Journal of Molecular Graphics and Modelling 81 (2018) 50–59

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Topical Perspectives

Nature of bonding and cooperativity in linear DMSO clusters: A DFT, AIM and NCI analysis

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ARTICLE INFO

Article history:
Received 6 January 2018
Received in revised form
22 February 2018
Accepted 22 February 2018
Available online 2 March 2018

Keywords:
AIM
Cooperativity
DFT
DMSO
Solvents

ABSTRACT

This study aims to cast light on the nature of interactions and cooperativity that exists in linear dimethyl sulfoxide (DMSO) clusters using dispersion corrected density functional theory. In the linear DMSO, DMSO molecules in the middle of the clusters are bound strongly than at the terminal. The plot of the total binding energy of the clusters *vs* the cluster size and mean polarizabilities vs cluster size shows an excellent linearity demonstrating the presence of cooperativity effect. The computed incremental binding energy of the clusters remains nearly constant, implying that DMSO addition at the terminal site can happen to form an infinite chain. In the linear clusters, two σ-hole at the terminal DMSO molecules were found and the value on it was found to increase with the increase in cluster size. The quantum theory of atoms in molecules topography shows the existence of hydrogen and S═O···S type in linear tetramer and larger clusters. In the dimer and trimer S═O···O═S type of interaction exists. In 2D non-covalent interactions plot, additional peaks in the regions which contribute to the stabilization of the clusters were observed and it splits in the trimer and intensifies in the larger clusters. In the trimer and larger clusters in addition to the blue patches due to hydrogen bonds, additional, light blue patches were seen between the hydrogen atom of the methyl groups and the sulphur atom of the nearby DMSO molecule. Thus, in addition to the strong H-bonds, strong electrostatic interactions between the sulphur atom and methyl hydrogens exists in the linear clusters.

1. Introduction

Dimethyl sulfoxide [DMSO] is an aprotic solvent with high dipole moment (3.96 D) and is miscible in organic and aqueous media [1]. Owing to the amphiphilic nature of DMSO and its lower activity on cell membranes they are frequently used as a solvent in biological studies and as a vehicle for drug therapy [2]. The boiling and melting point of DMSO is 189° C and 19° C, whereas that of Dimethyl sulfide is 37.3 and −98° C. The presence of extra oxygen atom in DMSO, has resulted in the such an unequivocal property for DMSO and has created interest towards the study on DMSO. Various experimental measurements made for DMSO indicates, that it is a highly associated liquid [3,4]. X-ray crystal structure of DMSO molecule has demonstrated the existence of CH···O hydrogen bonds, which can be altered using pressure and temperature [5]. Various molecular properties, such as geometries and vibrational frequencies, as well as physical properties of materials, are influenced by solvation using the intermolecular interactions, especially the hydrogen bonds (H-bonds) that exists between the solvent and the material [6,7]. Hence, much interest has been devoted to understanding the nature of intermolecular interactions especially that exists in the solvents [8–10].

Over the past decades, numerous theoretical and experimental studies have been devoted to studying the geometry and bonding in DMSO [11–13]. X-ray and neutron diffraction studies had satisfactorily elucidated the intermolecular geometry of DMSO in the liquid state. Furthermore, liquid DMSO is relatively unstructured, with a slight preference for the antiparallel ordering of the S–O dipoles [14]. High pressure Raman spectroscopic studies conclude that pressure favors the formation of aggregates and results in a more ordered local structure compared to the structure at ambient pressure [15]. A recent study shows that DMSO exists in α and β -phase. At 140 MPa, the crystal structure exists in α-phase and is dominated by electrostatic attraction and the CH···O hydrogen bonds and exists with a like chain structure. At a pressure of 540 MPa, the methyl H···H contacts are formed in the β–phase [5].

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https://doi.org/10.1016/j.jmgm.2018.02.010
1093-3263/

Varnali showed using semiemprical PM3 calculations, the existence of trimers in a linear fashion, which represents segment for higher polymers [16]. Very recently Venkataramanan et al. studied the nature of the interaction between the $(DMSO)_n$ (n = 2–13) clusters and observed the existence of cooperativity, which has led to the formation of oroborus structure [17].

The cooperativity is one of the interesting characteristics of noncovalent interactions, which find application in supramolecular chemistry [18,19]. Study of cooperative intermolecular interactions of molecules in the gas phase is important in understanding the process of solvation/reactivity, which is vital to control the chemical behavior of compounds and biological systems. The cooperativity, anti-cooperativity and non-cooperativity in small clusters of methanol, water and formaldehyde have been studied recently [20]. Formaldehyde clusters did not show cooperativity, while in methanol cooperativity is dominated by the presence of –OH group [21]. The nature of interaction in one-dimensional NCBr and NCCl are examined using DFT methods. The study suggest that electron localization leads to cooperative changes in the bond strength and electrostatic interaction to dominant in those clusters [22]. The three-body terms were found to determine the relative stabilities especially on the trimers to pentamer water clusters [23]. In a recent study hydrogen bonding cooperativity was found to strengthen the σ-hole interaction in the $FCl\cdots(NCH)_n$ system. However, in the larger cluster with n > 5, the effect saturates [24,25]. Song et al. studied the linear *trans*-Diazene and *cis*, *trans*-cyclotriazane clusters using the hybrid functionals, and found that cooperative phenomena are pervasive in the circular clusters, however, the neglected dispersion energies and the nonadditive energies in the calculation may affect the computed properties [26,27].

