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AB-INITIO COMPUTATIONAL STUDIES OF THE STRUCTURAL CONFORMATIONS OF DIMETHYLBIS (METHYLDITHIO CARBONATO) STANNUM (IV)

Bing Chuan Chua

Chemical Sciences Programme, School of Distance Education, Universiti Sains Malaysia

Lee Sin Ang*

Faculty of Applied Sciences, Universiti Teknologi MARA, Malaysia

Mohamed Ismail Mohamed-Ibrahim

Chemical Sciences Programme, School of Distance Education, Universiti Sains Malaysia

Shukri Sulaiman

Physical Sciences Programme, School of Distance Education, Universiti Sains Malaysia

ABSTRACT

The orientation of the dithiocarbonate ligands in dimethylbis(methyldithiocarbonato)stannum(IV) in a previous investigation involving experimental and theoretical studies are not in agreement. In this study, we modeled a cluster of 11 molecules in order to include the crystal packing effect. By performing ab initio calculations on the many-molecule cluster, we found that the S-, S-; S-, O-orientation is the most stable configuration for the ligands which agrees with the experimental results in the previous work. We show that the interactions between molecules would affect the orientations of the ligands, thus it is necessary to include neighbouring molecules in the conformational analysis. Furthermore, we also discuss a few possible interactions between the molecules that contribute to the stabilization of the solid state structure.

Keywords: Diorganotin complex, Conformational analysis, Hartree-Fock, Crystal packing, Cluster method.

1. INTRODUCTION

Organotin compounds are defined as those containing at least one Sn−C bond. They have many applications, such as catalysis (Cinnamon *et al.*, 1980; Ratier *et al.*, 1992), agrochemicals (Crowe, 1987; Saxena *et al.*, 1988) and as potential antitumor agents (Sherman *et al.*, 1988; Tabassum *et al.*, 2006). In order to understand the behavior of organotin complexes, insights into their molecular structure is desirable. The present investigation focused on a diorganotin dimethyldithiocarbonate complex, $Me_2Sn(S_2COMe)_2$ (herein labelled as structure **1**). This complex is a member of a series of substituted diorganotin dimethyldithiocarbonate complexes

$R_2Sn(S_2COMe)_2$, where their structures have been determined experimentally by Mohamed-Ibrahim et al. (Mohamed-Ibrahim *et al.*, 2000). The two other complexes are R=phenyl (structure **2**) and R=methylphenyl (structure **3**). The orientations of the dithiocarbonate ligands in **1**, **2** and **3** are shown in Table 1. It can be seen from Table 1 that structures **2** and **3** adopt the S-, S- ; S-, S-orientation mode that have been similarly observed for other dialkyl and diaryl tin dithiocarbonate while structure **1** has the S-, S-; S-, O- orientation. Thus, the structure of complex **1** was classified as odd and do not follow the trend observed for the $R_2Sn(S_2COMe)_2$ series.

Quantum mechanical DFT calculations on these complexes **1**, **2**, and **3** have been performed by the same researchers and they found that the S-, O-; S-, O- orientation is the preferred orientation for all three complexes (Mohamed-Ibrahim *et al.*, 2000). Cogordan et al. (Barroso-Flores *et al.*, 2006) have claimed to have performed an improved theoretical investigation on the same set of three complexes. Even though a higher quality basis set was used, their results still disagree with the experimental findings, in that the stable conformation for complex **1** is S-, S-; S-, S. It should however be noted that the geometry optimization calculations in these previous works had been performed on a single representative molecule in the gas phase, thus, the intermolecular interactions of the molecule with its neighbours had been ignored.

Due to the contradictory results from the theoretical investigations as stated above, we have performed theoretical calculations on structure **1**, with improvement on the intermolecular interactions. It has been suggested that despite the absence of intermolecular forces such as hydrogen bonding, the stabilization gained by maximizing intermolecular interaction in the crystalline phase is sufficient to induce a rearrangement of the ligand orientation (Buntine *et al.*, 1998). For the present study, we focused on R = methyl since experimentally, it is the odd case in the $R_2Sn(S_2COMe)_2$ series, and also, previous theoretical studies have predicted two different conformations. We perform these calculations on an 11-molecule system, where 10 neighbouring molecules are located around a central molecule. In this many-molecule cluster, the interactions of the molecule with its neighbours would be taken into account, hence the portrayal of the crystal packing effects.

