e; C(1), −0.756 e). Compared with H(2) (+0.456 e) and O(2) (−0.914 e) in structure **A**, more positive and negative charges are found on the relative atoms in structure **B**. The O(3) negative charge increases from −0.913 e in structure **C** to −0.917 e in structure **B**, while the H(3) positive charge increases from +0.463 e in structure **C** to +0.466 e in structure **B**. The polarization of these bonds is thus all mutually enhanced through the cycle of cooperative charge-transfer interactions mapped by NBO analysis.

Charge-transfer interaction plays also a significative role in two hydrogen bonds. The charge transfers in both hydrogen bonds were calculated at the MP2/6-311++G(d,p) level, and their results were also listed in Table 2. The charge transfer of the C(1)−H(1)···O(2) H-bond in structure **A** is 0.004 e, while that of the O(2)−H(2)···O(3) H-bond in structure **C** is 0.012 e. Evidently, the charge-transfer interaction is of more importance in the usual O−H···O H-bond. Although the electron density transferred in the C−H···O interaction is small, this value is chemically significant. Very roughly, 0.001 e of the charge transfer corresponds to 4 kJ/mol of stabilization energy.[33] In

structure **B**, however, the charge transfer of the C(1)−H(1)···O(2) H-bond (0.003 e) decreases a little and that of the O(2)−H(2)···O(3) H-bond (0.013 e) increases a little. The sum of the charge transfer of both the C(1)−H(1)···O(2) H-bond in structure **A** and the O(2)−H(2)···O(3) H-bond in structure **C** is equal to that of both hydrogen bonds in structure **B**. The result shows that the contribution of charge-transfer interaction to the cooperativity of two hydrogen bonds is minor.

The above analytical results on these parameters show that there is a larger cooperativity between the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds. The increase of respective atom positive/negative charge shows an increase of electrostatic interaction in two hydrogen bonds. The analysis on the donor−acceptor orbital interaction demonstrates that the hyperconjugation interaction is present in two hydrogen bonds. Therefore, the C(1)−H(1)···O(2) and O(2)−H(2)···O(3) hydrogen bonds have similarity in nature, both mainly resulting from electrostatic interaction and hyperconjugation interaction. Since there is a similarity in nature of both hydrogen bonds, it is easy to understand that the larger cooperativity happens between two hydrogen bonds.

3.2. Cooperativity in Heptane Solvent. Of course, most hydrogen bonds do occur in condensed phase. It is thus important to study how the cooperativity of both types of hydrogen bonds is affected by their surroundings. Three complexes were therefore immersed in heptane solvent, and their bond lengths of hydrogen bonds have been given in Table 3. As shown in Table 3, for the C(1)−H(1)···O(2) hydrogen bond, solvent effect makes the value of the r(H(1)···O(2)) smaller (0.0987 Å in **A** and 0.0445 Å in **B**). Similar results are found for the O2−H2···O3 hydrogen bond (0.0346 Å in **C** and 0.0250 Å in **B**). This indicates that the strengths of both types of hydrogen bonds are enhanced significantly in heptane solvent. The direct interaction energy DE[34] is adopted to demonstrate two interactions in heptane solvent, and their results are also listed in Table 3. The DE value of the C(1)−H(1)···O(2) hydrogen bond is increased by 30% from structure **A** to **B**. A similar result (19%) is also found for the O(2)−H(2)···O(3) hydrogen bond. Therefore, placement in solvent retains the general principle of cooperativity. The enhancement of the C(1)−H(1)···O(2) hydrogen bond is again larger than that of the O(2)−H(2)···O(3) hydrogen bond in heptane solvent.

Through comparison of the cooperativity between two hydrogen bonds in gas phase and in heptane solvent, it is found that there is a clear lessening of the cooperative effect when heptane solvent is used. Taking the C(1)−H(1)···O(2) hydrogen bond as an example, the r(H(1)···O(2)) value in structure **B** is smaller than that in structure **A** by 0.1177 Å in vacuum, whereas it is shorter by 0.0635 Å in heptane. The interaction energy difference of the C(1)−H(1)···O(2) hydrogen bond between in structure **A** and that in **B** decreases from −2.72 kJ/mol in gas

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phase to −2.29 kJ/mol in heptane solvent. The difference of the $E(n(O(2)) \rightarrow \sigma^*(C(1)-H(1)))$ value between structure **A** and structure **B** is 5.83 kJ/mol in the gas phase, while it is 3.95 kJ/mol in heptane solvent. Similar results of cooperativity in heptane solvent are also observed for the O(2)−H(2)···O(3) hydrogen bond. This is consistent with the idea that separated molecules are stabilized by interaction with a dielectric continuum. The result also indicates that the solvent has a more prominent effect on the C(1)−H(1)···O(2) hydrogen bond than on the O(2)−H(2)···O(3) hydrogen bond. We attribute it to the weaker strength of the C(1)−H(1)···O(2) hydrogen bond.

Compared with that in structure **A**, the C(1)−H(1)···O(2) interaction in structure **B** is still enhanced in heptane by the O(2)−H(2)···O(3) hydrogen bond. There are abundant C−H···O H-bonds in proteins formed mainly by glycine, phenylalanine, and tyrosine residues with water molecule.[35] Structure **A**, where the C(1)−H(1)···O(2) H-bond is formed between the methyl of DMSO and the oxygen atom of water, can be taken as such a model. According to the above calculation results, it is concluded that the C(1)−H(1)···O(2) H-bond is enhanced by addition of water molecule. These results here are helpful in understanding the role of the C−H···O H-bond in the structure and activity of biological systems such as nucleic acids, DNA, proteins, and carbohydrates.[36,37]

4. Conclusions

In summary, a chain structure involving a DMSO−water complex was constructed through the C−H···O and O−H···O H-bonds. On the basis of the structure, the cooperativity between the C−H···O blue-shift hydrogen bond and the O−H···O red-shift hydrogen bond has been investigated by quantum chemical calculations at the MP2/ 6-311++G(d,p) and B3LYP /6-311++G(d,p) levels. In the gas phase, for the C−H···O H-bond, the interaction energy is increased by 58% and its bond length is decreased by 0.0707 Å, while, for the O−H···O H-bond, the interaction energy is increased by 53% and its bond length is decreased by 0.0344 Å. These results showed a great cooperativity between both types of hydrogen bonds, as also shown in changes of OH bond length and stretching frequency. The orbital interaction was calculated at the HF/6-311++G(d,p) level, and the result indicated that enhancement of their cooperativity has a close relation with the orbital interaction. The polarized continuum model has been employed to study the solvent effect on their cooperativity at the B3LYP/6-311++G(d,p) level. A lessening result was found for their cooperativity in heptane. The increase of the C−H···O H-bond strength is larger than that of the O−H···O H-bond in both the gas phase and heptane. Although the cooperativity of the C−H···O H-bond decreases in heptane solvent, its strength still increases greatly. The findings may shed light on understanding of the role of the C−H···O hydrogen bond in chemical and biological systems.

Supporting Information Available: Interaction energies of both hydrogen bonds and Cartesian coordinates of complexes **A**−**C** in the gas phase and in heptane solvent. This material is available free of charge via the Internet at http://pubs.acs.org.

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