Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(18):46-55
(http://derpharmachemica.com/archive.html)

A DFT study of the structure and bonding in 1, 3-dithia -2-arsacyclopetane derivatives with oxygen and sulfur donor ligands such as Acetic acid and Thioacetic acid

S. Trivedi[1], B. R. Patil[1], R. Prasad[2] and S. Patil[3]

[1]*Department of Chemistry, Govt. Girls Degree College, Dhar*
[2]*School of Chemical Sciences, D. A .University, Indore*
[3]*Department of Chemistry, Govt. P.G. College, Dhar*

ABSTRACT

A quantum mechanical analysis of 1,3-dithia-2-arsacyclopentane derivatives with oxygen and sulfur donor ligands such as acetic acid (compound 1) and thioacetic acid (compound 2), have been performed with the objective of exploring their electronic, structural and spectral behavior on the basis of density functional theory. The geometrical parameters, band gap and assignment of important vibration frequencies are reported. In compound 2 the As-S (ligand) bond length 2.40 A^0 *is slightly higher than As-S (1, 3-dithia-2-arsacyclopentane moity) bond length 2.35* A^0*. In compound 2 the C-C bonds are more stable than C-S bonds and in compound 1 the C-O bonds are more stable than C-C bonds. The bond length suggests that compound 2 should be more reactive than compound 1. Bonds around heavy metal As are found longer than all other bonds suggesting that active sites in both undertaken compounds are centered around As. Bond angle analysis around heavy metal As suggest* SP^3 *hybridization on As atom. Therefore the structure of undertaken compounds can be assumed to be distorted tetrahedral. Analysis of dihedral angles reveals that cyclopetane moiety is not planer and ligand is not co planer to cyclopentane moiety.* As_1 *is most positive element it suggest maximum reactivity around* As_1*. The total energies of the two compounds are found to -3339.38 a.u and -3662.34 a.u. suggesting sulfur complex to be much more stable compared to oxygen complex. On the other hand compound1 is more polar than compound2. The energy gap in the two complexes is found to be 5.07 eV (245 nm) and 4.75 eV (261 nm) respectively. An important feature is that the compound 1 undergoes rotation about* O_2*-*C_3 *and* O_1*-As bonds to produce one more conformer in which ligand is cis to the 1, 3-dithia -2-arsacyclopetane group. The compound 1 is stabilized by hydrogen bonding. For compound 1 zero-point vibrational energy is found to be 291633.6 (Joules/Mol) or 69.70210 (Kcal/Mol) with zero-point correction 0.111077 (Hartree/Particle) and for compound 2 zero-point vibrational energy is found 283863.8 (Joules/Mol) or 67.84509 (Kcal/Mol) with zero-point correction 0.108118 (Hartree/Particle)*

Keywords: 1, 3-dithia -2-arsacyclopetane, DFT, Arsenic, Ligand

---

INTRODUCTION

For the last several years the chemistry of arsenic complexes having organic ligands has been an active area of interest because of their technological applications. These compounds are popular as poisoning materials at high concentrations. Toxicity of organic complexes of arsenic is less than inorganic complexes of arsenic. Arsenic compounds can be used as analytical reagents, lubricant additives for regeneration of cracking catalysts, fungicides and as antitumor agents. [1-3] Vulcanization of rubber is carried out by its metal complexes. They also work as rodent repellents. [4] They are used in glass manufacturing and in semiconductor Industry. Arsenic trioxide has been used successfully for treatment of leukaemia, prostate, and ovarian carcinoma. [5,6,7] Organoarsenical compounds are found useful for the treatment of haematological malignancies and solid tumours. [8,9] Now a day's arsenic thiolates are studied as building blocks in self-assembled macrocycles. [10,11,12] Dithiocarbamate complexes of arsenic are used in analytical chemistry,[13] medicines,[14]] as antioxidants,[15] polymer photo stabilizers,[16] precursor for creating sulfide film semiconductor,[17] and exhibitantialkylation,[18] and anti-HIV properties.[19] Dithiocarbamate ligands and their antimony derivatives are proved as multifunctional additives to lubricants.[20] Arsenic complexes find extensive applications as biocides, [21] Ternary compounds of group V metals are found useful in solar cells, photolithography, holographic recording, optical memory devices, photoconductors and as thermoelectric generators and in coolers. [22-36] Arsenic compounds show good activities as antibacterial and antifungal agents.[37] Recently, Chauhan et, al [37] 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 electronic, structural and spectral behavior in such compounds. In the present study we report, A DFT level computation of the derivatives of 1, 3-dithia -2-arsacyclopetane with oxygen and sulfur donor ligands such as acetic acid and thioacetic acid. While complex with acetic acid is abbreviated as compound 1 and the complex with thioacetic acid is termed as compound 2.

MATERIALS AND METHODS

A quantum mechanical analysis of 1, 3-dithia-2-arsacyclopentane derivatives have been performed on the basis of density functional theory. [38,39] Calculations for the current problem were performed on a Pentium IV/ 1.6 GHz personal computer using the Gaussian 09W suite of programs [40]. The Becke 3LYP keyword, which invokes Becke three parameter hybrid method [41] using the correlation function of Lee et al [42,43,44] and 6-31G-basis set [45,46] was used to locate the optimized geometries of the mixed 1,3-dithia-2-arsacyclopentane derivatives with oxygen and sulfur donor ligands such as acetic acid and thioacetic 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 [47] with symmetry consideration, vibrational frequency assignments were made.

