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Der Pharma Chemica, 2015, 7(10):202-211
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

A DFT study of the structure and bonding in 1, 3-dithia -2-arsacyclopetane derivative with oxygen and sulfur donor legends

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ABSTRACT

A density functional computation of few mixed 1,3-dithia-2-arsacyclopentane (1,3-D-2-A) derivatives with sulfur and oxygen donor legends such as thiobenzoic acid, and benzoic acid, have been performed with the objective of exploring their electronic, structural and spectral behavior. While complexes with thiobenzoic acid are abbreviated as compound1, the complexes with benzoic acid are termed as compound2. The geometrical parameters, band gap and assignment of important vibration frequencies are reported. The As-S (ligands) bond length 2.409 is slightly higher than As-S (1, 3-D-2-A) bond length. The two ring namely benzene and 1, 3-D-2-A are not co-planer. The C-S and C-O bonds are greater than C-C bond. In the two molecules under consideration As-S bond is > As-O bond. The total energies of the two compounds are found to -3851.61 a.u and -3530.86 a.u. suggesting sulfur complex to be much more stable compared to oxygen complex. On the other hand compound2 is more polar than compound1. The energy gap in the two complexes is found to be 4.33 and 4. 77 eV respectively. An important feature of the two complexes is that while 1 exists in only one stable form the compound 2 undergoes rotation about O2-C3 and O2-As bonds to produce one more conformer in which benzene ring is cis to the 1, 3-dithia -2-arsacyclopetane group. The compound 2 is stabilized by hydrogen bonding.

Keywords. 1, 3-dithia -2-arsacyclopetane, DFT, Arsenic

INTRODUCTION

The chemistry of arsenic, antimony and bismuth compounds derived from organic ligands has been an active area of research for the last thirty years. The reasons for continues interest in these compounds can be attributed to their great structural diversity ranging from monomeric to polymeric supramolecular assemblies and their extensive technological applications.

Although arsenic and its compounds are popular as poisoning materials at high doses some of these materials find applications in industries and medicines as well. Organic compounds of arsenic are much less toxic than inorganic. Arsenic compounds find their applications as analytical reagents, cracking catalyst regenerators, fungicides and as antitumor agents. Its metal complexes are also used for vulcanization of rubber. Arsenic compounds also find applications as a preservative in pressure-treated lumber, pesticides, preservative in animal hides, additive to certain metals such as lead and copper , glass manufacturing. Arsenic metal is extensively used in semiconductor technology [1-23].

Recently, Chauhan et, al [24] reported the synthesis, characterization and antimicrobial studies of few 1, 3-dithia-2-arsacyclopetane derivative with oxygen and sulfur donor complexes. To the best of our knowledge, there is no report on the quantum mechanical study of the structure and bonding in such compounds. In the present study we report, A DFT level computation of the derivatives of 1, 3-dithia -2-arsacyclopetane with benzoic acid and thiobenzoic acid.

MATERIALS AND METHODS

All of the DFT [25, 26] calculations for the current problem were performed on a Pentium IV/ 1.6 GHz personal computer using the Gaussian 09W suite of programs [27]. The Becke 3LYP keyword, which invokes Becke three parameter hybrid method[28] using the correlation function of Lee et al [29,30,31] and 6-31G-basis set [32,33] was used to locate the optimized geometries of the mixed 1,3-dithia-2-arsacyclopentane (1,3-D-2-A) derivatives with oxygen and sulfur donor legends such as benzoic acid, thiobenzoic acid. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming the molecules belongs to Cs point group symmetry by combining the result of Gauss view programme [34] with symmetry consideration, vibrational frequency assignments were made.

RESULTS AND DISCUSSION

Geometry of the molecule.

Chauhan et al have reported a tentative geometry of the molecule on the basis of their spectroscopic data. It is concluded that ligands exhibit a monodented mode of attachment to the As (III) and suggested three – coordinated distorted pyramidal structure. X-Ray crystal structure data of the molecule is also not available [24]. In view of this optimized geometry of the molecule at DFT level becomes more relevant. The optimized geometry of the complex 1, 3-dithia-2-arsacyclopentane with thiobenzoic acid is shown in Fig.1. The geometry of the complex with benzoic acid can be obtained simply by replacing S with O shown in Fig.2. It is found that the calculated bond lengths are in conformity with the bond lengths expected from reported atomic radii [35]. The total energy is calculated to be -3851.61 a.u and -3530.86 a.u. for sulfur and oxygen ligands respectively suggesting sulfur complex to be more stable compared to oxygen complex. As-S bond length of the cyclopentane group is calculated to be 2.36 A^o in both the molecules. On the other hand As-S bond length of the As-S (ligands) is 2.409A^o in compound 1. These data suggest the AS-S (ligands) bond to be more covalent than As-S (cyclopentane) bond. The corresponding As-O bond length in the complex with O ligands is 1.87 A^o. On similar grounds it can be concluded that As-S bond is more polar compared to As-O bond. The S-C, C=O and C-C bonds of the ligands moiety are calculated to be 1.92, 1.22 1nd 1.48 A^o respectively. An important feature of the two compounds is that while molecule 1 remains in one stable conformer, the molecule 2 undergoes rotation about O2-C3 and O2-As bond to produce one more conformation. The low energy conformer can be named as cis conformers in which the benzene ring and R groups are cis to each other. On the other hand the high energy conformer can be named as Trans conformer in which the benzene ring is Trans to the R group. The cis conformer is stabilized by hydrogen bonding. The O1-H1 hydrogen bond length is 2.18 A^o . The detailed data on bond lengths is shown in fig- 1, fig-2 and Table 1.

Table 1. Various bond lengths in molecules 1 and 2 in A^O
$R = CH_2CH_2\ S_2As –$

Bond length	R-SCOC6H5	R-OCOC6H5	Bond length	R-SCOC6H5	R-OCOC6H5
C_1-H_1	1.09	1.08	C_3-C_4	1.48	1.47
C_1-H_2	1.09	1.08	C_4-C_5	1.40	1.40
C_1-C_2	1.51	1.51	C_5-C_6	1.39	1.39
C_2-H_3	1.09	1.08	C_6-C_7	1.40	1.39
C_2-H_4	1.09	1.08	C_7-C_8	1.39	1.39
C_2-S_1	1.92	1.92	C_8-C_9	1.39	1.39
C_1-S_2	1.90	1.91	C_4-C_9	1.40	1.40
S_1 – As_1	2.36	2.36	C_5-H_5	1.08	1.08
S_2 – As_1	2.35	2.33	C_6-H_6	1.08	1.08
As_1- S_3 / As_1-O_2	2.41	1.87	C_7-H_7	1.08	1.08
C_3 -S_3 / C_3-O_2	1.89	1.37	C_8-H_8	1.08	1.08
C_3– O_1	1.22	1.23	C_9-H_9	1.08	1.07
O1-H1		2.18			

