

## **Synthesis, structural and spectroscopic properties of Tris (diethyldithiocarbamato) arsenic(III)**

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### **ABSTRACT**

*In this paper, vibrational and electronic spectral analysis of Tris (diethyldithiocarbamato) arsenic(III) were presented using experimental techniques(FTIR,UV) and quantum chemical calculations. HOMO-LUMO properties also discussed.*

**Keywords:** Tris (diethyldithiocarbamato) arsenic(III), Vibrational, Electronic spectra, HOMO-LUMO

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### **INTRODUCTION**

Dithiocarbamato complexes are useful in water purification, metal ion detector in water, lubricating oil and potent antioxidant agent, IR spectral detector. So dithiocarbamato complexes are interested in the current research. Arsenic dithiocarbamato complexes have potential applications in the field of medical, industrial and communication. Hence it is catalysed us to prepare arsenic dithiocarbamato complexes with simple synthesis root.

Inarida. M[1] has reported the electronic spectra of diethyl dithiocarbamate complex of central atoms with  $S^2$  electron configuration. Preparation and study of some arsenic trisdithiocarbamates have reported by A.I.Saklaet.al [2].

R. R .Schanta et.al.[3]have reported the synthesis and spectral study of new iodo bis (dialkyldithiocarbamato) complexes of arsenic.

Five coordinate Bromo bis (dibutyldtc) complex of Arsenic was reported by G. E. Monovshakis et.al [4] S.Eskerar et.al[5] has reported the synthesis and spectroscopic study of a new series of mixed ligand complexes of As III with dithio ligands.

### **MATERIALS AND METHODS**

#### **Experimental Method**

Arsenic oxide is dissolved in water using sodium hydroxide pellets and neutralised with hydrochloric acid. It is added to the aqueous solution of sodium diethyldithiocarbamate. White precipitate obtained, is filtered, dried and recrystallised from chloroform. Arsenic oxide and sodium diethyldithiocarbamate are taken in 1:1 molar proportion.

#### **Computational Method**

For supportive evidence to the experimental observations, the ab initio computations were performed with the aid of GAUSSIAN 09W [6] software package with internally stored HF/sto-3g\* basis set methods. At first, the global minimum energy structure of the title molecule was optimized. Subsequently, the vibrational normal mode wave

numbers in association with the molecule were derived along with their IR intensity, Raman activity and HOMO-LUMO properties also studied.

## RESULTS AND DISCUSSION

### Vibrational spectra

The FTIR spectrum of tris(diethyldithiocarbamato)arsenic(III) complex is shown in Figure(1). Silvrstein and webstor[7] assigned C=N stretching vibration in the range  $1471\text{--}1689\text{ cm}^{-1}$ ,  $1266\text{--}1382\text{ cm}^{-1}$  and  $1020\text{--}1250\text{ cm}^{-1}$ . We observed the C=N stretching vibration is at  $1486.9\text{ cm}^{-1}$ . Two more peaks at  $1450.2$  and  $1422.9\text{ cm}^{-1}$  are also observed. These peaks can be assigned to out of plane bending vibrations of the alkyl group. The corresponding in plane bending vibrations is assigned to the peaks at  $1373.8$  and  $1353.5\text{ cm}^{-1}$ . The C–N stretching vibration is also found to split between  $1200$  and  $1300\text{ cm}^{-1}$ . Origin of such multiple bands depending on the nature of alkyl amino groups has also been reported in the literature<sup>1</sup>. These experimental observations coordinate with computational analysis. Results are tabulated in the table (1).

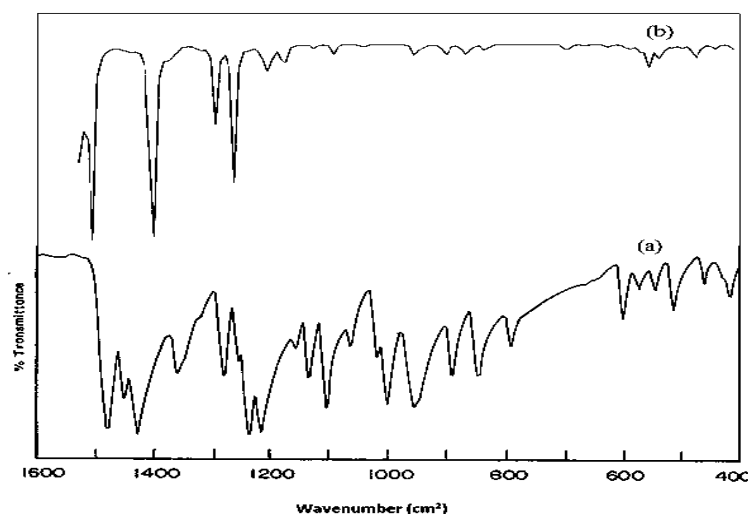


Figure 1. FTIR spectrum of tris(diethyldithiocarbamato)arsenic(III) (a) Experimental (b) Computational