RESULTS AND DISCUSSION

Geometry of the molecule

On the basis of spectroscopic data Chauhan et al have reported a tentative geometry of the molecules. Here ligands exhibit a monodented mode of attachment to the As (III) and have coordinated distorted pyramidal structure. X-Ray crystal structure data of the molecule is also not available [37]. Therefore optimized geometry of the molecule at DFT level becomes more relevant. The optimized geometry of the complex 1, 3-dithia-2-arsacyclopentane with acetic acid is shown in Fig.1 and geometry of the complex with thioacetic acid is shown in Fig.2. It is found that the calculated bond lengths are in conformity with the bond lengths expected from reported atomic radii [48]. The total energy is calculated to be -3339.39 a.u. and -3662.3 a.u.. for oxygen and sulfur ligands respectively suggesting sulfur complex to be less stable compared to oxygen complex. As-S bond length of the cyclopentane group is calculated to be 2.36 A^o approximately in both the molecules. On the other hand As-S bond length of the As-S (ligands) is 2.405 A^o in compound 2. The AS-S (ligands) bond is obtained 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 / O-C and C-C bonds of the ligands moiety are calculated to be 1.90and 1.50 A^o . respectively in com 2 while in com 1 corresponding values are 1.37, 1.50 A^0 Respectively The C=O bond in compound 1 (1.23 A^0) is slightly longer than in compound 2 (1.22 A^0) which can be attributed to hydrogen bond in compound 1. An important feature of the two compounds is that while molecule2 remains in one stable conformer, the molecule 1 undergoes rotation about O1-C3 and O1-As bond to produce one more conformation. The low energy conformer can be named as cis conformers in which the ligand 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 ligand is Trans to the R group. The cis conformer is stabilized by hydrogen bonding. The O_2-H_1 hydrogen bond length is 2.18 A^o .The bond length between cyclopentane moiety and ligand in compound 1 is less (1.87 A^0) than compound 2 (2.40 A^0) suggesting that compound 2 should be more reactive than compound 1. The study of bond lengths data suggest that bonds around heavy metal As are longer than all other bonds present in both the compounds. 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-$OCOCH_3$	R-$SCOCH_3$	Bond length	R-$OCOCH_3$	R-$SCOCH_3$
C_1-H_1	1.08	1.08	As_1-O_1/ As_1- S_3	1.87	2.40
C_1-H_2	1.09	1.09	C_3-O_1/ C_3 -S_3	1.38	1.90
C_1-C_2	1.51	1.51	C_3– O_1/ C_3– O_2	1.23	1.22
C_2-H_3	1.08	1.08	O_1-H_1	2.18	-------
C_2-H_4	1.09	1.09	C_3-C_4	1.50	1.50
C_2-S_2	1.92	1.92	C_4-H_5	1.09	1.09
C_1-S_1	1.91	1.91	C_4-C_6	1.09	1.09
S_1 – As_1	2.34	2.35	C_4-H_7	1.08	1.09
S_2 – As_1	2.36	2.36			

The optimized geometry of the molecule 1 and 2

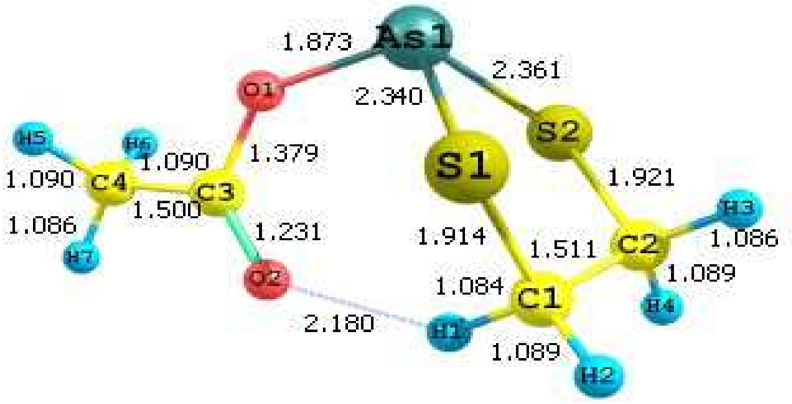


Fig.1.Optimized geometry of compound 1

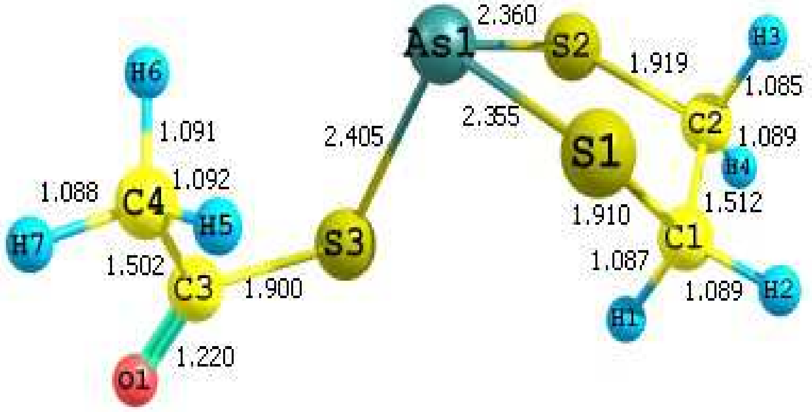


Fig.2. Optimized geometry of compound 2

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 is lower (93.4 ^{o}) compared to outer $S_1As_1O_1$ bonds (107^o) similarly in compound 2 the internal $S_2As_1S_1$ angle in cyclopantane moiety is lower (93.5 ^{o}) compared to outer $S_1As_1S_3$ bonds (102.8 ^{o}) which can be attributed to loan pair - loan pair repulsion over neibouring sulfur atoms. This also suggests SP^3 hybridization in the As atom in both the compounds. The structure of both the compounds can be assumed to be distorted tetrahedral due to the presence of lone pair on As and lp-bp repulsion around it. Similarly $As_1S_1C_1$ angle in com 1 and 2 are 96.90 ^{0} and 95.0 ^{0}**.** This is due to lp-lp repulsion on central S. As for as $As_1S_2C_2$ angle in com 1 and 2 are concern they are 98.9^0 and 98.4^0 respectively suggesting lp-lp repulsion on central S. We can also conclude that central S is in SP^2 hybridization. Bond angle $S_2As_1O_1$ in com 1 is 100.8 ^{0} and bond angle $S_2As_1S_3$ in com 2 is 94.8 ^{0} both are less than 109^{0}28'due to lp-bp repulsion. Since electronegativity of O is more than S therefore $S_2As_1S_3$ is less than $S_2As_1O_1$. Data also suggest that C_1, C_2, and C_4 carbon atoms of com. 1 and 2 are found in SP^3 hybridization. $O_1C_3O_2$/ $S_3C_3O_1$bond angle (123.6^0/ 116.8^0) and $O_2C_3C_4$/ $O_1C_3C_4$ bond angle(123.6^0/124.8^0) suggest SP^2 hybridisation in central C_3.Due to electronegativity difference between O and S bond angle of $O_1C_3O_2$ is more than $S_3C_3O_1$. It is interesting to discuss angle around As atoms bridging the two moieties namely 1, 3-dithia -2-arsacyclopetane and acetic acid / thioacetic acid. The $C_3S_3As_1$ angle in compound 2 is 106.8^o compared to $C_3O_1A_{S1}$

angle of 132.2° in the compound 1. 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 = CH_2CH_2 S_2As –