2. METHODOLOGY

Fractional coordinates of the solid state structure of the dimethyltin complex **1** were obtained from the paper reported by Mohamed-Ibrahim et al. (Mohamed-Ibrahim *et al.*, 2000). The structure of the complex is shown in Figure 1, where the dithiocarbonate ligands are in the S-, S-; S-, O-orientation, and $X(n)$ (n = 1, 2, 3, 4) are dummy atoms. These dummy atoms were used to specify the dihedral angle to be rotated. In performing the calculations, each of the ligands was rotated a full circle, in 5° steps, as shown by the arrows in Figure 1. Rotation of the S-, S- orientated ligand is designated R1 while R2 describes rotation of the S-, O- orientated ligand. Only one of the ligands is rotated at any one time. Rotating R1 to 175° (while holding R2 fixed at the original position) would give the S-, O-; S-, O orientation, while rotation of R2 to 185° (with R1 fixed the original position) would give the S-, S-; S-, S orientation.

To generate the 11-molecule system, only molecules within a 10 Å radius from the tin atom of the central molecule were selected. Molecules further than this radius were not considered as they were not expected to interact significantly with, and affect the geometry of the central molecule. The coordinates of the neighbouring molecules were generated based on the symmetry operations associated with the space group of the dimethyltin complex.

We used the Hartree-Fock cluster method, coupled with Gaussian basis sets in obtaining the wavefunctions of the systems considered in this study. In order to perform the calculations efficiently, the 3-21G basis set is used. The 3-21G basis set is a split valence basis set where the valence electrons are provided with extra functions for increased flexibility than those of the minimal basis set. Higher Pople-type basis sets, for example, 6-31G* is not suitable because this basis set is not defined for the Sn atom. Ab initio calculations were performed using the Gaussian98 suite of programs (Frisch *et al.*, 1998), with GaussView (Dennington *et al.*, 2006) providing the visualizations to the systems under considerations.

3. RESULTS AND DISCUSSION

Our preliminary results (not shown) for the single molecule using HF/3-21G model chemistry agrees with the orientation predicted in a previous study, the S-,O-; S-, O- orientation. In the following parts, we concentrate on our results of the 11-molecule system. The relative energies from the rotations of the ligands are presented in Figures 2 and 3 for the rotation of the dihedral angle of the S-, S- orientated and S-, O- orientated ligands, respectively.

In Figure 2, the curve showed that the global minimum (the lowest energy point anywhere on the potential surface scan) is located at 0° (corresponding to the S-, S-; S-, O- orientation mode). Since the dithiocarbonate ligand is capable of coordinating in two possible orientation modes, another minimum can be seen at 175° (corresponding to the S-, O-; S-, O- orientation mode). This point is the local minimum, which is the lowest point in some limited region of the potential surface scan. The energy difference between the global minimum and local minimum is 16.25 kJ mol^{-1}. The curve in Figure 2 is unsymmetrical with respect to the local minimum as the energy barrier located at around 90° is higher than that at around 270°. The difference in barrier energies at 90° and 270° is 573.72 kJ mol^{-1}.

For rotation of the S-, O- orientated ligand (Figure 3), the global minimum exists at 0° (corresponding to the S-, S-; S-, O- orientation mode) and the local minimum is at 185° (the S-, S-; S-, S- orientation mode). The local minimum was found to be higher than the global minimum by 575.25 kJ mol^{-1}. The curve is unsymmetrical as the energy barrier at 270° is slightly higher than that at 95°, giving a difference of 1141.66 kJ mol^{-1} in the barrier energy.

The energy barrier associated with rotation of the S-, O- oriented ligand is much higher compared to In In order to have a clearer picture for the S-, S- and S-, S-O rotations, the two rotations were combined as in Figure 4. In Figure 4, it can be seen that the energy barrier associated with rotation of the S-, O- orientated ligand is much higher compared to that for the rotation of the S-, S- orientated ligand. At the maximum at 95° and 270°, the difference in energy is 14505.98 kJ mol^{-1} and 16199.31 kJ mol^{-1} respectively. This can be attributed to the increased electronic interactions between neighbouring molecules in the crystal lattice environment for rotation of the S-, O- orientated ligand compared to that for the S-, S- orientated ligand. The detailed diagrams of the interactions (where the relevant atoms were labelled) are shown in Figures 5, 6, 7 and 8. In these figures, the interactions between OCH_3−, CHO−, and S− between central molecule and its neighbouring molecules are shown. To avoid a crowded representation of the molecules, only 3 molecules are included in the figures. The distances between the atoms of the central molecule that are closest to those of its nearest neighbours are collected in Tables 2 and 3. The central molecule is designated ‘a’ and its two neighbours ‘b’ and ‘c’ respectively. Any distances approaching the sum of the van der Waals radii of the atoms in questions indicate increased interactions, and distances which are less than the covalent radii of the pair of atoms are energetically unfavourable. The covalent and van der Waals’ radii for the relevant atom-pairs are listed in Table 4.

