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DFT Study of dimers of dimethyl sulfoxide in gas phase

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Abstract

Density functional (DFT) calculations at M05-2x/aug-cc-pVDZ level were used to analyze the interactions between dimethyl sulfoxide (DMSO) dimers. The structures obtained have been analyzed with the Atoms in Molecules (AIMs) and Natural Bond Orbital (NBO) methodologies. Four minima were located on the potential energy surface of the dimers. Three types of interactions are observed, $\mathrm{CH\cdots O}$, $\mathrm{CH\cdots S}$ hydrogen bonds and orthogonal interaction between the lone pair of the oxygen with the electron-deficient region of the sulfur atom. Stabilization energies of dimers including BSSE and ZPE are in the range 27–40 $\mathrm{kJmol^{-1}}$. The most stable conformers of dimers at DFT level is cyclic structure with antiparallel orientation of $\mathrm{S{=}O}$ groups pairing with three $\mathrm{C{-}H\cdots O}$ and a $\mathrm{S\cdots O}$ interactions.

Keywords: Hydrogen bonding; DMSO; DFT; dimers.

Introduction

Noncovalent interactions between molecules play an important role in supramolecular chemistry, molecular biology, and materials science. The hydrogen bond (HB) is the most important weak interaction due to its role in many chemical and biological processes [1-3]. Although research has traditionally focused on the most common hydrogen-bonded interactions [4,5], more recently, interest has grown for another type of H-bonds involving proton donors and acceptors other than elec-

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tronegative atoms [5-20]. The S atom has been known to act as proton acceptor in a few H-bonds [21-25], albeit normally weaker than its O analogues. The motivation for study of H-Bonds between molecular moieties involving S atoms is due to its presence in proteins and in atmospheric systems and because of its analogy to the closely related O atom as well, to which it provides an interesting counterpoint.

Pure DMSO, like its aqueous solutions, is widely used in chemical practices as an extremely effective solvent. At the same time, the permeability of DMSO through the skin covering and its good compatibility with biological tissues have given rise to numerous applications for the solvent in medicine. In the present work, to analyze the potential of the intermolecular interactions in the DMSO-DMSO complexes, we used the density functional M05-2X method. The optimized geometry obtained by this method and also the electronic structure of the complexes formed by two molecules of DMSO in the different orientations are given and discussed.

Computational Details

Calculations were performed using the GAMESS suite of programs [26]. The structures were optimized at the M05-2x [27] using aug-cc-pVDZ basis set. The recently described DFT functional, M05-2x, have proven to be very efficient in the calculation of weak complexes as those studied here [28]. The stabilization energy (ΔE) was calculated as the difference of the total energy of the complexes and the sum of the isolated monomers in their minima configuration. Frequency calculations were performed at the same computational level to confirm that the geometries obtained correspond to true minima. Basis set superposition error (BSSE) was corrected by the full counterpoise method [29].

The atom in molecules (AIMs) methodology [30] has been used to analyze the electron density of the systems considered at the M05-2x/aug-cc-pVDZ computational level. The topological analysis has been carried out with the AIM2000 program [31]. The Natural Energy Decomposition Analysis (NEDA) [32,33] within the Natural Bond Orbital methodology [34] has been performed to obtain insight of the source of the interaction energy. This methodology divides the interaction energy into several attractive components as orbital charge transfer that arises from the delocalization of electron from one monomer to the other, electrostatic interaction of the monomers, polarization and exchange correlation terms. Finally, a repulsive component is considered which takes into account the electronic deformation due to the complex formation in each monomer. These calculations have been performed at the M05-2x/aug-cc-pVDZ computational level with the NBO-5G [35] on the GAMESS program [36].

Results and discussion

Monomer

The geometry of the DMSO molecule has been determined using microwave spectroscopy in gas phase [37]. The calculated results nicely reproduce the experimental geometry within 0.04 Å in the bond distances and 1° in the bond angle (Table 1).