Angle	R-$OCOCH_3$	R-$SCOCH_3$	Angle	R-$OCOCH_3$	R-$SCOCH_3$
$H_1C_1H_2$	111.4	109.9	**$As_1S_2C_2$**	98.9	98.4
$H_2C_1C_2$	110.9	111.0	**$S_2As_1S_1$**	93.4	93.5
$H_1C_1C_2$	112.4	112.3	**$S_2As_1O_1$/ $S_2As_1S_3$**	100.8	94.8
$H_3C_2H_4$	110.3	110.3	**$S_1As_1O_1$/ $S_1As_1S_3$**	107.0	102.8
$H_3C_2C_1$	112.2	111.6	**$As_1O_1C_3$/ $As_1S_3C_3$**	132.2	106.8
$H_4C_2C_1$	110.6	110.8	**$O_1C_3O_2$/ $S_3C_3O_1$**	123.6	116.8
$S_1C_1H_1$	106.0	107.7	**$H_6C_4H_7$**	109.8	35.5
$S_1C_1H_2$	104.5	104.7	**$O_2C_3C_4$/ $O_1C_3C_4$**	125.3	124.8
$S_1C_1C_2$	111.1	110.6	**$C_3C_4H_5$**	110.0	110.6
$S_2C_2H_3$	107.0	107.4	**$C_3C_4H_6$**	110.0	111.1
$S_2C_2H_4$	103.8	103.8	**$C_3C_4H_7$**	109.6	108.8
$S_2C_2C_1$	112.6	112.5	**$H_5C_4H_6$**	107.3	108.0
$As_1S_1C_1$	96.9	95.0	**$H_5C_4H_7$**	110.0	109.0

Dihedral Angles

The dihedral angles of the two undertaken molecules are listed in Table 3. Analysis of dihedral angles $S_1C_1C_2S_2$ (-59.13^0/-61.07^0),$C_2C_1S_1As_1$(49.86^0/53.55^0),$C_1C_2S_2As_1$(34.18^0/32.41^0) and $C_1S_1As_1S_2$(-21.73^0/-25.44^0) in com 1 and 2 reveals that 1, 3-dithia-2-arsacyclopetane moiety is not planer. Similarly analysis of dihedral angles $S_2As_1O_1C_3$/$S_2As_1S_3C_3$ (55.590/-175.880) and $S_1As_1O_1C_3$/$S_1As_1S_3C_3$(-41.43^0/89.40^0) in compound 1 and 2 suggest that the ligand and cyclopentane moiety are not planer. we can also conclude that 1, 3-dithia-2-arsacyclopetane moiety is in cis position to ligand in com 1 while data analysis confirm the trans position of ligand to 1, 3-dithia-2-arsacyclopetane moiety.

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

Dihedral angles	R-$OCOCH_3$	R-$SCOCH_3$	Dihedral angles	R-$OCOCH_3$	R-$SCOCH_3$
$H_1C_1C_2H_4$	-56.18	-56.29	$H_1C_1S_1A_{S1}$	-72.57	-69.64
$H_1C_1C_2H_3$	-179.75	-179.76	$C_2C_1S_1A_{S1}$	49.86	53.55
$H_1C_1C_2S_2$	59.49	59.44	$C_1C_2S_2A_{S1}$	34.18	32.41
$H_2C_1C_2H_4$	69.39	67.29	$H_4C_2S_2A_{S1}$	153.85	152.32
$H_2C_1C_2H_3$	-54.18	-56.17	$H_3C_2S_2A_{S1}$	-89.52	-90.79
$H_2C_1C_2S_2$	-174.94	-176.96	$C_1S_1A_{S1}O_1$/ $C_1S_1A_{S1}S_3$	80.71	70.26
$S_1C_1C_2S_2$	-59.13	-61.07	$C_1S_1A_{S1}S_2$	-21.73	-25.44
$S_1C_1C_2H_3$	61.63	59.71	$C_2S_2A_{S1}O_1$/ $C_2S_2A_{S1}S_3$	-109.80	-101.68
$S_1C_1C_2H_4$	-174.80	-176.81	$C_2S_2A_{S1}S_1$	-1.72	1.48
$S_2A_{S1}O_1C_3$/ $S_2A_{S1}S_3C_3$	55.59	-175.88	$A_{S1}O_1C_3C_4$/ $A_{S1}S_3C_3C_4$	-176.52	-4.48
$S_1A_{S1}O_1C_3$/ $S_1A_{S1}S_3C_3$	-41.43	89.40	$A_{S1}O_1C_3O_2$/ $A_{S1}S_3C_3O_1$	3.72	176.32
$H_2C_1S_1A_{S1}$	169.58	173.29	$O_2C_3C_4H_5$/ $O_1C_3C_4H_5$	123.02	117.51
$O_1C_3C_4H_5$/ $S_3C_3C_4H_5$	-56.72	-61.61	$O_2C_3C_4H_6$/ $O_1C_3C_4H_6$	-118.99	-122.43
$O_1C_3C_4H_6$/ $S_3C_3C_4H_6$	61.26	58.43	$O_2C_3C_4H_7$/ $O_1C_3C_4H_7$	1.85	-2.25
$O_1C_3C_4H_7$/ $S_3C_3C_4H_7$	-177.89	178.62			

Electronic structure

Atomic charges depend on how the atoms are defined [49] it plays an important role in the application of theoretical 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. Table shows that 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 ligand [50] it can be attributed to the presence of more electronegative sulfur with C_1 and C_2 while in ligand less electronegative carbon is attached to C_4. C_1, C_2 of cyclopentane moiety in both the compounds are negative due to the presence of electropositive hydrogen atoms it concludes they accept electron. C_4 in both the compounds is negative, here C_4 of com 1 is more charged than C_4 of com 2 because $C_3O_1O_2$ system of com 1 is more electronegative than $C_3O_1S_3$ system of com 2. Strong electronegative O / S is attached to C_3 results in positive charge on it. Here C_3 of com 1 is more charged than com 2 it can be attributed to more electro negativity of sulfur over oxygen. Less charge on S_1, S_2, and S_3 is due to less electro negativity of sulfur and charge on O_1 and O_2

is higher than sulfur due to its high electro negativity. As_1 is most positive element in both the undertaken compounds because it is present in a moiety made of strong electronegative elements S_1, S_2, O_1 it suggest maximum reactivity around As_1 in both the compounds.

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

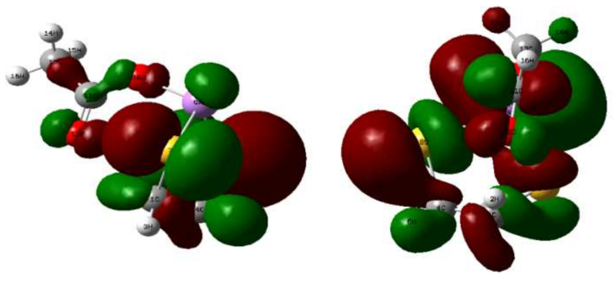
Atomic charges	R-$OCOCH_3$	R-$SCOCH_3$	Atomic charges	R-$OCOCH_3$	R-$SCOCH_3$
C_1	-0.64	-0.65	**O_2/O_1**	-0.32	-0.29
C_2	-0.59	-0.59	**H_1**	0.24	0.25
C_3	0.53	0.02	**H_2**	0.24	0.24
C_4	-0.73	-0.58	**H_3**	0.26	0.26
S_1	-0.08	-0.04	**H_4**	0.26	0.25
S_2	0.01	0.01	**H_5**	0.23	0.22
O_1/ S_3	-0.61	-0.01	**H_6**	0.23	0.23
As_1	0.75	0.45	**H_7**	0.23	0.22