From Table 2, it can be seen that rotation of the S-, S- orientated dithiocarbonate ligand through to R1 = 90° and 270° caused certain atoms on the central molecule and those of its closest neighbours to be brought closer together. For the C···S and H···S interactions, the interatomic distance decreased to below the sum of the van der Waals’ radii for these atoms. There is also a decrease in the S···O distance, but to a lesser extent. In addition, the data in Table 3 shows that rotation of the S-, O- orientated ligand produced a more dramatic change. While some of the interatomic distances decreased to below the sum of the van der Waals’ radii for the atoms, there are also interactions where the interatomic distances decreased to below the sum of the covalent radii of the atoms, indicating extreme interactions. Thus, the much higher increase in the torsion potential energy on rotation of the S-, O- orientated ligand as compared to rotation of the S-, S- orientated ligand (Figure 4) can be attributed to the increased intermolecular interactions as the distances became closer.

From the discussion above, the configuration where the $Me_2Sn(S_2COMe)_2$ molecules were arranged with the dithiocarbonate ligands in the S-,S-; S-,O- orientation mode (R1 = 0°, R2 = 0°) has the least interaction between the central molecule and its nearest neighbours, and is thus the most energetically stable arrangement of the molecules in the crystal lattice. This result agrees with the configuration found in the solid state structure (Mohamed-Ibrahim *et al.*, 2000). The use of 11-molecule cluster provided interactions that are absent from investigations using single molecule. The cluster method employed here provided a more realistic environment for the molecules. Disagreements of the previous calculations may be due to the neglect of the intermolecular interactions in their investigations.

Finally, it can be seen that the S-,S-;S-,S- orientation mode (after a R2 = 185° rotation of the S-,O- orientated ligand) gave a higher relative energy compared to the S-,O-; S-,O- orientation mode (after a R1 = 180° rotation of the S-,S- orientated ligand), which in turn has a higher relative energy compared to the S-, S-; S-, O- orientation mode (the initial orientation at R1 = 0° and R2 = 0°). Thus, the order of conformational stability of $Me_2Sn(S_2COMe)_2$ in a crystal lattice environment is predicted to be in the order.

S-, S-; S-, O- > S-, O-; S-, O- > S-, S-; S-, S-

4. CONCLUSIONS

Our calculations showed that it is important to include the intermolecular interactions in the conformational study of $Me_2Sn(S_2COMe)_2$ complex. The results from our calculations on the 11-

molecule system show that the most stable conformation for the $Me_2Sn(S_2COMe)_2$ complex is the S-,S-; S-,O orientation, which is in agreement with the experimental results. Furthermore, our results also show that for this complex, the S-, S-; S-, O- orientation is more stable than S-, S-; S-, S- orientation found for other members in the diorganotin dimethyldithiocarbonate series. Further validations to this trend, by varying basis set and level of theory, are being carried out and will be reported elsewhere.

5. ACKNOWLEDGEMENTS

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Table-1. Orientation modes of experimentally determined structures and geometry optimized structures of $R_2Sn(S_2COMe)_2$ (Mohamed-Ibrahim *et al.*, 2000).

$R_2Sn(S_2COMe)_2$	**Orientation mode of dithio carbonate ligands**	
	Experimentally determined structures	**Theoretical predictions**
1 (R = Me)	S-, S- ; S-, O-	S-, O- ; S-, O-
2 (R = Ph)	S-, S- ; S-, S-	S-, O- ; S-, O-
3 (R = Me, Ph)	S-, S- ; S-, S-	S-, O- ; S-, O-

Figure-1. A molecule of dimethyltin complex, where the ligands are in the S-, S-; S-, O-orientation.