Table 1. Calculated and microwave geometrical data (bond length in Å and bond angle in °) for DMSO monomer

	M05-2x/aug-cc-pVDZ	**Exp. [37]**
SO	1.53	1.49
SC	1.81	1.80
OSC	105.2	106.4
CSC	96.5	96.5

Among the electronic characteristics of the isolated monomer, it is worth to mention the presence of minima in the molecular electrostatic potential (MEP), two of them associated to the lone pairs of the oxygen and sulphur atoms. At the M05-2x/aug-cc-pVDZ computational level, the minima associated to the oxygen have a value of -0.1015 kcalmol^{-1} and the one associated to the sulfur only -0.0154 kcalmol^{-1} (Figure 1).

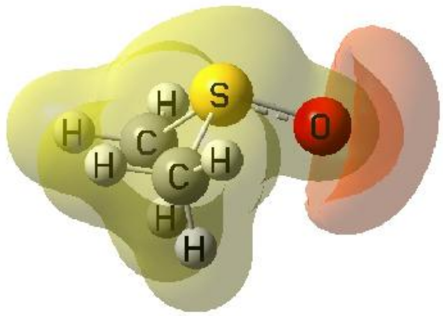


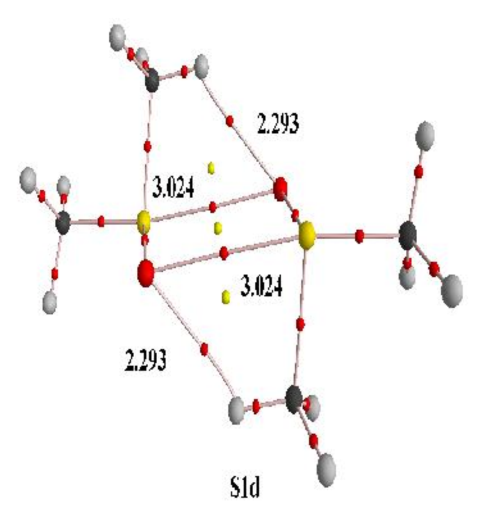
Figure 1. Molecular electrostatic potential of the DMSO molecule at ±0.08 au isosurfaces calculated at the M05-2x/aug-cc-pVDZ computational level

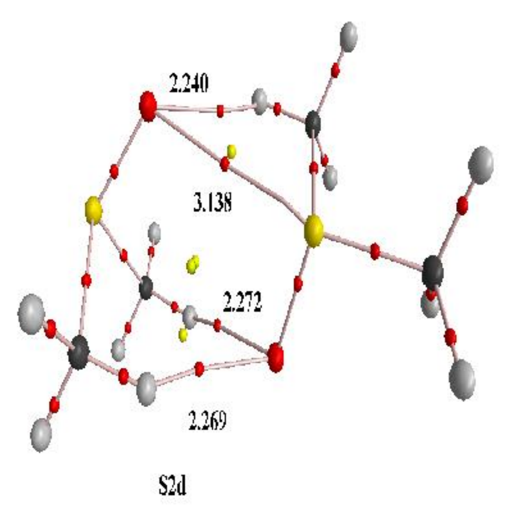
Dimers

Association of two DMSO molecules leads to formation of four minima. The binding energies of these complexes are reported in Table 2 and their structures are depicted in Figure 2. Binding energies of the DMSO dimers including zero-point vibrational corrections and BSSE lie in the range of 27–40 kJmol^{-1} at M05-2x/aug-cc-pVDZ computational level. S2d is the most stable conformer at the DFT level.

Table 2. Stabilization energies of DMSO dimers (kJmol^{-1})

Complex	**M05-2x /aug-cc-pVDZ**			
	ΔE	**BSSE**	**ΔE+BSSE**	**ΔE+BSSE+ZPE**
S1d	-42.96	4.05	-38.74	-34.74
S2d	-49.56	4.59	-44.78	-40.11
S3d	-36.07	4.73	-31.15	-27.31
S4d	-37.30	4.94	-32.16	-28.51