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

5. Table R = $CH_2CH_2S_2As$ –

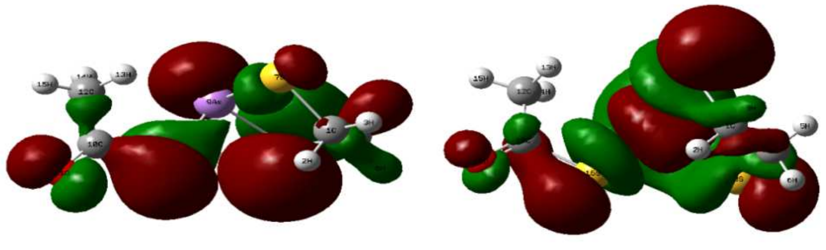
	R-$OCOCH_3$	R- $SCOCH_3$		R-$OCOCH_3$	R- $SCOCH_3$
Dipole Moment	0.31 Debye	4.0 Debye	**HOMO**	-0.25 Hartree	-0.26 Hartree
Total Energy	-3339.39 a.u.	-3662.3 a.u.	**LUMO**	-0.06 Hartree	-0.08 Hartree
Point group	C1	C1	**Energy GAP**	0.19 Hartree	0.18 Hartree
			Energy GAP	5.17 eV	4.89 eV

The frontier molecular orbitals HOMO and LUMO gap (band gap) helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small band gap is more polarizable and is suppose to posses high chemical reactivity and can be termed as soft molecule [51, 52]. HOMO is electron donor and LUMO is electron accepter [53] the band gaps for molecule 1 and 2 are computed to be 5.17 eV (240 nm) and 4.89 eV (253 nm) respectively which matches well with the observed value in the range 210 -270 nm. It suggest high chemical reactivity of compound 2 than compound 1. The electron movement between these orbitals could easily occur [54] 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 0.18 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 molecules 1, 3-dithia-2-arsacyclopentane derivatives with oxygen and sulfur donor legends such as acetic acid (compound 1) and thioacetic acid (compound 2) both has 16 atoms as a result of it 42 fundamental modes of vibrations are present in both the molecules. The molecules belong to the Cs point group and all vibrations are supposed to IR as well as Raman active.

C-H Stretching Vibrations;

For molecule 1 seven frequencies are computed at 3170.1, 3136.8, 3076.9 ,3065.9, 3155.2, 3111.9 and 3046.3 cm.$^{-1}$ `Consideration of Cartesian displacements revealed that frequencies appeared at 3170.1, 3136.8, 3076.9 and 3065.9 cm^{-1} should be assigned to C-H stretching modes of cyclopentane moiety and 3155.2, 3111.9 and 3046.3 cm^{-1} should be assigned to C-H stretching modes of methyl group. Out of this only one mode at 2962 cm-1 is observed by Chauhan et al. The nearest calculated frequency corresponding to the reported observed frequency at 3050 cm^{-1} is 3046.3 cm^{-1}. Its dependence on Cartesian coordinates suggests it belong to methyl group. Similarly in molecule 2 the four bands computed at 3151.3,3132.5,3075.6 and 3066.1 cm^{-1} can be assigned to C-H stretching modes of cyclopentane moiety and three modes appeared at 3132.3, 3098.9 and 3029.8 cm^{-I} can be assigned to methyl group. 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 [55-60] and Cartesian displacement of normal modes. The nearest calculated frequency corresponding to the reported observed frequency at 2930 cm^{-1} is 3029.8 cm^{-1}. Its dependence on Cartesian coordinates suggests it to belong to methyl group.

Heavy Atoms Stretching Modes:

Frequencies computed at 1689.8 and 1712.9 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 1650 and 1650 cm^{-1} respectively. Frequencies computed that 599.3 and 604.3 cm^{-1} can be assigned to C-S stretching modes of the compound 1 and 2 respectively. Corresponding observed bands have appeared at 625 and 610 cm^{-1}. Calculated vibrational frequencies are found in well conformity with experimental values.

Metal Legend Stretching Vibrations:

These include As-S and As-O stretching modes. Frequency calculated at 320.0 cm $^{-1}$ can be assigned to As-S stretching modes in molecule 1 Corresponding observed band has appeared at 315 cm. $^{-1}$ For compound 2 frequency lie at 348.4 cm. $^{-1}$ and for it observed freaquency is at 335 cm. $^{-1}$ Data show an excellent agreement between the observed and calculated frequencies. While in molecule 1 As_1-O_1 stretching mode is calculated and observed at 542.4 cm $^{-1}$ and 510 cm $^{-1}$ respectively.

Other vibration modes:

In molecule 1 the frequencies calculated at 1225.7 cm^{-1} and 1037.3 cm^{-1} are assigned to C_3-C_4 and C_1-C_2 stretching modes respectively. In molecule 2 these modes are calculated at 959.9 and 1034.6 cm $^{-1}$. For molecule 1 assignment of frequencies computed in the range 53.6-1512.9 cm^{-1} belong to different C-H bending modes and are shown in Table 7.similarly for molecule 2 assignment of frequencies computed in the range 24.3-1516.8 cm^{-1} belong to different C-H bending modes and are shown in Table 7.1. In compound 1 O-C-O, C_3-O_1-As_1, and O_1-As_1-S_1 bending modes are calculated at 633.4 cm $^{-1}$,195.8 cm $^{-1}$ and 177.2 cm $^{-1}$ respectively while for compound 2 O_1-C_3-C_4, C_4-C_3-S_3, S_2-As_1-S_1,C_3-S_3-As_1 bending modes are calculated at 584.1 cm $^{-1}$,374.3 cm $^{-1}$, 262.6 cm $^{-1}$and 146.5 cm.$^{-1}$ respectively.

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

A(Cyclopantane moiety), B(Methyle group)