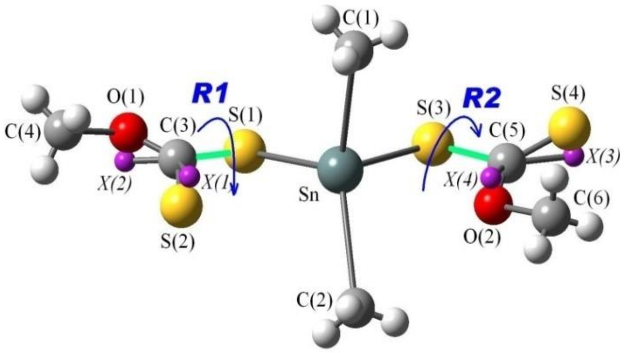


Figure-2. Torsion potential curve for rotation of the S-, S- orientated ligand (R1) in the dimethyltin complex in a 11-molecule crystal lattice system.

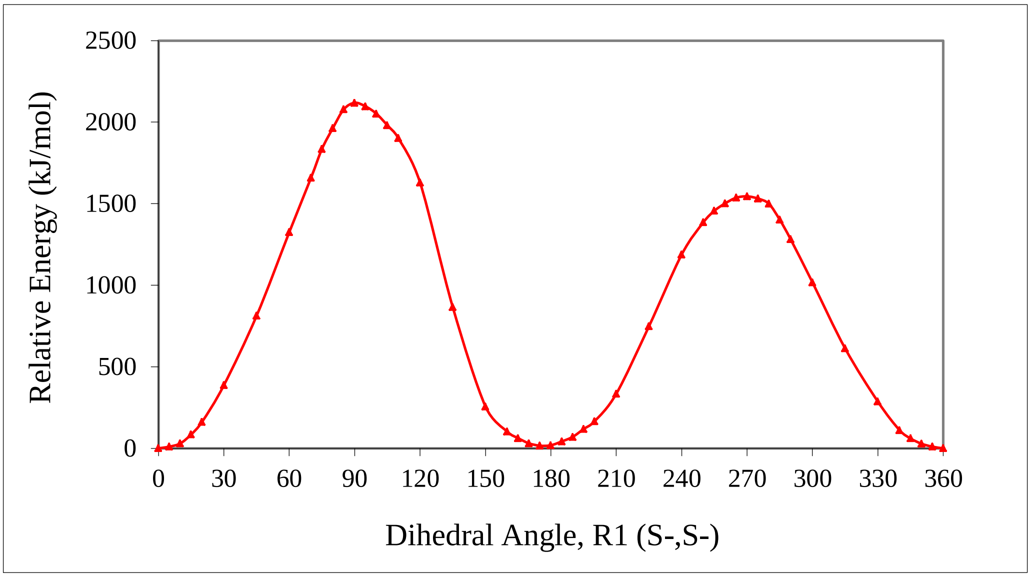


Figure-3. Torsion potential curve for rotation of the S-, O- orientated ligand (R2) in the dimethyltin complex in an 11-molecule crystal lattice system.