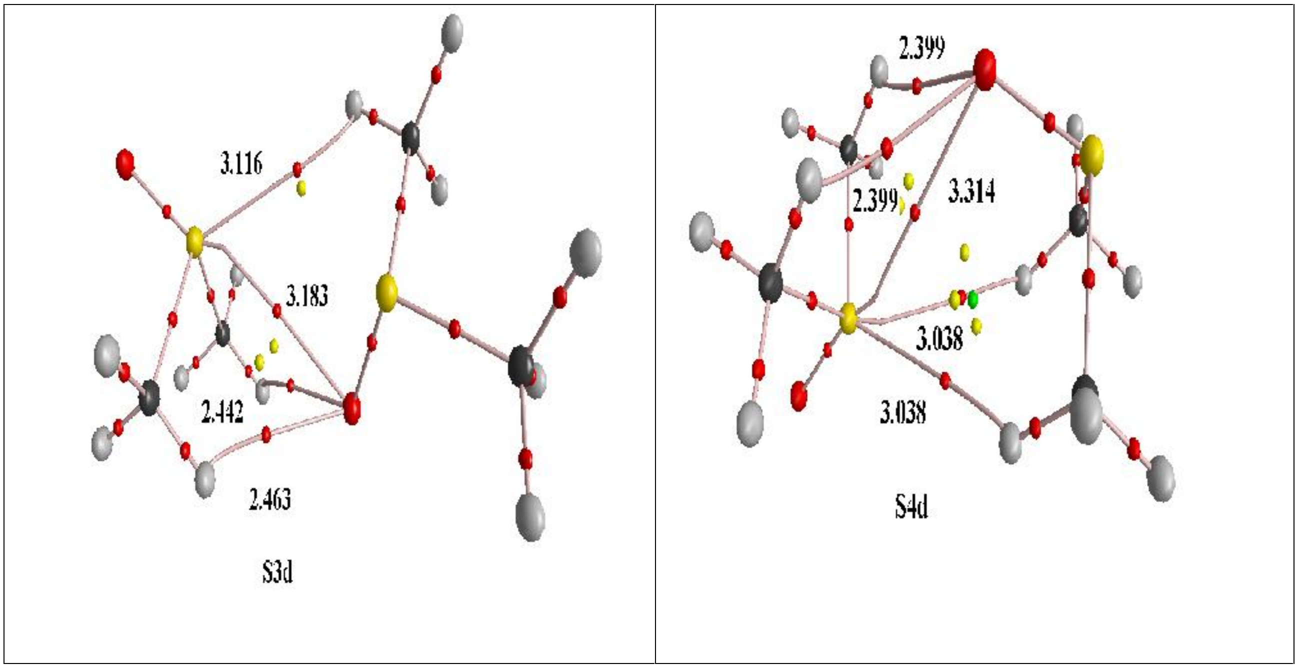


Figure 2. Molecular graph of the dimer minima obtained at the M05-2x/aug-cc-pVDZ computational level. The red and yellow dots represent the position of the bond and ring critical points, respectively. The interatomic distances (Å) of those atoms that shows intermolecular interactions.

The principal intermolecular interaction within the most stable minimum S2d corresponds to a cyclic structure with three C–H···O interactions. There is also an interaction of the oxygen lone pair with the MEP positive region surrounding the sulfur atom (S···O interaction). This kind of interactions has been named as orthogonal interactions [38-40]. We could locate three additional minima on the potential energy surface of dimers. S1d presents a pair of CH···O hydrogen bond interaction and a pair of orthogonal S···O interactions. S3d present a bifurcated CH···O interactions along with CH···S and S···O interactions. Finally, the S4d dimer is an interesting structure that presents a pair of CH···O and CH···S bifurcated interactions along with an S···O orthogonal interaction.