SN.	Frequency (Calculated)	Freq. Obs.	Assignt.	Force Const	Cartesian Displacement
1.	3170.1(4.1)	-----	Asym $\nu(C_1\text{-}H_1)$A	6.5	C_1(-0.09X) + H_1(0.76X) + H_2(0.27Y) + H_3(0.22X)
2.	3155.2(9.6)	-----	Asym $\nu(C_4\text{-}H_7)$B	6.5	C_4(0.09Y) + H_5(-0.27Z) +H_6(0.24Z) + H_7(-0.82Y)
3.	3136.7(11.4)	-----	Asym $\nu(C_2\text{-}H_3)$A	6.4	H_2(-0.10Y) + C_2(0.06Y) + H_3(0.70X) + H_4(-0.38Z)
4.	3111.9(5.9)	-----	Asym $\nu(C_4\text{-}H_6)$B	6.3	C_4(0.09Z) + H_5(-0.54Z) + H_6(-0.56Z) + H_7(-0.04Y)
5.	3076.9(21.8)	-----	Sym $\nu(C_1\text{-}H_2)$A	5.9	C_1(-0.05Y) + H_1(-0.37X) + H_2(0.47X) + H_4(0.29Z)
6.	3065.0(2.5)	-----	Sym $\nu(C_2\text{-}H_4)$A	5.8	H_2(-0.29X) + C_2(-0.04X) + H_3(0.41X) + H_4(0.51Z)
7.	3046.2(3.0)	2962	Sym $\nu(C_4\text{-}H_5)$B	5.7	C_4(0.05X) + H_5(-0.48Z) + H_6(0.55Z) + H_7(0.41Y)
8.	1689.7(137.3)	1650	$\nu(C_3=O_2)$	15.0	C_3(0.53Y) + O_2(-0.35Y) + C_4(-0.08X) + H_7(0.29X)
9.	1225.7(431.1)	-------	$\nu(C_3\text{-}C_4)$B	3.2	C_3(0.32X) + C_4(0.14Y) + H_6(-0.26Y) + H_7(-0.72X)
10.	1037.3(1.8)	-------	$\nu(C_1\text{-}C_2)$A	1.6	C_1(0.19Z) + H_2(0.52Z) + C_2(-0.19Z) + H_4(-0.44Z)
11.	892.3(161.0)	-----	$\nu(C_3\text{-}O_1)$	3.4	O_1(0.42Y) + C_3(-0.15Y) + O_2(-0.24Y) + C_4(0.32X)
12.	599.3(6.7)	625	$\nu(C_1\text{-}S_1)$	0.8	C_1(0.29Y) + H_1(0.41Y) +S_1(-0.11Y) + H_2(0.31X)
13.	582.3(7.8)	-----	$\nu(C_2\text{-}S_2)$	1.2	C_2(0.34X) + C_1(0.30Y) + H_4(0.41X) + S_2(-0.13Y)
14.	542.4(21.8)	510	$\nu(As_1\text{- }O_1)$	0.8	As_1(0.06X)+O_1(-0.33X) + C_3(0.21Y) +O_2(0.22X)
15.	351.9(16.5)	-----	$\nu(As_1\text{- }S_1)$	1.8	H_4(-0.26Y)+ S_1(0.49z)+S_2(-0.48Z)+As_1(0.20Y)
16.	320.0(13.5)	315	$\nu(As_1\text{- }S_2)$	0.9	H_4(-0.30Y)+S_1(0.26Y)+S_2(-0.32Z)+As_1(0.25Z)

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

A(Cyclopantane moiety), B(Methyle group)

SN.	Frequency (Calculated)	Freq. Obs.	Assignt.	Force Const	Cartesian Displacement
1.	3151.3(5.8)	-----	Asym $\nu(C_2\text{-}H_3)$A	6.5	H_1(0.30X) + C_2(0.06Z) + H_3(0.47X) + H_4(-0.28Z)
2.	3132.5(0.2)	-----	Asym $\nu(C_1\text{-}H_1)$A	6.4	H_1(0.42X) + H_2(0.37Y) + H_3(-0.27X) + C_1(-0.06X)
3.	3132.3(15.1)	-----	Asym $\nu(C_4\text{-}H_7)$B	6.4	C_4(-0.09X) + H_5(0.24Y) + H_6(-0.29Z) + H_7(0.83X)
4.	3098.9(3.8)	-----	Asym $\nu(C_4\text{-}H_6)$B	6.2	C_4(0.06Y) + H_5(-0.53Y) + C_6(-0.62Z) + H_7(0.03Y)
5.	3075.6(12.8)	-----	Sym $\nu(C_2\text{-}H_4)$A	5.9	H_1(-0.30X) + H_2(0.35Y) + C_2(-0.05X) + H_4(0.42Z)
6.	3066.1(4.1)	-----	Sym $\nu(C_1\text{-}H_2)$A	5.8	H_1(-0.29X) + H_2(0.42Y) + C_1(-0.04Z) + H_4(-0.40Z)
7.	3029.8(0.8)	2930	Sym $\nu(C_4\text{-}H_5)$B	5.6	C_4(0.04Z) + H_5(0.49Y) + H_6(0.14Y) + H_7(-0.43X)
8.	1712.9(368.0)	1650	$\nu(C_3=O_1)$	16.7	C_3(0.49X) + O_1(-0.36X) + H_5(0.31Z) + H_7(-0.29Y)
9.	1034.6(1.6)		$\nu(C_1\text{-}C_2)$A	1.7	C_1(0.20X) + H_2(-0.42Y) + C_4(0.16Z) + H_4(0.49Y)
10.	959.9(115.8)		$\nu(C_3\text{-}C_4)$A	1.6	H_5(-0.44Y) + C_3(0.18Y) + C_4(0.20Z) +H_7(0.40Z)
11.	604.3(3.9)	610	$\nu(C_1\text{-}S_1)$	0.9	C_1(0.29Z) + S_1(-0.11Z) + H_1(0.42Z) + H_2(0.39X)
12.	587.7(13.8)	-----	$\nu(C_2\text{-}S_2)$	1.0	C_2(0.30X) + S_2(-0.10X) + H_3(0.17Y) + H_4(0.38X)
13.	418.8(32.2)	-----	$\nu(C_3\text{-}S_3)$	1.3	C_3(0.29X) + S_3(-0.41X) + O_1(0.42X) + C_4(-0.07Z)
14.	348.4(24.9)	335	$\nu(As_1\text{-}S_1)$	1.5	As_1(-0.18X)+S_2(-0.40Y) + S_1(0.47Y) + C_2(-0.12Y)
15.	318.2(9.7)	-----	$\nu(As_1\text{-}S_2)$	1.2	As_1(-0.18X)+S_2(-0.30X) +H_3(-0.32X)+C_2(-0.15X)
16.	245.5(10.1)	-----	$\nu(As_1\text{-}S_3)$	0.2	As_1(0.11X)+S_3(-0.07X) +S_1(0.09Y)+C_3(-0.08X)

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

A(Cyclopantane moiety), B(Methyle group)