The optimized geometry of the molecule 1 and 2

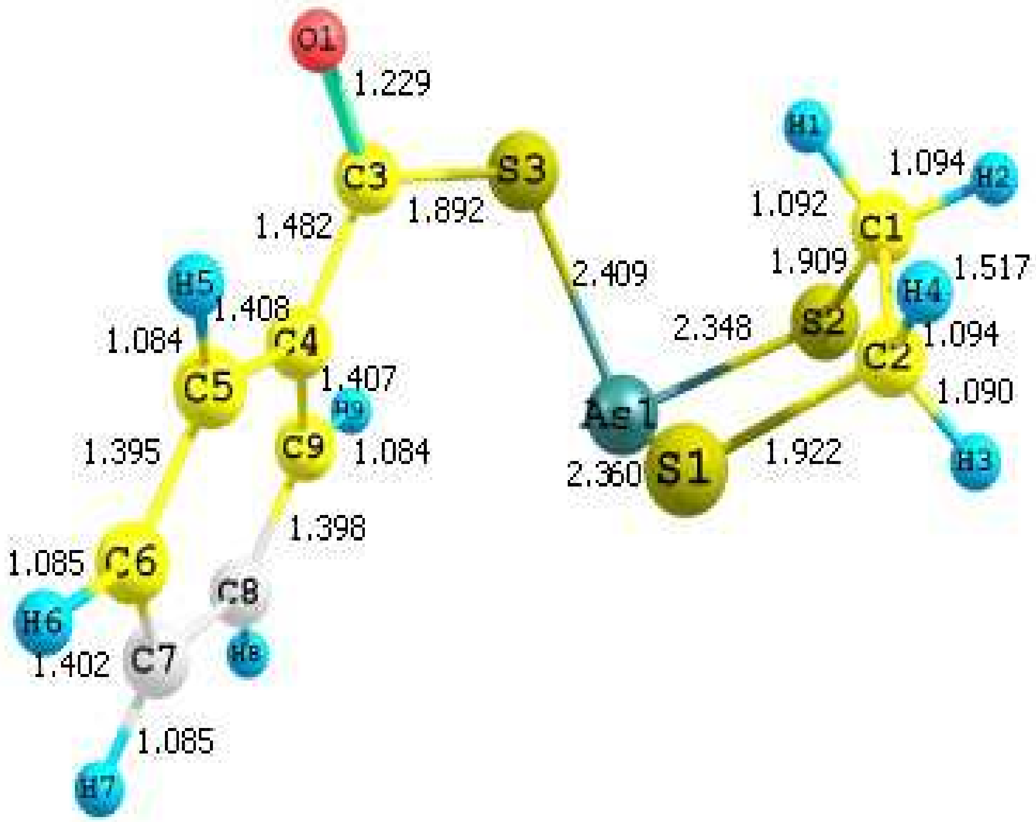


Fig.1.Optimized geometry of compound1

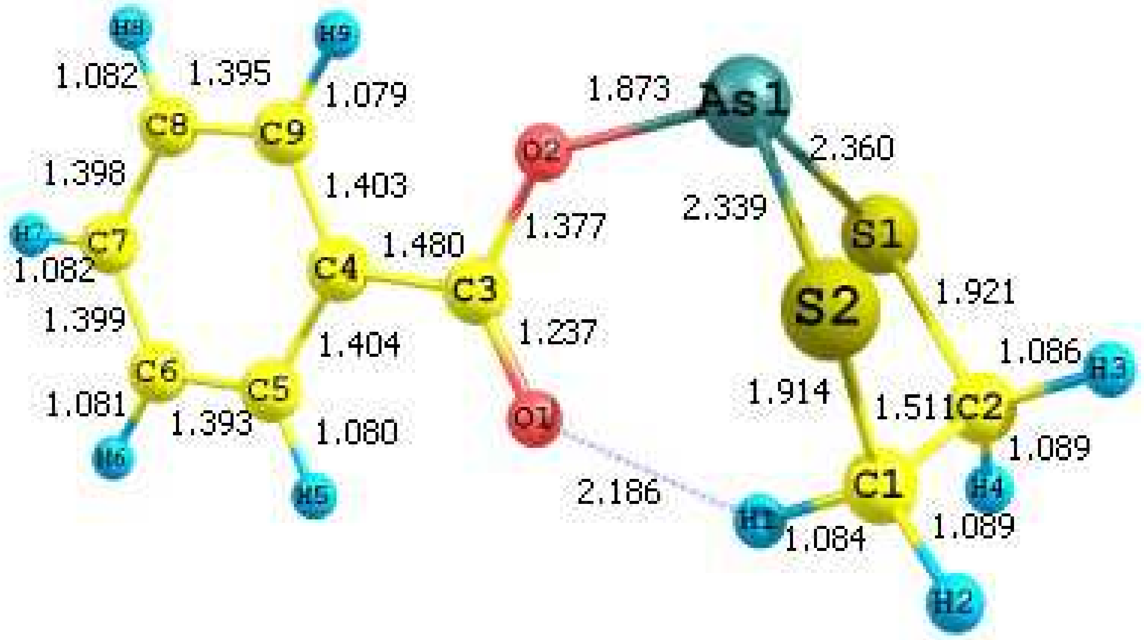


Fig.2. Optimized geometry of compound 2

The bond angles in compound 1 and 2 are listed in Table 2. In compound 1 the internal $S_2As_1S_1$ angle in cyclopantane moiety R is lower (93.72 ^{o}) compared to outer $S_1As_1S_3$ bonds (98.5^o) similarly in compound 2 the internal $S_2As_1S_1$ angle in cyclopantane moiety R is lower (93.5 ^{o}) compared to outer $S_1As_1O_2$ bonds (101.4^o) which can be attributed to loan pair - loan pair repulsion over neibouring sulfur atoms. This also suggests SP^3 hybridization on the As atom in both the compounds. The structure of both the compounds can be assumed to be distorted tetrahedral. Data also suggest C_1 and C_2 carbon atoms of com. 1 & 2 to posses SP^3 hybridization and all carbon atoms of the benzene ring to posses SP^2 hybridization. It is interesting to discuss angle around As atoms bridging the two moieties namely 1, 3-dithia -2-arsacyclopetane and benzoic acid / thiobenzoic acid. The $C_3S_3As_1$ angle in compound 1 is 104.7° compared to $C_3O_2A_{S1}$ angle of 131.1° in the compound 2. This can be attributed to the higher electro negativity of oxygen as compared to sulfur.