### HOMO-LUMO analysis

The energies of two important molecular orbitals of the complex of arsenic III, the highest occupied molecules (HOMO), the lowest unoccupied molecules (LUMO) were calculated and are presented in fig(3). The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [8]

Molecular orbitals (HOMO and LUMO) and their properties such as energy are very useful for physicists and chemists and are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in  $\pi$ -electron systems and also explains several types of reaction in conjugated system [9]. The conjugated molecules are characterized by a small highest occupied molecular orbital – lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of intramolecular charge transfer from the end-capping electron-donor groups to the efficient electron-acceptor groups through  $\pi$ -conjugated path [10]. This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital [11]. Recently, the energy gap between HOMO and LUMO has been used to prove the NLO, bioactivity from the intramolecular charge transfer from SCN to carbamato molecules [12, 13].

Table 1. Vibrational Frequency Assignments

Frequency	FT-IR	Raman	Experiment value	Vibrational Assignment
	HF/sto-3g*			
1008.8755	32.5558	7.5333		
1103.308	2.8607	11.113		
1109.5155	3.4851	5.4705		
1116.703	1.0912	10.7502		
1163.8526	20.8903	5.3114		
1179.7013	0.1136	10.1606		
1202.1505	7.7405	12.2816	1200	C-N stretching
1257.5421	24.7187	7.1594		
1259.6436	26.1271	7.4688		
1260.8244	16.296	40.4271		
1277.8639	8.8333	9.6516		
1279.26	1.1218	0.7342		
1282.8987	7.2976	3.2562		
1285.0502	4.0821	2.3827		
1289.0812	28.2147	4.6307		
1290.0546	22.6275	5.4055		
1301.6766	16.5943	9.5968	1300	C-N stretching
1304.1201	8.228	2.7057		
1324.0485	7.7128	4.985		
1354.0256	268.4371	20.4253		
1389.6599	154.5205	11.4954		
1420.7101	13.9013	10.7965	1422.9	C=N stretching
1463.5986	10.2717	3.7893	1450.2	C=N stretching
1474.9355	27.3086	7.6047		
1484.3353	24.0553	7.0188	1486.9	C=N stretching
1507.1334	348.8419	11.6992		
1515.6255	148.0355	6.9774		
1539.5573	3.475	12.3452		
1548.8288	8.7318	6.2207		
1557.499	6.9902	27.3075		
1566.8733	4.9349	0.8486		
1626.7507	547.4304	95.427		