SN	Frequency (Calculated)	Freq. Obs.	Assignt.	Force Const	Cartesian Displacement
1	1512.9(13.1)	-----	π β (C-H)B	1.4	$C_4(0.05Z)+H_5(0.38Y)+H_6(0.33X)+H_7(-0.72Z)$
2	1508.7(25.1)	-----	π β (C-H)B	1.4	$C_4(0.05Y)+H_5(-0.49Y)+H_6(-0.52Y)+H_7(0.40Y)$
3	1494.7(10.9)	-----	π β (C-H)A	1.4	$H_1(0.44Y)+H_2(-0.37X)+H_3(0.39Z)+H_4(0.40X)$
4	1488.9(11.2)	-----	π β (C-H)B	1.4	$H_1(-0.35Y)+H_2(0.32X)+H_3(0.40Z)+H_4(0.52X)$
5	1441.1(35.9)	-----	W β (C-H)B	1.5	$C_4(0.14X)+H_5(-0.51X)+H_6(-0.57X)+H_7(-0.46X)$
6	1361.5 (7.9)	-----	τ β (C-H)A	1.3	$H_1(0.65Z)+H_2(0.20Y)+H_3(0.37)+H_4(0.13X)$
7	1313.4(14.5)	-----	W β (C-H)B	1.2	$H_1(0.27Z)+H_2(0.46Z)+H_3(-0.43Y)+H_4(0.37Z)$
8	1183.1(1.9)	-----	τ β (C-H)A	1.0	$H_1(-0.13Z)+H_2(0.64Z)+H_3(0.14X)+H_4(0.43Y)$
9	1165.6(4.7)	-----	τ β (C-H)A	0.8	$C_3(0.32X)+C_4(0.14Y)+H_6(-0.26Y)+H_7(-0.72X)$
10	1093.3(8.5)	-----	R β (C-H)B	1.2	$C_4(-0.16Z)+H_5(-0.58X)+H_6(0.63X)+H_7(0.35Z)$
11	1029.8(108.2)	-----	W β (C-H)B	1.2	$C_4(-0.17Y)+H_5(-0.49X)+H_6(-0.45X)+H_7(0.59X)$
12	972.8(8.6)	-----	R β (C-H)A	0.8	$H_1(0.43Y)+H_2(-0.44Y)+H_3(0.43Y)+H_4(-0.44X)$
13	869.1(13.5)	-----	R β (C-H)A	0.7	$H_1(0.30Y)+H_2(-0.49Y)+H_3(-0.31Z)+H_4(0.57X)$
14	633.4(38.7)	-----	π β (O-C-O)	1.9	$O_1(0.33Y)+C_3(-0.15X)+O_2(-0.26Y)+C_4(-0.39X)$
15	590.1(6.2)	-----	R β (C-H)B	0.6	$O_2(0.13Z)+H_5(-0.50X)+H_6(0.59X)+H_7(0.33Z)$
16	422.2(3.4)	-----	R β (C-H)A	0.4	$H_1(0.32Z)+H_2(-0.29X)+C_2(0.21Z)+H_3(0.43Z)$
17	310.2(40.2)	-----	β (C-H)B	0.3	$C_4(0.24\ Y)+H_5(-0.36X)+H_6(0.33Y)+H_7(0.36Y)$
18	265.9(9.8)	-----	β (C-H)A	0.4	$H_1(0.33Z)+H_2(-0.36X)+H_3(-0.37Z)+H_4(0.45X)$
19	257.7(0.5)	-----	β (C-H)A	0.1	$H_1(0.34Y)+H_2(0.45X)+H_3(0.33Z)+H_4(-0.27X)$
20	195.8(6.3)	-----	β(C_3-O_1-As_1)	0.2	$S_2(0.16X)+As_1(0.08Z)+O_1(-0.60Z)+C_3(-0.20Z)$
21	177.2(10.5)	-----	β(O_1-As_1-S_1)	0.1	$S_1(0.19X)+As_1(-0.09X)+O_1(-0.23Y)+C_3(-0.17Y)$
22	123.5(2.7)	-----	β (C-H)A	0.04	$H_1(0.21X)+C_2(0.21X)+H_3(-0.31Y)+H_4(0.40X)$
23	110.9(2.1)	-----	β (C-H)A	0.04	$H_1(0.27X)+H_2(0.28X)+H_3(-0.45Y)+H_4(0.46X)$
24	101.7(0.1)	-----	R β (C-H)B	0.008	$O_2(-0.11Z)+H_5(0.49Y)+H_6(-0.51Y)+H_7(0.58Z)$
25	75.5(0.6)	-----	R β (C-H)B	0.01	$O_2(0.32Z)+H_5(0.43Y)+H_6(-0.41Y)+H_7(0.46Z)$
26	53.6(3.3)	-----	R β (C-H)B	0.006	$C_4(0.33Z)+H_5(0.55Z)+H_6(0.51Z)+H_7(0.46Z)$

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

A(Cyclopantane moity), B(Methyle group)

SN	Frequency (Calculated)	Freq. Obs.	Assignt.	Force Const	Cartesian Displacement
1	1516.8(23.5)	-----	π β (C-H)B	1.4	$C_4(0.04Y)+H_5(0.39X)+H_6(-0.38X)+H_7(-0.51Y)$
2	1504.3(44.4)	-----	π β (C-H)B	1.4	$C_4(0.05X)+H_5(-0.41X)+H_6(-0.57X)+H_7(-0.35Z)$
3	1491.6(2.8)	-----	π β (C-H)A	1.4	$H_1(0.28Z)+H_2(0.28Z)+H_3(0.45X)+H_4(0.48X)$
4	1487.2(13.5)	-----	π β (C-H)A	1.4	$H_1(0.41Z)+H_2(0.46Z)+H_3(-0.27X)+H_4(-0.33X)$
5	1438.1(29.4)	-----	W β (C-H)B	1.5	$C_4(-0.10Z)+H_5(0.55Z)+H_6(-0.55Y)+H_7(0.36Z)$
6	1347.2(20.6)	-----	W β (C-H)A	1.3	$H_1(-0.48Y)+H_2(0.16Z)+H_3(0.55Y)+H_4(0.15X)$
7	1309.9(5.2)	-----	W β (C-H)A	1.2	$H_1(-0.31X)+H_2(0.40Y)+H_3(0.29Z)+H_4(0.46Y)$
8	1183.8(0.4)	-----	W β (C-H)A	1.0	$H_1(0.15Z)+H_2(0.47X)+H_3(0.16X)+H_4(0.53Y)$
9	1151.3(4.0)	-----	τ β (C-H)A	0.8	$H_1(0.41Y)+H_2(0.31X)+H_3(0.46Y)+H_4(-0.32Y)$
10	1141.9(172.7)	-----	R β (C-H)B	1.5	$C_4(0.17X)+H_5(0.26Y)+H_6(-0.29X)+H_7(0.58Z)$
11	1068.7(2.9)	-----	R β (C-H)B	1.0	$C_4(0.11Y)+H_5(-0.56Z)+H_6(-0.55Y)+H_7(-0.25Y)$
12	962.6(3.2)	-----	R β (C-H)A	0.8	$H_1(-0.40Z)+H_2(0.45Z)+H_3(-0.36X)+H_4(0.44X)$
13	869.9(15.8)	-----	R β (C-H)A	0.6	$H_1(-0.29Z)+H_2(0.55Z)+H_3(-0.12Z)+H_4(0.33X)$
14	584.1(105.7)	-----	π β (O_1-C_3-C_4)	0.9	$O_1(0.23X)+C_3(0.16Y)+C_4(0.19Z)+H_6(0.54Z)$
15	505.9(1.7)	-----	R β (C-H)B	0.5	$C_4(-0.02Z)+H_5(-0.49Z)+H_6(-0.51Y)+H_7(-0.28Y)$
16	425.9(3.5)	-----	R β (C-H)A	0.4	$H_1(0.41Z)+H_2(0.24Y)+H_3(-0.42X)+H_4(0.22Y)$
17	374.3(0.2)	-----	π β (C_4-C_3-S_3)	0.4	$C_4(-0.26X)+C_3(0.06Y)+S_3(-0.19Y)+O_1(-0.13Z)$
18	262.6(4.4)	-----	π β (S_2-As_1-S_1)	0.2	$S_1(0.15X)+As_1(-0.09Z)+s_2(0.13Z)+c_1(-0.15Y)$
19	255.5(32.8)	-----	R β (C-H)A	0.2	$H_1(-0.27Y)+H_2(-0.27X)+H_3(0.22Y)+H_4(-0.18Z)$
20	164.8(0.9)	-----	R β (C-H)B	0.01	$C_4(0.01X)+H_5(-0.41X)+H_6(0.56X)+H_7(-0.38Y)$
21	146.5(2.9)	-----	β (C_3-S_3-As_1)	0.09	$C_3(-0.04x)+S_3(-0.23y)+As_1(0.09Z)+S_1(0.21X)$
22	131.7(0.7)	-----	β (A and B)	0.08	$H_6(-0.40X)+H_5(-0.49X)+C_4(-0.35X)+S_2(0.24X)$
23	86.3(1.6)	-----	β (A and B)	0.04	$H_7(-0.37X)+H_6(-0.28X)+H_2(0.27X)+C_4(-0.26X)$
24	61.6(4.1)	-----	β (A and B)	0.01	$H_1(-0.31X)+H_3(036Z)+H_4(0.34X)+O_1(-0.23Y)$
25	43.9(4.2)	-----	β (A and B)	0.006	$H_7(-0.39Y)+O_1(0.26Z)+H_2(-0.21X)+H_1(-0.23X)$
26	24.3(2.0)	-----	β (A and B)	0.002	$H_6(0.36Y)+H_7(0.37Y)+H_5(0.22X)+C_4(0.25Y)$