The topological analysis of the electron density within the Atoms in Molecules (AIM) theory characterized those points of space where the gradient is null (critical points). Based on the number and sign of the eigenvalues of these critical points they are classified as bond critical point (3,-1), ring critical points (3,+1) and cage critical points (3,+3). The bond critical points are located along a maximum electron density trajectory that connects two atoms, known as bond path. In Figure 2, the corresponding critical points and bond path of the dimers obtained are represented showing a variety of complex graph forms (Figure 2). Thus, S1d presents a bcp between the oxygen of DMSO molecule with sulfur and hydrogen atoms of another molecule. In the S2d complex, only a bcp is observed between the oxygen and sulfur atoms of the two molecules and three bcp between oxygen of one DMSO molecule with two hydrogen of two methyl group of another DMSO molecule. In the S3d complex, a bcp between sulfur of one DMSO with hydrogen and oxygen of another molecule along with two bcp between oxygen of one DMSO molecule with two hydrogen of two methyl group of another DMSO molecule are presented. Finally, S4d presents three bcp between oxygen of one DMSO molecule with two hydrogen of two methyl group of another DMSO molecule and sulfur atom. In addition, three bcp between sulfur of one DMSO molecule with two hydrogen of two methyl group of another DMSO molecule and oxygen atom are presented.

The results obtained for the electron density, its Laplacian, and kinetic (G) and potential electron energy density (V) at the bond critical points are evaluated at the M05-2x/aug-cc-pVDZ level and displayed in Table 3. A G_C/V_C ratio greater than 1 generally indicates a noncovalent interaction with covalent nature introduced as the ratio becomes smaller than unity. The small value of the electron density and the positive value of the Laplacian and G_C/V_C grater than 1 indicate that these intermolecular bonds correspond to weak interactions as proposed previously [41,42].

Table 3. Electron density, Laplacian and Total energy density (a.u.) of the intermolecular bond critical points

	Interaction	**Distance(Å)**	**ρ_{BCP}**	**Laplacian**	**-G/V**
S1d	O…H	2.339	0.0148	0.0460	1.023
	S…O	2.339	0.0116	0.0403	1.127
S2d	O…H	2.240	0.0151	0.0490	1.052
	O…H	2.272	0.0140	0.0415	1.021
S3d	O…H	2.269	0.0150	0.0422	0.985
	S…O	3.138	0.0093	0.0316	1.170
	O…H	2.442	0.0104	0.0354	1.106

S4d	O…H	2.463	0.0114	0.0350	1.030
	S…H	3.116	0.0060	0.0174	1.317
	S…O	3.186	0.0101	0.0308	1.087
	O…H	2.399	0.0111	0.0358	1.070
	S…H	3.038	0.0061	0.0162	1.213
	S…O	3.314	0.0074	0.0236	1.125

In order to obtain insights of the source of the interactions, the Natural Energy Decomposition Analysis (NEDA) within the NBO methodology has been carried out (Table 4). In all the complexes, the most important stabilizing component is the charge transfer one followed by the electrostatic one, except in S1d. Similar results have been described for water clusters stabilized by conventional red shifting hydrogen bonds [32]. The polarization term only became important in the S1d complex which shows a different pattern to the other ones.

Table 4. NEDA components (kcal/mol) f the interaction energy calculated at the M05-2x/aug-cc-pVDZ computational level

	S1d	**S2d**	**S3d**	**S4d**
Charge Transfer	-17.59	-22.21	-14.18	-14.67
Electrostatic	-15.31	-16.39	-10.78	-10.18
Polarization	-25.48	-21.64	-13.52	-11.49
Exchange-Correlation	-14.12	-13.81	-10.44	-9.78
Total Electronic deformation	62.96	63.11	41.34	38.41

The NCI (noncovalent interactions) index, based on the reduced gradient of the electron density, has been calculated to identify attractive and repulsive interactions with the NCI program [43] and plotted with the VMD program. As depicted in Figure 3, the green colors in nocovalent regions of studied complexes show weak nature of interactions in complexes pairing two DMSO molecules.