Table 2. Various bond angles (degree) in molecules 1 and 2
R = CH2CH2 S2As -

Angle	R-SCOC6H5	R- OCOC6H5	Angle	R-SCOC6H5	R- OCOC6H5
$H_1C_1H_2$	109.65	111.42	$O_1C_3C_4$	124.11	124.11
$H_2C_1C_2$	110.85	110.88	$C_3C_4C_9$	122.56	121.96
$H_1C_1C_2$	112.22	112.52	$C_4C_9H_9$	119.95	119.20
$H_3C_2H_4$	110.11	110.25	$C_4C_9C_8$	119.99	119.85
$H_3C_2C_1$	111.97	112.16	$H_9C_9C_8$	119.96	120.93
$H_4C_2C_1$	110.58	110.58	$C_9C_8H_8$	119.72	119.81
$S_2C_1H_1$	107.49	106.03	$C_9C_8C_7$	120.14	120.16
$S_2C_1H_2$	104.53	104.44	$H_8C_8C_7$	120.12	120.02
$S_2C_1C_2$	111.74	111.13	$C_8C_7H_7$	119.96	119.96
$S_1C_2H_3$	106.93	106.96	$C_8C_7C_6$	120.03	120.07
$S_1C_2H_4$	104.30	103.82	$H_7C_7C_6$	120.00	119.95
$S_1C_2C_1$	112.60	112.67	$C_7C_6H_6$	120.10	120.11
$As_1S_2C_1$	93.35	97.18	$C_7C_6C_5$	120.07	119.99
$As_1S_1C_2$	98.50	98.86	$H_6C_6C_5$	119.82	119.89
$S_2As_1S_1$	93.72	93.49	$C_6C_5H_5$	120.97	121.22
$S_1As_1S_3$ / $S_1As_1O_2$	98.51	101.42	$C_6C_5C_4$	120.13	120.06
$S_2As_1S_3$/ $S_2As_1O_2$	93.84	107.28	$H_5C_5C_4$	118.88	118.71
$As_1S_3C_3$/ $As_1O_2C_3$	104.76	131.06	$C_5C_4C_3$	117.79	118.18
$S_3C_3O_1$/ $O_2C_3O_1$	117.66	122.71	$C_5C_4C_9$	119.59	119.84

Dihedral Angles.

The dihedral angles of the two molecules are listed in Table 3. Inspection of Table 3 reveals the dihedral angles of the benzene ring moiety to planar. The dihedral angles $S_2A_{S1}S_3C_3$ and $S_2A_{S1}O_2C_3$ In compound 1 and 2 are respectively -148.60 and -41, 10 degrees which again confirm the cis position of 1, 3-dithia -2-arsacyclopetane moiety cis to the benzene ring in compound 2. Similar conclusion is provided by the dihedral angles $A_{S1}S_3C_3O_1$and $A_{S1}O_2C_3O_1$, $C_2S_1A_{S1}S_3$ and $C_2S_1A_{S1}O_2$, $A_{S1}S_3C_3C_4$ / $As_1O_2C_3C_4$.

Table 3. Various Dihedral angles in molecules 1 and 2
R = CH_2CH_2 S_2As -

Dihedral angles	R-C_6H_5COS	R-C_6H_5COO	Dihedral angles	R-C_6H_5COS	R-C_6H_5COO
$H_1C_1C_2H_4$	-54.15	-55.85	$H_1C_1S_2A_{S1}$	-67.43	-73.48
$H_1C_1C_2H_3$	-177.35	-179.38	$C_2C_1S_2A_{S1}$	56.12	49.09
$H_1C_1C_2S_1$	62.09	59.83	$C_1C_2S_1A_{S1}$	26.15	34.67
$H_2C_1C_2H_4$	68.83	69.69	$H_4C_2S_1A_{S1}$	146.10	154.3
$H_2C_1C_2H_3$	-54.36	-53.83	$H_3C_2S_1A_{S1}$	-97.24	-89.03
$H_2C_1C_2S_1$	-174.91	-174.61	$C_1S_2A_{S1}S_3$ /$C_1S_2A_{S1}O_2$	68.82	82.16
$S_2C_1C_2S_1$	-58.74	-58.91	$C_1S_2A_{S1}S_1$	-29.99	-20.94
$S_2C_1C_2H_3$	61.81	61.86	$C_2S_1A_{S1}S_3$ /$C_2S_1A_{S1}O_2$	-87.11	-110.86
$S_2C_1C_2H_4$	-174.98	-174.60	$C_2S_1A_{S1}S_2$	7.34	-2.45
$S_1A_{S1}S_3C_3$ /$S_1A_{S1}O_2C_3$	-54.24	56.25	$A_{S1}S_3C_3C_4$ / $As_1O_2C_3C_4$	-26.41	-178.12
$S_2A_{S1}S_3C_3$ /$S_2A_{S1}O_2C_3$	-148.60	-41.10	$S_3C_3C_4C_5$ / $O_2C_3C_4C_5$	148.69	-179.42
$A_{S1}S_3C_3O_1$/$A_{S1}O_2C_3O_1$	152.25	2.32	$C_3C_4C_9H_9$	-2.28	0.04
$S_3C_3C_4C_9$ / $O_2C_3C_4C_9$	-33.84	0.48	$C_3C_4C_5H_5$	-1.33	-0.05
$C_3C_4C_9C_8$	-178.94	-179.94	$C_3C_4C_5C_6$	179.67	179.93
$O_1C_3C_4C_9$	147.58	-179.96	$O_1C_3C_4C_5$	-29.87	0.12
$C_4C_9C_8H_8$	179.19	-179.99	$C_5C_6C_7H_7$	-179.87	-179.97
$C_4C_9C_8C_7$	0.04	0.02	$C_5C_6C_7C_8$	-0.24	0.00
$C_4C_5C_6H_6$	178.82	-179.99	$C_5C_4C_9H_9$	175.13	179.95
$C_4C_5C_6C_7$	-1.25	-0.01	$C_5C_4C_9C_8$	-1.53	-0.03
$H_5C_5C_4C_9$	-178.87	-179.97	$H_5C_5C_6C_7$	179.78	179.98
$H_5C_5C_6H_6$	-0.13	0.00	$C_6C_7C_8H_8$	-178.29	-179.99
$C_6C_7C_8C_9$	0.85	-0.01	$C_6C_5C_4C_9$	2.14	0.02
$H_6C_6C_7H_7$	0.03	0.00	$H_7C_7C_8H_8$	1.33	-0.00
$H_6C_6C_7C_8$	179.66	179.98	$H_7C_7C_8C_9$	-179.51	179.96
$C_7C_8C_9H_9$	-176.62	-179.95	$H_8C_8C_9H_9$	2.53	0.02
$H_2C_1S_2A_{S1}$	176.08	168.70			

Electronic structure

We know that the atomic charges are very much dependent on how the atoms are defined [36] it also plays an important role in the application of quantum chemical calculations to molecular system. The Mullikan atomic charges calculated at B3LYP level with 6-31 +G (d, p) basis set on various atoms in molecules 1 and 2 are shown in table 4. All hydrogen atoms in both the compounds carry positive charge. In both the compounds positive charge on hydrogen atoms of cyclopentane moiety is more than the hydrogen of organic ring. C1, C2 of cyclopentane moiety in both the compounds are most negative and As1 is most positive.