CONCLUSION

Density function theory (DFT) computations are carried out for the model compounds CH_2CH_2 S_2As – $ACOCH_3$ (A=S, O) with the objectives of suggesting their geometry, electronic structure, and bonding. The geometrical parameters, band gap and assignment of important vibration frequencies are reported. The As-S (ligands) bond length of 2.40 A^0 is slightly higher than As-S (1, 3-dithia-2-arsacyclopentane moity) bond length 2.35 A^0. It is found that the calculated bond lengths are in conformity with the bond lengths expected from reported atomic radii. The bond length between cyclopentane moiety and ligand in compound 1 and 2 suggest that compound 2 should be more reactive than compound 1. By analyzing the bond lengths data in both the compounds bonds around heavy metal As are found longer than all other bonds suggesting that active sites in both undertaken compounds are centered around As. Bond angle analysis around heavy metal As suggest SP^3 hybridization on As atom in both the compounds Therefore the structure of undertaken compounds can be assumed to be distorted tetrahedral. We can also conclude that ALL S atoms are in SP^2 hybridization. Data analysis also suggests C_1, C_2, and C_4 carbon atoms of com. 1 & 2 to posses SP^3 hybridization and C_3 is in SP^2 hybridization. Analysis of dihedral angles reveals that 1, 3-dithia-2-arsacyclopetane moiety is not planer. It can also be concluded that ligand and cyclopentane moiety are not planer. Analysis also suggest that 1, 3-dithia-2-arsacyclopetane moiety is in cis position to ligand in com 1 while in com 2 it is trans.As_1 is most positive element in both the undertaken compounds. It suggests maximum reactivity around As_1 in both the compounds. Energetically sulfur complex is found to be less stable compared to oxygen complex. On the other hand compound 2 is more polar than compound 1. The band gaps for molecule 1 and 2 are computed to be 5.07 eV (245 nm) and 4.75 eV (261 nm) respectively It suggest high chemical reactivity of compound 2 than compound 1. An important feature of the two complexes is that while compound 2 exists in only one stable form the compound 1 has one more conformer. The compound1 is stabilized by hydrogen bonding. Zero-point vibrational energy for compound 1 and 2 is reported to be 291633.6 (Joules/Mol) with zero-point correction 0.111077 (Hartree/Particle) and 283863.8 (Joules/Mol) with zero-point correction 0.108118 (Hartree/Particle) respectively. Calculated vibrational frequencies are found in well conformity with experimental values reported by Chauhan at al [37].

REFERENCES

[1] Mehrotra, M.S.; Srivastava, G.; Chauhan, H. P. S. *Coord. Chem. Rev.* **1984,** *55*, 207–259.

[2] Garje, S. S.; Jain, V. K. *Coord. Chem. Rev.* **2003,** *236*, 35–56.

[3] Silvestru, C.; Haiduc, I. *Coord. Chem. Rev.* **1996,** *147*, 117–146.

[4] Ludwing, R. A.; Thorn, G. D. *Adv. Pest Control Res.* **1960,** *3*, 219–252.

[5] Gallagher, R. E. *N. Engl. J. Med.* **1998,** *339*, 1389–1391.

[6] Shen, Z. Y.; Shen, W. Y.; Chen, M. H.; Shen, J.; Cai, W. J.; Zeng, Y. M. *Int. J. Mol. Med.* **2002,** *9*, 385–390.

[7] Uslu, R.; Sanli, U. A.; Sezgin, C.; Karabulut, B.; Terzioglu, E.; Omay, S. B.; Goker, E. *Clin. Cancer Res.* **2000,** *6*, 4957–4964.

[8] P.J. Dilda, P.J. Hogg, Cancer Treatment Rev. 33 (2007) 542–564.

[9] S.J. Ralph, Met-Based Drugs (2008) 1–13. Article ID 260146.

[10] W.H.C. Rueggeberg, A. Ginsberg, W.A. Cook, J. Am. Chem. Soc. 68 (1946) 1860–1862.

[11] W.J. Vickaryous, E.R. Healey, O.B. Berryman, D.W. Johnson, Inorg. Chem. 44 (2005) 9247–9252.

[12] W.J. Vickaryous, R. Herges, D.W. Johnson, Angew. Chem. Int. Ed. 43 (2004) 5831

[13] Kenneth, W. W.; Houghton, C. L.; Sedlak, D. L. *Anal. Chem.* **1998,** 70, 4800-4804.

[14] Cvek, B.; Melacic, V.; Taraba, J.; Dou, Q. P. *J. Med. Chem.* **2008,** 51, 6256-6258.

[15] Kateva, J.; Ivanou, S. K.; *J. Polym. Sci. Part A: Polym. Chem.* **1979,** 17, 2707-2718.