In the present work we carry out a thorough investigation of the structural growth and nature of interaction in the linear $(DMSO)_n$ clusters (n = 1–8) using the dispersion corrected density functional theory. Special attention has been paid to the hydrogen bond cooperativity effect and the nature of interactions between DMSO molecules using the pairwise energy calculation, atoms-in-molecules (AIM) and non-covalent interactions-reduced density gradient (NCI-RDG) analysis. This manuscript is organized as follows. The next section gives the computational details. Results are presented and discussed in the third section. Conclusions are inferred in the last section.

2. Computational details

All density functional theory calculations reported here were carried out using the Gaussian 09 (revision D.01) suite of programs [28]. The geometries of the linear DMSO clusters were optimized without any geometrical constraints using the dispersion corrected B3LYP functional and 6–311++G (d,p) basis set. It is well known that Grimme's dispersion correction D3 is essential in systems which are dominant by noncovalent interactions [29,30]. The counterpoise correction is sensitive to the use of diffuse basis functions. The use of diffuse basis functions can considerably reduce the basis set superposition errors (BSSE). Very recently, Baerends et al., have pointed out that the use of larger basis set is essential to get accurate result, than performing a counterpoise correction. Furthermore, the use of larger basis set significantly reduces the BSSE and all the errors arising from the basis set truncation [31,32]. The use of B3LYP-D3/6–311++G(d,p) method in these calculations is justified as a compromise between reliable results and reasonable computational cost. Harmonic vibrational frequencies were carried out on the reported structures and are found to have no negative frequencies, indicating that they are all in the minima in the potential energy surface and are not the saddle points.

Total binding energies for the $(DMSO)n$ clusters are calculated as

$$BE = E(DMSO)n - nE(DMSO) \quad (1)$$

while incremental binding energy for the successive DMSO addition is computed as

$$IBE = E(DMSO)n - E(DMSO)n\text{-}1 - E(DMSO) \quad (2)$$

where the $E(DMSO)$ is the monomer energy and $E(DMSO)n$ and $E(DMSO)n\text{-}1$ are the energy of the nth and n-1st DMSO clusters, which are determined at the same level of theory.

Wave function analysis–surface analysis suite (WFA-SAS) suite of the program was employed to calculate quantitative electrostatic potential and to visualize the 3D surface [33]. The electrostatic potential in the space around a molecule can be evaluated rigorously using the formula,

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|} \quad (3)$$

V(r) is the potential created at any point r by the nuclei and electrons of the molecule; Z_A is the charge on nucleus A, located at R_A, and ρ(r) is the molecule's electronic density. The sign in any region depends upon the effects of the nuclei (positive) or the electrons (negative) predominate. The surface was considered with 0.001 a.u. (electrons/$Bohr^3$) contour of the electronic density, as suggested by Bader et al. [34,35]. When plotted on a molecular surface, V(r) is designated VS(r) and its local most positive and most negative values (of which there may be several) are identified as the $VS,_{max}$ and $VS,_{min}$.

In order to gain further insights into the bonding that exists, topological analysis has been performed using AIMALL package and the corresponding wave functions were generated at the B3LYP-D3/6-311 + G(d,p) level of theory [36]. The characteristics of the bond critical point (BCP) were obtained in terms of the electron density (ρ) and it's Laplacian ($\nabla^2\rho$), the total electron energy density (H(r)), the potential electron energy density (V(r)), and the Lagragian kinetic energy (G(r)). More details about AIM analysis can be found in our previous publications [37,38].

Noncovalent interaction (NCI)-reduced density gradient (RDG) method has been used to visualize the nature of interactions between the molecules. The NCI indices rely on the electron density and the reduced density gradient (s), as shown in equation

$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}} \quad (4)$$

By using the three components along the three principal axes of maximal variation, the Laplacian can be expressed as $\nabla^2 = \lambda_1 + \lambda_2 + \lambda_3$. Blue, green, and red color codes are used to represent stabilizing hydrogen bonding, weak van der Waals, and destabilizing steric interactions, in the NCI isosurfaces. The NCI-RDG analysis is performed using the MultiWfn program with larger size grids [39]. The visualization of the gradient isosurface in real-space was made using Chemcraft program [40].

3. Results and discussions

The X-crystal packing mode for DMSO molecule was found to alter with pressure and temperature [5]. At room temperature, the X-ray structure appears like two antiparallel linear infinite chains stacking in opposite direction. The electrostatic attraction is the driving force which helps in the assembly of the linear chains into a