The results show that (a) all the hydrogen atoms in both the molecules lost electrons and electron releasing tendency of hydrogen of cyclopentane moiety is more than hydrogen of benzene ring [37] (b) C1, C2 of cyclopentane moiety in both the compounds accept electron (c) As1 in both the compounds accept electron.

Table 4. Atomic charges (coulomb) on various atoms in molecules 1 and 2
R = CH_2CH_2 S_2As -

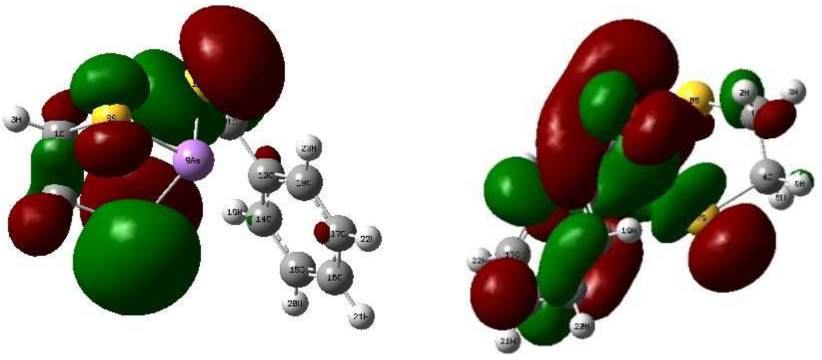
Atomic charges	R-SCOC6H5	R- OCOC6H5	Atomic charges	R-SCOC6H5	R- OCOC6H5
C_1	-0.49	-0.58	As_1	0.24	0.74
C_2	-0.44	-0.54	O_1	-0.36	-0.38
C_3	0.05	0.53	H_1	0.23	0.29
C_4	0.04	-0.19	H_2	0.20	0.23
C_5	-0.15	-0.06	H_3	0.20	0.24
C_6	-0.12	-0.17	H_4	0.20	0.24
C_7	-0.10	-0.10	H_5	0.17	0.18
C_8	-0.13	-0.18	H_6	0.14	0.15
C_9	-0.09	-0.03	H_7	0.14	-0.10
S_1	-0.02	-0.08	H_8	0.14	0.15
S_2	-0.007	-0.07	H_9	0.17	0.18
S_3/O_2	-0.01	-0.69			

The dipole moments, energies, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies and the energy gap for the studied molecules have been calculated and given in Table 5.

Table 5. Dipole moment/Total energy/Point group/ HOMO-LUMO/Energy GAP
R = CH_2CH_2 S_2As -

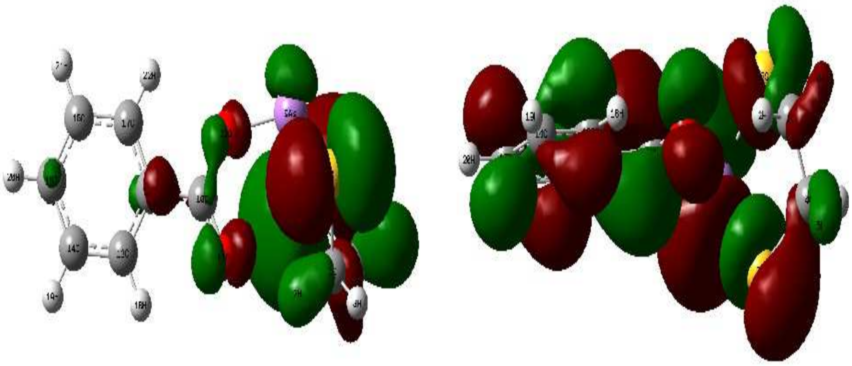
	R-SCOC6H5	R- OCOC6H5		R-SCOC6H5	R- OCOC6H5
Dipole Moment	3.81 Debye	5.60 Debye	**HOMO**	-0.25 Hartree	-0.25 Hartree
Total Energy	-3851.61 a.u.	-3530.86 a.u.	**LUMO**	-0.08 Hartree	-0.07 Hartree
Point group	C1	C1	**Energy GAP**	0.17 Hartree	0.18 Hartree
			Energy GAP	4.33 eV	4.77 eV

The frontier molecular orbitals HOMO and LUMO gap (band gap) helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small band gap more polarizable and is suppose to posses high chemical reactivity and can be termed as soft molecule [38, 39]. HOMO is electron donor and LUMO is electron accepter [40] the band gaps for molecule 1 and 2 are computed to be 4.33 eV (287 nm) and 4.77 eV (260 nm) respectively which matches well with the observed value in the range 210 -270 nm. The electron movement between these orbitals could easily occur [41] it makes molecule soft and more polarizable with a high chemical reactivity. 3D plots of HOMO and LUMO of the studied molecules are shown in Fig 3. The highest occupied molecular orbital is concentrated around 1, 3-dithia-2-arsacyclopentane moiety in both the compounds. The lowest unoccupied molecular orbital is concentrated around the whole molecule The HOMO and LUMO orbital's of compound 1 and 2 are shown in Figure 3 ,4, The band gap is found to be 0.16 Hartree and 0.17 Hartree for compound 1 & 2 respectively.



A **B**

Fig 3. (A) HOMO and (B) LUMO molecular orbitals of compound 1



A **B**

Frig. 4. (A) HOMO and (B) LUMO molecular orbitals of compound 2

Vibrational analysis

The title molecules 1, 3-dithia-2-arsacyclopentane (1, 3-D-2-A) derivatives with oxygen and sulfur donor legends both has 23 atoms as a result of it 63 fundamental modes of vibrations are present in both the molecules. The molecule belongs to the Cs point group and all vibrations are supposed to IR as well as Raman active.

C-H Stretching Vibrations; Nine frequencies computed at 3097.8, 3105.4, 3166 ,3182.6, 3202.8, 3213.5, 3223.3, 3232.8, 3238.9 cm^{-1} can be assigned to four C-H stretching modes of cyclopentane moiety and five to benzene ring. Consideration of Cartesian displacements revealed that frequencies appeared at 3097.8, 3105.4, 3166 and 3182.6 cm^{-1} should be assigned to C-H stretching modes of cyclopentane moiety. Out of this only one mode at 3050 cm-1 is observed by Chauhan et al. The nearest calculated frequency corresponding to the reported observed frequency at 3050 cm^{-1} is 3097.8 cm^{-1}. Its dependence on Cartesian coordinates suggests it belong to cyclopentane moiety. Similarly in molecule 2 the four bands computed at 3064.8, 3076.4, 3136.4, 3167.6 cm^{-1} can be assigned to C-H stretching modes of cyclopentane moiety and five modes appeared at 3171.1, 3181.0, 3193.8, 3209.2, 3220.8 cm^{-1} can be assigned to benzene ring. Some relevant vibrational modes, their observed as well as computed frequencies along with their force constants and intensities are shown in Table. The assignments have been made on the basis of earlier published work [42-47] and Cartesian displacement of normal modes. The nearest calculated frequency corresponding to the reported observed frequency at 3050 cm^{-1} is 3097.8 cm^{-1}. Its dependence on Cartesian coordinates suggests it to belong to cyclopentane moiety.

