

Hydrogen bonded complexes between dibenzyl sulfoxide and HX (X= F, Cl or CN): A theoretical study

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Introduction

It is well known that hydrogen bonds are important in biomolecular systems^{1,2}. These interactions influence several physical properties of the system, such as: stability, structural properties and chemical reactivity. In this work we studied the molecular and vibrational properties of hydrogen bonded complexes between dibenzyl sulfoxide (DBSO, Fig.1) and different monoprotic acids HX (X=F, Cl or CN). We have employed B3LYP calculations with the 6-311++G (d, p) basis set, available in Gaussian 2009, to obtain structural, electronic and vibrational properties of the hydrogen bonded complexes considered in this work.

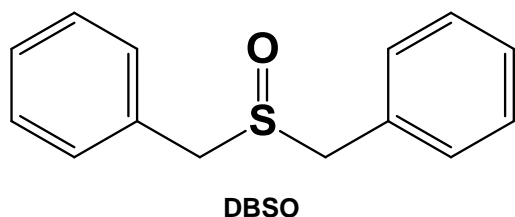


Figure 1. Molecular structure of the dibenzyl sulfoxide (DBSO).

Results and Discussion

First, all geometries were fully optimized and no imaginary frequencies were obtained, indicating that the structures are associated with the true energy minima. Subsequently, the force constants were calculated, which are necessary for the calculation of the thermodynamic properties. Then, we obtained the uncorrected binding energies of the hydrogen bonds in the complexes DBSO---HX (ΔE). Further, we added the correction of zero-point energy (E^{ZPE}) to the values of the uncorrected binding energies of the complexes (ΔE^{ZPE}). Table 1 presents the values of the energies of the hydrogen bonded complexes without correction ΔE , the energy of the hydrogen bonded complexes with ZPE correction ΔE^{ZPE} and Gibbs free energies for the complexation reactions. The results indicate that all complexes are energetically favorable to be formed and its order of spontaneity is: DBSO---(HF) > DBSO---(HCl) > DBSO---(HCN).

Table 2 shows the changes in the vibrational properties of H-X due the hydrogen bonds.

Table 1. Uncorrected binding energies (ΔE), binding energies corrected for ZPE (ΔE^{ZPE}), and Gibbs free energies (ΔG) of hydrogen bonds in complexes.

Complex	ΔE (kJ/mol)	ΔE^{ZPE} (kJ/mol)	ΔG (kJ/mol)
DBSO---(HF)	-65.5	-56.4	-23.1
DBSO---(HCl)	-47.0	-42.9	-7.7
DBSO---(HCN)	-36.0	-31.7	-0.1

Table 2. B3LYP/6-311++G(d,p) values for the harmonic frequency shifts ($\Delta\nu_{H-X}$) and the ratio of the infrared intensities of the H-X stretching in the complex and the corresponding H-X stretching in the isolated molecule ($A^{H-X \text{ in complex}} / A^{H-X, \text{ isolated}}$) in complexes.

Complex	$\Delta\nu_{H-X}$ (cm^{-1})	$\frac{A^{H-X \text{ in complex}}}{A^{H-X, \text{ isolated}}}$
DBSO---(HF)	-1116	11.5
DBSO---(HCl)	-1149	41.4
DBSO---(HCN)	-249	10.6

Our results indicate that the H-X bonds are weakened by the hydrogen bond. This effect is associated with intermolecular charge density transfer from a lone pair on the oxygen atom to the σ^* antibonding orbital of the monoprotic acid.

Conclusion

We performed calculations of the molecular and vibrational properties of the hydrogen bonded complexes between DBSO and HX (X=F, Cl or CN). The results indicate that all complexes are energetically favorable to be formed and its spontaneity order is: DBSO---(HF) > DBSO---(HCl) > DBSO---(HCN).

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