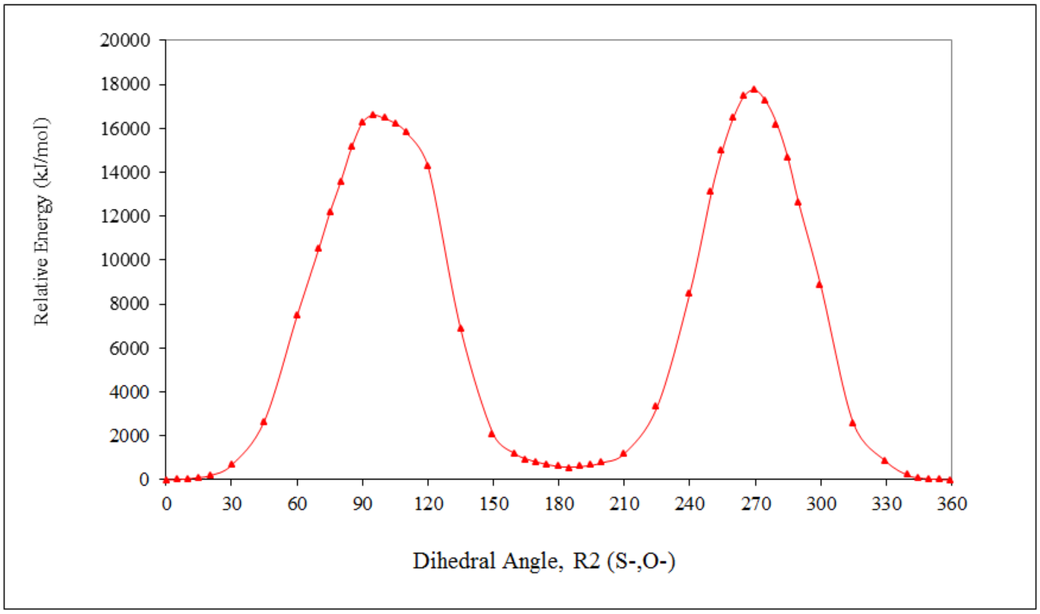
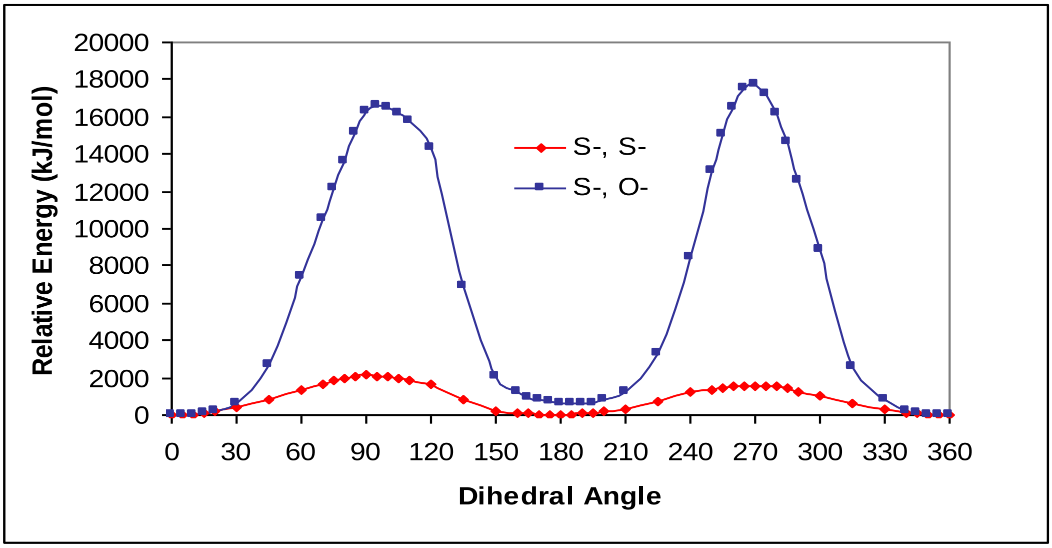


Figure-4. Torsion potential curve obtained for rotation of the R1 (S-, S-) and R2 (S-, O-) orientated ligands in the dimethyltin complex in an 11-molecule crystal lattice system.



A: Dihedral angle 0° indicating the S-, S-; S-, O- orientation mode

B: Dihedral angle 175° indicating the S-, O-; S-, O- orientation mode

C: Dihedral angle 185° indicating the S-, S-; S-, S- orientation mode

Figure-5. Close interactions between atoms of the central molecule and those of its nearest neighbour molecules with R1=90°, viewed along the 'p' axis. The $OCH_3 \cdots S$ interactions between molecules are marked with green broken lines.