Heavy Atoms Stretching Modes; Frequencies computed at 1632.3 and 1653 cm^{-1} are assigned to C=O stretching modes of compound 1 and 2 respectively on the basis of their dependence of atomic coordinates. Corresponding observed frequencies are 1640 and 1690 cm^{-1} respectively. Frequencies computed that 618 and 610.1 cm^{-1} can be assigned to C-S stretching modes of the compound 1 and 2 respectively. Corresponding observed bands have appeared at 620 and 610 cm^{-1}. Data show an excellent agreement between the observed and calculated frequencies.

Metal Legend Stretching Vibrations: These include As-S and As-O stretching modes. Frequencies calculated in the range 356 – 319 cm $^{-1}$ are assign to As-S stretching modes in both the molecules. While As1-O2 stretching mode in molecule 2 is calculated at 610.1 cm $^{-1}$

Table 6: Computed stretching frequencies (cm^{-1}), force constants (mDyne/A°), and atomic Cartesian displacement of vibrational motions in molecule 1

S.No.	Frequency (Calculated)	Freq. Obs.	Assignt.	Frce Const	Cartesian Displacement
1.	3238.9(9.5)	-----	$\nu(C_5-H_5)B$	6.8	$C_5(-0.06Z) + H_5(0.64Z) + C_6(-0.03Z) + H_6(0.34Z)$
2.	3232.8(6.9)	-----	$\nu(C_9-H_9)B$	6.7	$C_8(0.04Z) + H_8(-0.44Z) + C_9(-0.04Z) + H_9(-0.52Z)$
3.	3223.3(20.2)	-----	$\nu(C_7-H_7)B$	6.7	$C_9(0.04Z) + H_9(-0.44Z) + C_7(-0.04Y) + H_7(0.47Y)$
4.	3213.5(8.3)	-----	$\nu(C_8-H_8)B$	6.6	$C_8(0.05Z) + H_8(-0.53Z) + C_6(-0.04Z) + H_6(-0.48Z)$
5.	3202.8(0.2)	-----	$\nu(C_6-H_6)B$	6.6	$C_9(0.01X) + H_9(0.15Z) + C_6(-0.03Z) + H_6(0.36Z)$
6.	3182.7(3.3)	-----	Asym ν(C-H)A	6.6	$C_1(0.05X) + H_3(0.58Y) + H_4(0.39Z) + C_2(-0.06Y)$
7.	3165.7(1.0)	-----	Asym ν(C-H)A	6.5	$C_2(0.04Y) + H_1(0.53Y) + H_2(-0.47X) + C_1(0.06X)$
8.	3105.4(12.4)	-----	Sym ν(C-H)A	6.0	$C_1(-0.04Y) + H_1(0.39Y) + H_2(0.51X) + C_2(-0.04Z)$
9.	3097.8(2.4)	3050	Sym ν(C-H)A	6.0	$C_1(-0.03Y) + H_1(0.34Y) + H_2(0.56X) + C_2(0.04Z)$
10.	1701.8(254.3)	1640	$\nu(C_3=O_1)$	21.6	$C_3(0.66Y) + O_1(-0.42Y) + C_4(-0.10Z) + C_5(-0.06X)$
11.	1654.2(16.7)	-----	$\nu(C_5-C_6)B$	8.8	$C_7(-0.12Y) + C_4(0.16Y) + C_5(-0.21Y) + C_6(0.24Y)$
12.	1632.3(9.6)	-----	$\nu(C_6-C_7)B$	8.2	$C_7(0.34Z) + C_8(-0.19Z) + C_5(0.15Z) + C_6(-0.18Z)$
13.	1503.0(11.5)	-----	$\nu(C_7-C_8)B$	2.7	$C_7(0.10Z) + C_8(-0.11Y) + C_9(0.07X) + C_6(0.11Y)$
14.	1384.9(5.1)	-----	$\nu(C_8-C_9)B$	2.0	$C_7(0.12Z) + C_8(0.05Y) + C_9(-0.12Z) + C_4(-0.02Z)$
15.	1367.1(1.1)	-----	$\nu(C_4-C_9)B$	3.8	$C_5(0.09X) + C_8(0.12X) + C_9(-0.09Z) + C_4(-0.11Y)$
16.	1245.7(67.1)	-----	$\nu(C_4-C_5)B$	1.8	$C_5(-0.05X) + C_6(0.07Y) + C_9(-0.05Y) + C_4(-0.16Y)$
17.	1227.3(78.6)	-----	$\nu(C_3-C_4)$	1.3	$C_5(-0.02Z) + C_3(0.07X) + O_1(0.02Y) + C_4(-0.12Y)$
18.	1038.6(2.2)	-----	$\nu(C_1-C_2)A$	1.6	$S_1(0.01X) + C_2(-0.22Y) + S_2(0.01X) + C_1(0.21Y)$
19.	618.0(3.2)	620	$\nu(C_1-S_2)$	0.9	$S_1(0.07X) + C_2(-0.21X) + S_2(-0.14Z) + C_1(0.34Z)$
20.	598.2(7.8)	-----	$\nu(C_2-S_1)$	1.2	$S_1(-0.18X) + C_2(0.37X) + S_2(-0.12Z) + C_1(0.20Z)$
21.	394.3(5.5)	-----	$\nu(C_3-S_3)$	0.7	$S_3(-0.17X) + C_3(0.14Y) + O_1(0.34X) + C_4(-0.12Z)$
22.	356.8(23.3)	-----	$\nu(As_1-S_2)$	1.7	$C_1(-0.08Y) + S_1(0.42Z) + S_2(0.53X) + As_1(-0.16X)$
23.	347.3(7.0)	-----	$\nu(As_1-S_3)$	1.0	$S_3(0.43Y) + S_1(0.03X) + S_2(-0.13X) + As_1(-0.14X)$
24.	330.3(9.3)	331	$\nu(As_1-S_1)$	1.2	$C_2(0.23Y) + S_1(0.43Z) + S_2(-0.39X) + As_1(0.20X)$

Table 6.1: Computed stretching frequencies (cm^{-1}), force constants (mDyne/A°), and atomic Cartesian displacement of vibrational motions in molecule 2