[16] Plyusnin, V. F.; Kolomeets, A. V.; Grivin, V. P.; Larinov, S. V.; Lemmetyinen, H. *J. Phys. Chem.A.* **2011,** 115, 1763-1773.

[17] Regulacio, M. D.; Tomson, N.; Stoll, S. L. *Chem. Mater.* **2005,** 17, 3114-3121.

[18] Jian, F.; Bei, F.; Zhao, P.;Wang, X.; Fun, H.; Chinnakali, K. *J. Coord. Chem.* **2002,** 55, 429-437.

[19] Sheng, T.; Wu, X.; Lin, P.; Zhang, W.; Wang, Q.; Chen, L. *Polyhedron* **1999,** 18, 1049-1054.

[20] Phillips, D. J.; Oscar, F. L. Additives for lubricants: Mobil oil. W01995/0199441. **1995** Jul –5833

[21] Shivram S.; Garje; Vimal K. Jain; *Coordination Chemistry Reviews* 236 (**2003**) 35_ 56

[22] P. Lostak, C. Drasar, A. Krejcova, L. Benes, J.S. Dyck, W.Chen, C. Uher, *J. Cryst. Growth* 222 (**2001**) 565;

[23] L. Iordanidis, P.W. Brazis, T. yratsi, J. Ireland, M. Lane,C.R. Kannewurf, W. Chen, J.S. Dyck, C. Uher, N.A. Ghelani,T. Hogan, M.G. Kanatzidis, *Chem. Mater*. 13 (**2001**) 622;

[24] V.A. Greanya, W.C. Tonjes, R. Liu, C.G. Olson, D.Y.Chung, M.G. Kanatzidis, *Phys. Rev*. B 62 (**2000**) 16425;

[25] A.L. Prieto, M.S. Sander, M.S. Martin-Gonzalez, R.Gronsky, T. Sands, A.M. Stacy, *J. Am. Chem. Soc*. 123 (**2001**)7160.

[26] Y. Rodriguez-Lazcano, M.T.S. Nair, P.K. Nair, *J. CrystGrowth* 223 (**2001**) 399;

[27] B. Mednikarov, *Bulg. Chem. Commun*. 26 (**1993**) 502;

[28] B. Mednikarov, *Chem. Abstr*. 122 (**1997**) 302676;

[29] Y. Rodriguez-Lazcano, L. Guerro, O.G. Daza, M.T.S. Nair,P.K. Nair, Superficies y Vacio 9 (**1999**) 100;

[30] K. Nagaro, Y. Watanabe, B. Huybrechts, M. Takata, Surf.Modf. Technol. VII Proc. *Int. Conf.* **1993**.

[31] K. Nagaro, Y. Watanabe, B. Huybrechts, M. Takata, *Chem.Abstr*. 123 (**1995**) 325628;

[32] O. Salminen, A. Ozols, P. Riihola, P. Moenkkoenn, *J. ApplPhys*. 78 (**1993**) 718;

[33] M.S. Iovu, E.G. Khanchevskaya, *Phys. Status Solidi A* 156(**1996**) 375;
[34] M.S. Iovu, E.G. Khanchevskaya, *Chem. Abstr.* 125 (**1996**)312301;
[35] M.N. Kozieki, S.W. Hsia, U.S. Patent 531477A, **1994**.;
[36] M.N. Kozieki, S.W. Hsia, *Chem. Abstr.* 121 (**1994**) 96058.
[37] H.P.S. Chauhan; Sumit Bhatia; Abhilash Bakshi; K. S. Makwana*;Phosphorus, Sulphure And Silicon,* **2011,** 186, 511-519.
[38] W. Kohn; L. J. Sham; *Phys. Rev*.,**1965,** 140, A1133.
[39] P. Hohenberg; W.Kohn; *Phys. Rev*., **1964**, 136, B864.
[40] M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria et al., Gaussian 09, Revision A02, Gaussian Inc, Wallingford CT, **2009**.
[41] Beack A D*; J Chem Phys*, **1993,** 98, 5648.
[42] Lee C; Yang W & Parr R. G.; *Phys Rev B*, **1998,** 37, 785.
[43] B. Miehlich; A. Savin; H. Stroll; H. Preuss;, *Chem. Phys. Lett*., **1989**, 157, 200.
[44] C.Lee;W. Yang; R.G. Parr;. *Phys. Rev*., **1988**, 37 B787.
[45] Francl M.M.; Pietro W. J.; HehreW. J.; Binkley J.S.; Gordan M.S. ;Defrees D. J.; Pople J.*A.; Journal of Chemical Physics*, **1982**, 77, 3654.
[46] R. Ditch field; W. J. Hehre; J.A. Pople; *J. Chem. Phys*., **1971,** 54, 724.
[47] Frisch A; Nielson A B ; Holder A J; Gauss view Users Manual, Gaussian Inc, Pittsburgh PA,**2000**.
[48] Pekka Pyykkö, Michiko Atsumi, *Chemistry - A European Journal*, Vol.15, Issue 46, **2009,** Vol.15, 12770.
[49] A. B. Sawant; R. S. Nirwan; *Indian Journal of Pure & Applied Physics*, **2012**,50, 308.
[50] Y. Zalaoglu; G. Yildirim; A. T. Ulgen; *J. Sci. Tech.,***2011**, *1*, 36.
[51] R. Kurtaran; S. Odabasoglu; A. Azizoglu; H. Kara;O. Atakol; *Polyhedron,* **2007**,26,5069.
[52] I. Fleming; *Frontier Orbitals and Organic Chemical Reactions,* J. Wiley and Sons, New York, **1976**.
[53] R. K. Srivastav; V. Narayan; O. Prasad and L. Sinha;*Journal Of chemical and Pharmaceutical Research,* **2012**, 4(6) , 3287.
[54] S. Sagdinc; H. Pir; *Spectrochimica Acta A,* **2009**, 73, 181.
[55] H. P. S. Chauhan; S. Bhatiya; A. Bakshi; *Spectrochim. Acta Part* A,**2009,** *74*, 67.
[56] K. R. Chaudhari; V. K. Jain; V. S. Sagoria;E. R. T. Tiekink;*J. Organometal. Chem,* **2007,** *692*, 4928.
[57] L.Yu; J. S.Li;Z. Xuan; R. Liu; *J. Organometal. Chem.*, **2004,** *620*, 235.
[58] S. Bhattacharya; S. *Spectrochim. Acta Part A,* **2005,** *61*, 3145.
[59] K. Nakamoto; Infrared *and Raman Spectra of Inorganic and Coordination Compounds Part B*, 5th ed.,John Wiley & Sons, New York, **1997**, Sect. III, 74.
[60] D. N. Sathyanarayana; *Vibrational Spectroscopy Theory and Applications* 2nd ed.,New Age International Limited: New Delhi, **2005,** 390.