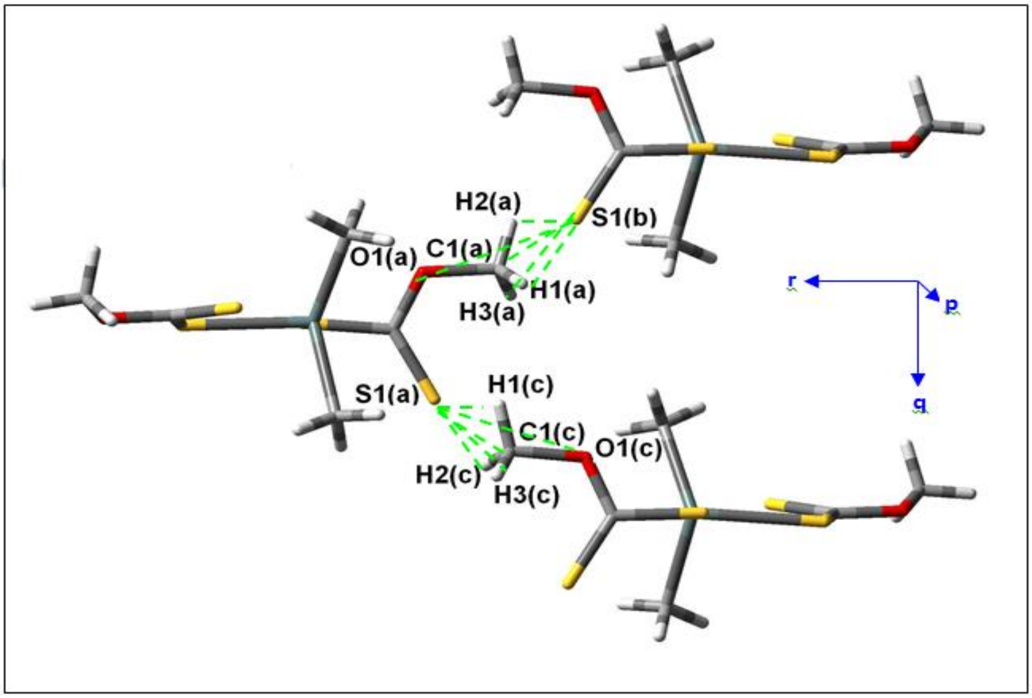


Figure-6. Close interactions between atoms of the central molecule and those of its nearest neighbour molecules with R1=270°, viewed along the 'p' axis. The $OCH_3 \cdots S$ interactions between molecules are marked with green broken lines.

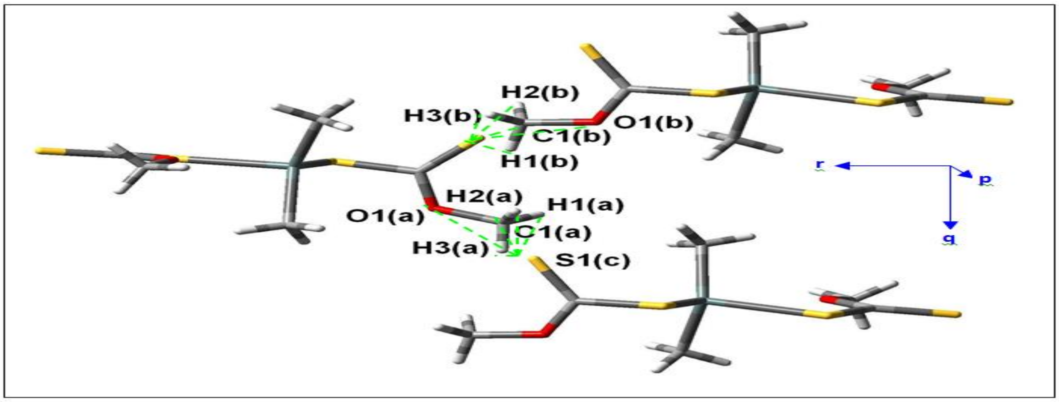


Figure-7. Close interactions between atoms of the central molecule and those of its nearest neighbour molecules with R2=95°, viewed along the 'p' axis. The $H_2 \cdots S$ interactions between molecules are marked with green broken lines. The CHO—S interactions between molecules are marked with red lines.