SN.	Frequency (Calculated)	Freq. Obs.	Assignt.	Frce Const	Cartesian Displacement
1.	3220.9	-----	$\nu(C_8-H_8)B$	6.7	$C_7(0.02Y) + H_7(-0.24Y) + C_8(0.07Y) + H_8(-0.78Y)$
2.	3209.2	-----	$\nu(C_9-H_9)B$	6.6	$C_5(-0.03Y) + H_5(0.31Y) + C_9(0.80Y) + H_9(0.0Y)$
3.	3193.8	-----	$\nu(C_7-H_7)B$	6.6	$C_5(0.03Y) + H_5(-0.31Y) + C_7(-0.04Y) + H_7(0.45Y)$
4.	3181.0	-----	$\nu(C_5-H_5)B$	6.5	$C_5(0.05Y) + H_5(-0.56Y) + C_9(0.21Y) + H_9(0.0Y)$
5.	3171.1	-----	Asym ν(C-H)A	6.5	$C_1(-0.09X) + H_1(0.80X) + H_2(0.27Y) + C_2(-0.02X)$
6.	3167.6	-----	ν(C6-H6)B	6.4	$C_5(-0.03Y) + H_5(0.41Y) + C_6(-0.06X) + H_6(0.71X)$
7.	3136.4	-----	Asym ν(C-H)A	6.4	$C_1(0.03X) + H_3(0.73X) + H_4(-0.40Y) + C_2(-0.06Y)$
8.	3076.4	-----	Sym ν(C-H)A	6.0	$C_1(-0.05Y) + H_1(-0.37X) + H_2(0.48Y) + C_2(-0.03X)$
9.	3064.8	2970	Sym ν(C-H)A	5.8	$C_1(0.03Y) + H_3(0.42X) + H_4(0.51Y) + C_2(-0.03Y)$
10.	1653.0	1690	$\nu(C_3=O_1)$	16.6	$O_1(-0.24Y) + C_3(-0.36Y) + C_4(0.11Y) + O_2(0.56Y)$
11.	1642.5	-----	$\nu(C_4-C_9)B$	8.3	$C_4(-0.30X) + C_9(0.34X) + C_5(0.26X) + C_8(-0.27X)$
12.	1615.6	-----	$\nu(C_5-C_6)B$	8.6	$C_4(-0.20Y) + C_5(0.35Y) + C_4(0.16Y) + C_7(-0.18Y)$
13.	1536.9	-----	$\nu(C_5-C_6)B$	2.8	$C_5(0.09Y) + C_6(-0.11Y) + C_9(0.43X) + C_6(0.10X)$
14.	1496.9	-----	$\nu(C_6-C_7)B$	2.7	$C_6(0.12Y) + C_7(-0.14Y) + C_5(0.13X) + C_8(0.07X)$
15.	1374.3	-----	$\nu(C_8-C_9)B$	1.6	$C_8(-0.10X) + C_9(-0.51X) + C_4(0.10X) + C_7(0.02X)$
16.	1347.7	-----	$\nu(C_7-C_8)B$	6.6	$C_7(0.24X) + C_8(-0.19X) + C_6(0.24Y) + C_9(0.13X)$
17.	1268.3	-----	$\nu(C_3-C_4)$	4.3	$O_1(0.36X) + C_3(-0.09Y) + C_4(0.09Y) + O_2(-0.29X)$
18.	1073.3	-----	$\nu(C_3-O_2)$	2.0	$O_1(0.16X) + C_3(-0.05X) + C_4(0.11Y) + O_2(0.20X)$
19.	1036.9	-----	$\nu(C_1-C_2)A$	1.7	$C_1(0.16X) + H_1(-0.25Y) + H_3(-0.23X) + C_2(-0.20Z)$
20.	610.1	540	$\nu(As_1-O_2)$	2.5	$C_3(0.22Y) + O_1(-0.06X) + O_2(0.29Y) + As_1(0.08X)$
21.	595.8	610	$\nu(C_1-S_2)$	0.9	$C_1(0.29Y) + S_1(0.07X) + S_2(-0.11Y) + C_2(-0.18X)$
22.	582.1	-----	$\nu(C_2-S_1)$	1.2	$C_1(0.33Y) + S_1(-0.14Y) + S_2(-0.12Y) + C_2(0.31Y)$
23.	352.1	-----	$\nu(As_1-S_2)$	24.5	$S_2(-0.51Z) + S_1(0.50Z) + O_2(0.03Y) + As_1(-0.21Y)$
24.	319.8	320	$\nu(As_1-S_1)$	13.3	$S_2(-0.31Y) + S_1(0.39Z) + O_2(0.01X) + As_1(-0.29Y)$

Other vibration modes: C=C stretching modes in benzene ring appear in the regions 1600-1585 cm^{-1} and 1500-1400 cm^{-1} [48]. On the basis of Cartesian displacements the frequencies listed at al No. 11-16 in Table six can be assigned to these vibrations. The frequencies calculated at 1227 cm^{-1} and 1038.6 cm^{-1} are assigned to C3-C4 and C1-C2 stretching modes respectively. In molecule 2 these modes are calculated at 1268.3 & 1036.3 cm^{-1} .

Assignment of frequencies computed in the range 700-1654 cm^{-1} belong to different C-H bending mode, few C- C stretching modes of benzene ring are assigned on the basis of movement of atoms in these frequencies and are shown in Table 7. The benzene ring breathing modes in molecule 1 and 2 are computed at 891.0 cm^{-1} and 1049.9 cm^{-1} respectively. These vibrations could be recognized because of their high intensities of 241.5 and 159.9.

Table 7: Computed Bending frequencies (cm^{-1}), force constants (mDyne/A°), and atomic Cartesian Displacement of vibrational motions in Com 1