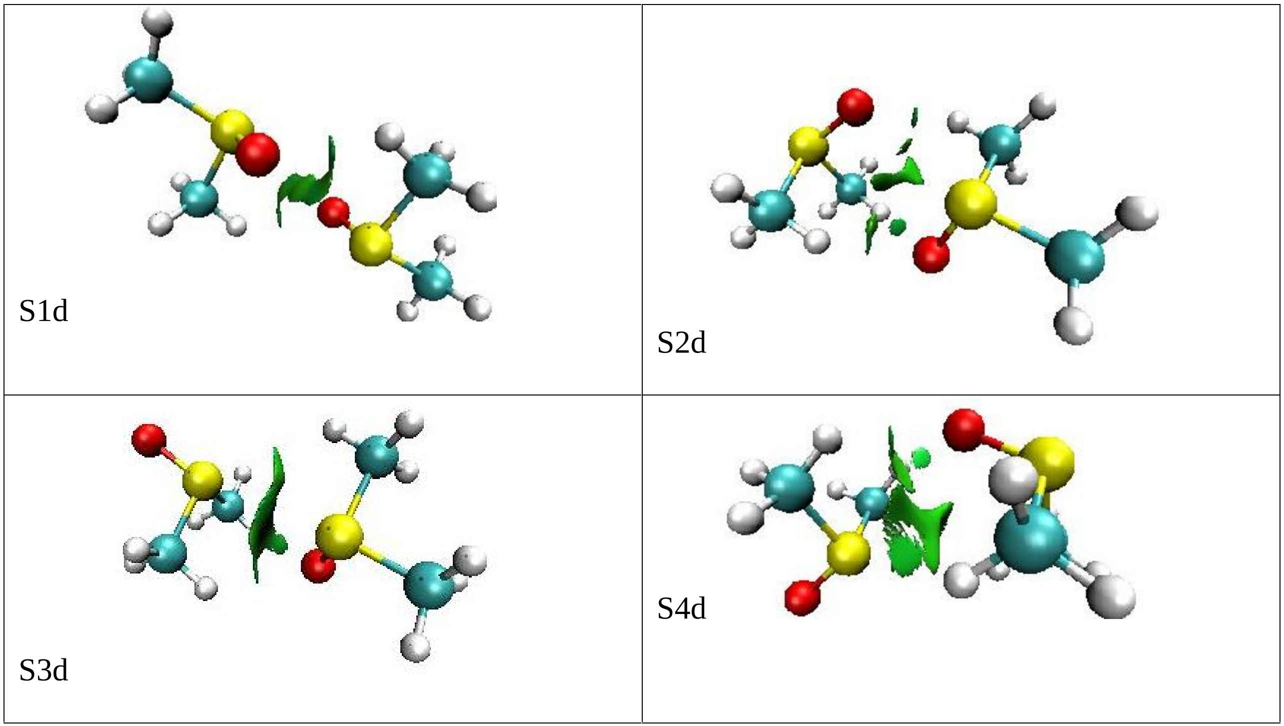


Figure 3. Noncovalent region between interacting atoms in complexes pairing DMSO molecules

Let us compare the results of the present study with those of previous studies regarding association of DMSO molecules. According to the recent quantum-chemical calculations [44], dipole···dipole interactions are the main forces leading to the aggregation of molecules into dimers in vapor, whereas the MD, X-ray, and neutron diffraction results [44] show that no dimers or chains of molecules interacting by dipole···dipole forces are formed in the liquid state, but only a slight preference for antiparallel orientation of S=O groups was observed. There is also evidence from the X-ray and neutron diffraction and from MD simulations of the existence of intermolecular hydrogen bonds CH···O in liquid DMSO [44]. The structural studies of DMSO revealed very short CH···O contacts, approaching 2.3 Å [45], which is consistence with calculated values of CH···O distance in the range between 2.24-2.46 Å in the present study. Finally, our calculations at M05-2x/ aug-cc-pVDZ computational level reveals more stability for structure with antiparallel orientation of S=O groups that pairing with three C–H···O and a S···O interactions(S2d) than structure stabilized via dipole-dipole interaction (S1d) and other local minimums located on the potential energy surface of DMSO dimers.

Conclusion

A theoretical study of dimers of the DMSO molecule have been carried out by means of DFT (M05-2x/ aug-cc-pVDZ) calculations. Four structures have been characterized for the dimers. The most stable conformers of dimers at DFT level is cyclic structure with antiparallel orientation of S=O groups that pairing with three C–H…O and a S…O interactions.

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Supporting Information Available

Optimized geometries of the complexes at the M05-2x/ aug-cc-pVDZ computational level.

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