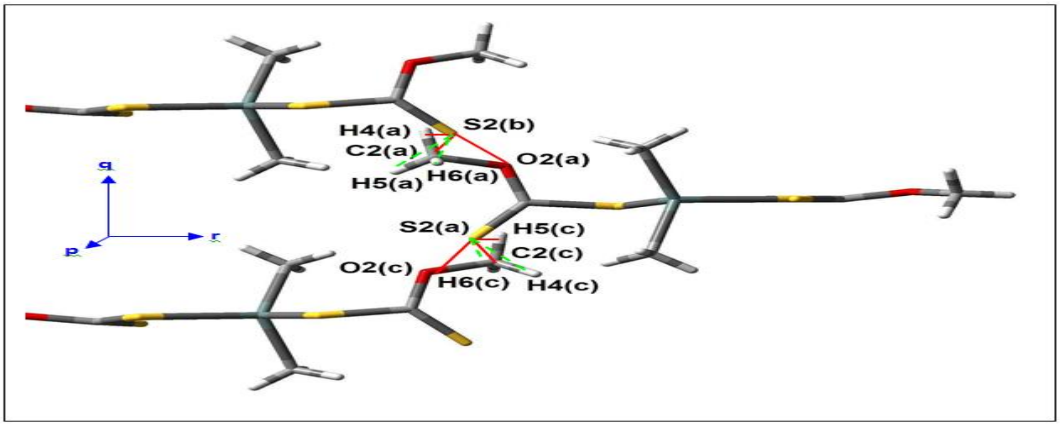


Figure-8. Close interactions between atoms of the central molecule and those of its nearest neighbour molecules with R2=270°, viewed along the 'p' axis. The $H_2 \cdots S$ interactions between molecules are marked with green broken lines. The CHO—S interactions between molecules are marked with red lines.

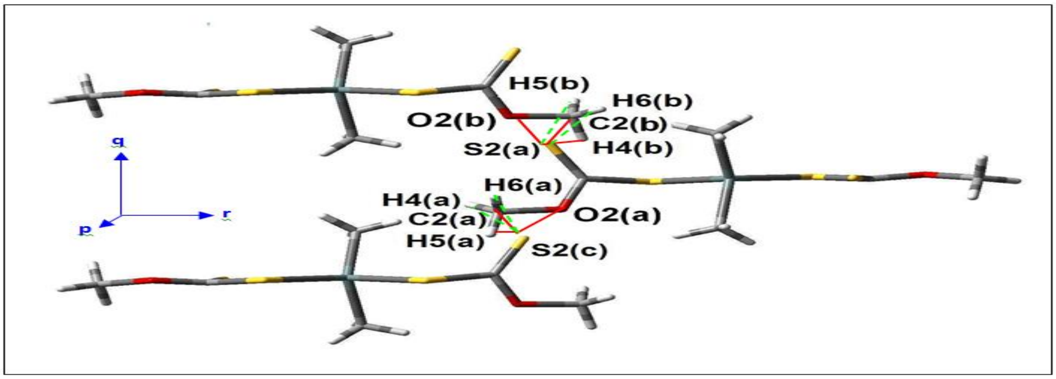


Table-2. Selected bond distance (Å) between atoms of the central molecule and those of its nearest neighbour molecules with R1 at 0°, 90° and 270° respectively. The values in green denotes a bond distance of less than the sum of the van der Waal's radii of the atoms involved.

Atomic Interaction	Rotation		
	R1 = 0°	**R1 = 90°**	**R1 = 270°**
S1(a)···C1(c)	4.31	2.32	2.31
S1(a)···H1(c)	3.34	1.82	1.82
S1(a)···H2(c)	4.80	2.04	2.04
S1(a)···H3(c)	4.59	2.97	2.96
S1(a)···O1(c)	4.99	3.38	3.67
C1(a)···S1(b)	4.31	2.31	2.31
H1(a)···S1(b)	4.60	2.03	2.03
H2(a)···S1(b)	3.34	1.80	1.80
H3(a)···S1(b)	4.80	2.96	2.97
O1(a)···S1(b)	5.00	3.36	3.67

Table-3. Selected bond distance (Å) between atoms of the central molecule and those of its nearest neighbour molecules with R2 at 0°, 95° and 270° respectively. The values in green denotes a bond distance of less than the sum of the van der Waal's radii of the atoms involved. The values in red denotes a bond distance of less than the sum of the covalent radii of the atoms involved.

Atomic Interaction	Rotation		
	R2 = 0°	**R2 = 95°**	**R2 = 270°**
S3(a)···C2(b)	3.86	1.23	1.23
S3(a)···H4(b)	3.31	0.81	0.89
S3(a)···H5(b)	4.77	2.03	2.03
S3(a)···H6(b)	3.98	1.80	1.84
S3(a)···O2(b)	3.99	1.56	1.45
C2(a)···S3(c)	3.85	1.22	1.23
H4(a)···S3(c)	4.75	2.04	2.01
H5(a)···S3(c)	3.30	0.80	0.88
H6(a)···S3(c)	3.97	1.79	1.83
O2(a)···S3(c)	4.01	1.56	1.46

Table-4. Sum of the covalent and van der Waals radii (Å) for selected atom-pairs (Bondi, 1964).

	covalent radii	**van der Waals radii**
C···S	1.81	3.50
H···S	1.41	3.00
S···O	1.78	3.32