SN	Frequency (Calculated)	Freq Obs.	Assignt.	Frce Const	Cartesian Displacement
1	1545.4(2.8)	-----	β (C-H)B	2.9	$H_5(-0.34X)+H_6(-0.37Y)+H_8(-0.33X)+H_9(-0.33Y)$
2	1514.1(8.7)	-----	β (C-H)A	1.5	$H_1(0.59X)+H_2(0.58Y)+H_3(0.32Z)+H_4(-0.23Y)$
3	1507.1(10.1)	-----	β (C-H)A	1.4	$H_1(-0.27X)+H_2(-0.29Y)+H_3(0.64Z)+H_4(-0.54Y)$
4	1352.2(14.7)	-----	W β (C-H)A	1.3	$H_1(0.23Z)+H_2(0.18Z)+H_3(0.43X)+H_4(-0.13Y)$
5	1310.5(7.7)	-----	W β (C-H)A	1.2	$H_1(0.29Z)+H_2(0.51Z)+H_3(-0.50X)+H_4(-0.46X)$
6	1225.8(32.8)	-----	β (C-H)B	1.1	$H_6(-0.26Y)+H_7(0.55Z)+H_8(0.40X)+H_9(-0.31Y)$
7	1185.7(0.9)	-----	τ β (C-H)A	1.0	$H_1(0.15Y)+H_2(0.63Z)+H_3(0.16Z)+H_4(0.57X)$
8	1152.4(3.7)	-----	τ β (C-H)A	0.8	$H_1(0.54Z)+H_2(-0.38Z)+H_3(-0.49X)+H_4(0.36X)$
9	1127.6(3.2)	-----	β (C-H)B	1.2	$H_5(0.39X)+H_7(-0.53Z)+H_8(0.22X)+H_9(-0.32Y)$
10	1065.5(1.4)	-----	β (C-H)B	1.5	$H_5(-0.34X)+H_6(-0.37Z)+H_8(0.35Z)+H_9(-0.31Z)$
11	1038.8(1.9)	-----	β (ring)B	0.9	$H_6(0.37X)+H_7(-0.37X)+H_8(0.31X)+H_9(-0.19X)$
12	1034.6(5.3)	-----	β (ring)B	2.2	$H_5(0.34Y)+H_6(0.35X)+H_7(-0.49X)+H_9(0.20X)$
13	1010.7(4.4)	-----	π β (C-H)B	0.8	$H_5(-0.32X)+H_6(0.29X)+H_8(-0.39X)+H_9(0.31X)$
14	981.1(8.2)	-----	R β (C-H)A	0.9	$H_1(-0.41Z)+H_2(0.52Y)+H_3(-0.40X)+H_4(-0.26Y)$
15	964.7(3.1)	-----	π β (C-H)B	0.7	$H_5(0.35X)+H_7(-0.36X)+H_8(-0.11X)+H_9(0.44X)$
16	891.0(204.5)	-----	Ring Breathing	2.3	$H_5(-0.21X)+H_6(-0.48X)+H_8(-0.29Y)+H_9(-0.25Y)$
17	884.4(3.5)	-----	π β (C-H)B	0.6	$H_5(-0.33X)+H_6(0.33Y)+H_8(0.38X)+H_9(0.36X)$
18	880.5(3.1)	-----	R β (C-H)A	0.7	$H_1(0.28X)+H_2(-0.44Y)+H_3(-0.45Z)+H_4(0.42X)$
19	793.0(32.9)	-----	π β (C-H)B	0.6	$H_6(0.36X)+H_7(0.38X)+H_8(0.38X)+H_9(0.16X)$
20	724.6(48.4)	-----	π β (C-H)B	0.6	$H_5(0.36Y)+H_6(0.13X)+H_7(0.40X)+H_9(0.34Z)$
21	692.4(69.2)	-----	β (ring)B	2.1	$H_6(-0.22X)+H_7(0.22X)+H_8(-0.31X)+H_9(0.17X)$
22	652.9(26.0)	-----	β (ring)B	1.5	$C_6(0.24X)+C_8(-0.23Y)+H_6(0.43X)+H_8(-0.32Y)$
23	642.2(14.5)	-----	β (ring)B	1.4	$C_5(-0.20Z)+H_6(0.33Z)+H_8(0.33Z)+H_9(-0.19Z)$
24	520.6(1.0)	-----	β (ring)B	1.1	$H_6(0.32Y)+H_7(-0.27Y)+H_8(-0.34X)+H_9(-0.23X)$
25	440.5(16.3)	-----	π β (C-H)B	0.5	$C_9(0.15X)+H_6(0.36X)+H_7(-0.30X)+H_9(0.33X)$
26	439.1(1.5)	-----	β (C-H)A	0.4	$C_1(0.22X)+H_1(0.51X)+H_2(0.29X)+H_3(-0.48Z)$
27	430.9(3.0)	-----	π β (ring)B	0.4	$H_5(0.37X)+H_6(-0.24X)+H_8(0.37X)+H_9(-0.25X)$
28	274.2(23.7)	-----	β (S-C-O)	0.5	$As_1(0.16Y)+S_3(-0.21X)+C_3(-0.09Y)+O_1(0.40X)$
29	268.3(14.6)	-----	R β (C-H)A	0.1	$H_1(-0.44X)+H_2(0.47Y)+H_3(-0.40Z)+H_4(-0.37Y)$
30	252.6(1.4)	-----	τ β (C-H)A	0.2	$H_1(0.49X)+H_2(-0.38Y)+H_3(0.43Z)+H_4(0.25Y)$
31	193.6(1.5)	-----	β (C-C-O)	0.5	$S_3(0.12X)+C_3(-0.08Y)+O_1(-0.14Y)+C_4(-0.25Z)$
32	173.6(3.4)	-----	τ β (S-As-S)	0.2	$S_1(0.29Y)+S_2(0.13Y)+As_1(-0.16Y)+S_3(0.21Z)$
33	155.9(0.6)	-----	β (C-H)B	0.1	$H_5(-0.26X)+H_6(-0.24Y)+H_7(0.34X)+H_9(0.32Y)$
34	121.0(2.2)	-----	β (HA)	0.1	$H_4(-0.46Y)+S_2(0.26Y)+As_1(0.09Y)+S_3(-0.15Z)$
35	94.2(3.1)	-----	β (C-H)A	0.02	$H_1(-0.23Z)+H_2(0.26Y)+H_3(0.27Y)+H_4(0.38Y)$
36	87.0(0.8)	-----	π β (C-H)B	0.02	$H_5(0.25X)+H_6(0.23X)+H_8(-0.33X)+H_9(-0.21X)$
37	42.5(1.4)	-----	π β (C-H)A	0.01	$H_1(-0.22X)+H_2(-0.22X)+C_2(-0.23X)+H_4(-0.36X)$
38	36.3(0.4)	-----	β (C-H)B	0.005	$H_5(-0.25X)+H_6(-0.41X)+H_7(-0.29X)+H_9(-0.21Y)$
39	25.0(1.6)	-----	β (C-H)A	0.003	$H_2(-0.19Z)+C_2(0.18Y)+H_3(0.18Y)+H_4(0.28Y)$

Table 7.1: Computed Bending frequencies (cm^{-1}), force constants (mDyne/A^o), and atomic Cartesian Displacement of vibrational motions in Com 2

SN	Frequency (Calculated)	Freq. Obs.	Assignt.	Frce Const	Cartesian Displacement
1	1491.9(10.7)	-----	β (C-H)A	1.4	$H_1(0.29Y)+H_2(-0.27X)+H_3(0.49Z)+H_4(0.56X)$
2	1485.5(13.1)	-----	β (C-H)A	1.4	$H_1(0.46Y)+H_2(-0.45X)+H_3(-0.25Z)+H_4(-0.37X)$
3	1357.9(9.3)	-----	τ β (C-H)A	1.3	$H_1(0.62Z)+H_2(0.19Y)+H_3(-0.47Z)+H_4(0.13X)$
4	1312.1(22.3)	-----	W β (C-H)A	1.2	$H_1(0.29Z)+H_2(0.47Z)+H_3(-0.40Y)+H_4(0.39Z)$
5	1217.8(86.4)	-----	β (C-H)B	1.0	$H_5(0.46X)+H_6(-0.33X)+H_8(-0.42X)+H_9(0.47X)$
6	1212.7(0.5)	-----	β (C-H)B	1.0	$H_5(0.19X)+H_6(-0.42X)+H_8(0.67Y)+H_9(0.42X)$
7	1182.8(0.6)	-----	τ β (C-H)A	1.0	$H_1(-0.15Z)+H_2(0.65Z)+H_3(0.13X)+H_4(-0.43Z)$
8	1164.3(9.9)	-----	τ β (C-H)A	0.9	$H_1(0.44Z)+H_2(-0.33Z)+H_3(0.44Z)+H_4(-0.39Z)$
9	1117.2(45.8)	-----	β (C-H)B	1.3	$H_5(0.56X)+H_7(-0.53Y)+H_8(0.35X)+H_9(-0.36X)$
10	1049.9(159.9)	-----	Ring Breathing	2.3	$H_5(-0.33X)+H_6(-0.41Y)+H_8(0.40Y)+H_9(-0.32Y)$
11	1043.4(0.1)	-----	π β (C-H)B	0.8	$H_5(-0.40Z)+H_6(0.53Z)+H_7(-0.51Z)+H_8(0.44Z)$
12	1026.9(16.5)	-----	β (ring)B	3.4	$C_7(0.41X)+H_5(-0.32X)+H_7(0.43X)+H_9(-0.30X)$
13	1024.6(0.1)	-----	π β (C-H)B	0.8	$H_5(-0.54Z)+H_6(0.39Z)+H_8(-0.51Z)+H_9(0.50Z)$
14	986.1(1.5)	-----	π β (C-H)B	0.8	$C_7(0.11Z)+H_5(0.49Z)+H_7(-0.62Z)+H_9(0.57Z)$
15	970.4(8.9)	-----	R β (C-H)A	0.8	$H_1(0.46Y)+H_2(-0.40Y)+H_3(0.45Y)+H_4(-0.44X)$
16	887.9(0.04)	-----	π β (C-H)B	0.6	$H_5(-0.45Z)+H_6(-0.54Z)+H_8(0.51Z)+H_9(0.48Z)$
17	866.9(20.8)	-----	R β (C-H)A	0.7	$H_1(0.31X)+H_2(-0.49Y)+H_3(-0.31Z)+H_4(0.55X)$
18	825.1(7.7)	-----	π β (C-H)B	1.0	$C_7(0.12Z)+H_6(-0.54Z)+H_7(-0.52Z)+H_8(-0.56Z)$
19	819.9(58.0)	-----	β (OCO)	3.6	$C_3(0.12Z)+O_1(-0.54Z)+H_8(-0.52Z)+O_2(-0.56Z)$
20	726.3(97.0)	-----	π β (C-H)B	0.5	$H_5(-0.46Z)+H_7(-0.55Z)+H_8(-0.34Z)+H_9(-0.47Z)$
21	705.2(9.7)	-----	β (ring)B	1.4	$H_6(0.47Z)+H_7(-0.33Z)+H_8(0.47Z)+H_9(-0.24Z)$
22	687.4(18.1)	-----	β (ring)B	2.4	$H_6(0.31X)+H_7(-0.30X)+H_8(0.32X)+O_2(-0.30Y)$
23	649.7(0.2)	-----	β (ring)B	1.6	$H_6(-0.32X)+H_7(0.25Y)+H_8(-0.33Y)+H_9(0.31Y)$
24	457.8(0.02)	-----	π β (ring)B	0.4	$H_6(-0.41Z)+H_7(0.47Z)+H_8(-0.39Z)+H_9(-0.34Z)$
25	448.9(28.7)	-----	β (ring)B	1.0	$H_7(-0.25X)+H_8(-0.24X)+H_9(-0.35X)+O_2(0.21X)$
26	424.8(0.002)	-----	π β (C-H)B	0.3	$H_5(0.47Z)+H_6(0.44Z)+H_8(0.44Z)+H_9(-0.47Z)$
27	419.5(3.3)	-----	R β (C-H)A	0.4	$H_1(-0.46Y)+H_2(-0.29X)+H_3(0.22Z)+H_4(0.44Z)$
28	295.9(2.2)	-----	β (C-H)B	0.3	$H_5(-0.38X)+H_6(-0.34X)+H_7(-0.22Y)+H_9(0.26Y)$
29	268.3(11.8)	-----	β (C-H)A	0.4	$C_1(-0.23X)+H_1(-0.42Y)+H_2(-0.42X)+H_3(-0.22X)$
30	262.5(15.4)	-----	R β (C-H)A	0.1	$H_1(-0.29X)+H_2(-0.49X)+H_3(-0.38Z)+H_4(-0.39X)$
31	216.8(13.3)	-----	β (C-H)A	0.3	$H_1(-0.22Y)+H_2(-0.20X)+C_2(-0.13Y)+H_3(-0.19Y)$
32	210.6(11.9)	-----	β (C-H)A	0.2	$H_1(-0.25Y)+H_2(-0.32X)+H_3(-0.28Z)+H_4(0.29X)$
33	142.7(0.4)	-----	β (C-H)B	0.1	$H_5(-0.32Z)+H_7(0.52Z)+H_9(-0.26Z)+O_2(-0.30Z)$
34	129.3(0.8)	-----	β (O-As-S)	0.1	$S_1(0.16X)+S_2(0.28X)+As_1(0.07Y)+C_3(-0.14X)$
35	109.3(3.6)	-----	β (As-S-C)	0.03	$C_1(-0.23X)+C_2(-0.20X)+S_1(0.16X)+As_1(-0.33X)$
36	90.3(0.7)	-----	π β (HA)	0.04	$S_1(-0.14X)+S_2(0.16X)+C_3(0.19Z)+O_1(0.49Z)$
37	73.5(1.2)	-----	R β (C-H)B	0.02	$H_5(0.25X)+H_6(0.24X)+H_7(0.30Y)+H_8(-0.20X)$
38	38.4(0.1)	-----	R β (C-H)B	0.004	$H_5(0.38Z)+H_6(0.46Z)+H_8(-0.36Z)+H_9(-0.40Z)$
39	25.6(1.2)	-----	τ β (HA)	0.003	$S_1(-0.21X)+S_2(0.17X)+C_3(-0.18Z)+O_1(-0.28Z)$

CONCLUSION

Density function theory (DFT) computations are carried out for the model compounds **CH_2CH_2 S_2As – $ACOC_6H_5$ (A=S, O) with the objectives of reporting their** geometry, electronic structure, and bonding. While complexes with thiobenzoic acid are termed compound1, the complexes with benzoic acid are termed compound2. The geometrical parameters, band gap and assignment of important vibration frequencies are reported. The As-S (ligands) bond length of 2.409 is slightly higher than As-S (1, 3-D-2-A) bond length. Computations reveal that the benzene ring is not co-planar with the 1, 3-D-2-A rings. Energetically sulfur complex are found to be much more stable compared to oxygen complex. On the other hand compound2 is more polar than compound1. The energy gap in the two complexes is found to be 4.33 and 4. 77 eV respectively. An important feature of the two complexes is that while compound1 exists in only one stable form the compound2 undergoes rotation about O2-C3 and O2-As bonds to produce one more conformer in which benzene ring is cis to the 1, 3-dithia -2-arsacyclopetane group. The compound2 is stabilized by hydrogen bonding.

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