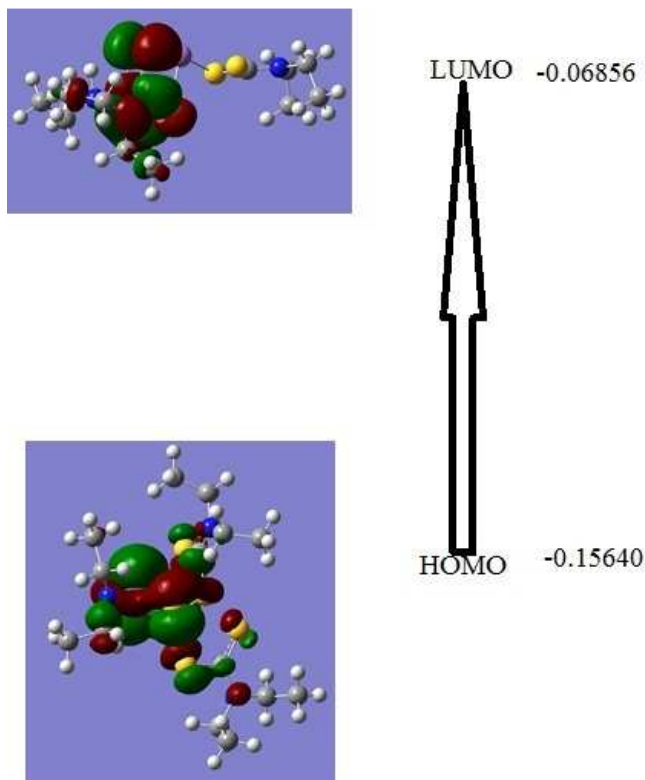


Figure 3. HOMO- LUMO Plot

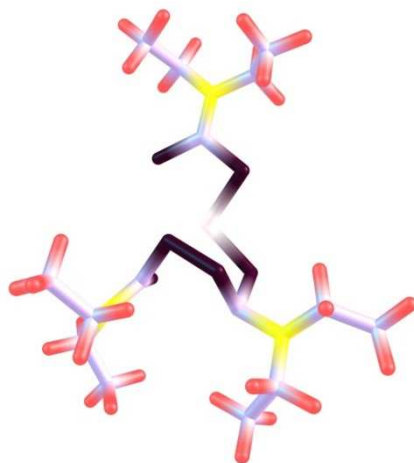


Figure 4. Optimized structure using HF/STO-3G\*

Table 2. Bond angle and bond length optimized for HF/STO-3G\*

Bond Angle				Bond length Å	
A(C2-S1-S9)	110.0	A(C13-C14-H41)	111.6	R(S1-C2)	1.827
A(S1-C2-3)	113.5	A(H35-C13-H36)	107.2	R(S1-S9)	1.931
A(S1-C2-N4)	118.1	A(H39-C14-H40)	108.6	R(C2-S3)	1.588
A(S1-S9-C10)	97.6	A(H39-C14-H41)	108.3	R(C2-N4)	1.384
A(S3-C2-N4)	128.1	A(H40-C14-H41)	108.1	R(N4-C5)	1.482
A(C2-N4-C5)	123.6	A(C16-C15-H37)	108.8	R(N4-C7)	1.482
A(C2-N4-C7)	118.9	A(C16-C15-H38)	109.1	R(C5-C6)	1.546
A(C5-N4-C7)	117.3	A(C15-C16-H42)	110.3	R(C5-H25)	1.090
A(N4-C5-C6)	112.8	A(C15-C16-H43)	110.4	R(C5-H26)	1.090
A(N4-C5-H25)	107.6	A(C15-C16-H44)	110.0	R(C6-H29)	1.086
A(N4-C5-H26)	109.0	A(H37-C15-H38)	106.7	R(C6-H30)	1.086
A(N4-C7-C8)	113.0	A(H42-C16-H43)	108.7	R(C6-H31)	1.086
A(N4-C7-H27)	107.7	A(H42-C16-H44)	108.4	R(C7-C8)	1.545
A(N4-C7-H28)	108.1	A(H43-C16-H44)	109.0	R(C7-H27)	1.091
A(C6-C5-H25)	109.7	A(S17-C18-S19)	117.5	R(C7-H28)	1.091
A(C6-C5-H26)	110.2	A(S17-C18-N20)	124.6	R(C8-H32)	1.085
A(C5-C6-H29)	110.7	A(S19-C18-N20)	117.9	R(C8-H33)	1.086
A(C5-C6-H30)	109.6	A(C18-S19-As55)	90.0	R(C8-H34)	1.085
A(C5-C6-H31)	110.8	A(C18-N20-C21)	119.6	R(S9-C10)	1.835
A(H25-C5-H26)	107.4	A(C18-N20-C23)	121.8	R(C10-S11)	1.844
A(H29-C6-H30)	108.6	A(C21-N20-C23)	118.6	R(C10-N12)	1.483
A(H29-C6-H31)	108.5	A(N20-C21-C22)	114.0	R(S11-As55)	2.105
A(H30-C6-H31)	108.6	A(N20-C21-H45)	108.0	R(N12-C13)	1.493
A(C8-C7-H27)	110.1	A(N20-C21-H46)	108.0	R(N12-C15)	1.487
A(C8-C7-H28)	109.8	A(N20-C23-C24)	114.2	R(C13-C14)	1.545
A(C7-C8-H32)	110.8	A(N20-C23-H47)	108.5	R(C13-H35)	1.090
A(C7-C8-H33)	109.6	A(N20-C23-H48)	107.8	R(C13-H36)	1.096
A(C7-C8-H34)	110.4	A(C22-C21-H45)	109.7	R(C14-H39)	1.085
A(H27-C7-H28)	108.0	A(C22-C21-H46)	109.1	R(C14-H40)	1.087
A(H32-C8-H33)	108.7	A(C21-C22-H49)	110.3	R(C14-H41)	1.085
A(H32-C8-H34)	108.6	A(C21-C22-H50)	111.1	R(C15-C16)	1.541
A(H33-C8-H34)	108.8	A(C21-C22-H51)	109.5	R(C15-H37)	1.090
A(S9-C10-S11)	107.9	A(H45-C21-H46)	107.9	R(C15-H38)	1.097
A(S9-C10-N12)	108.4	A(H49-C22-H50)	108.7	R(C16-H42)	1.085
A(S11-C10-N12)	105.2	A(H49-C22-H51)	108.5	R(C16-H43)	1.087
A(C10-S11-As55)	106.7	A(H50-C22-H51)	108.5	R(C16-H44)	1.084
A(C10-N12-C13)	119.0	A(C24-C23-H47)	109.2	R(S17-C18)	1.616
A(C10-N12-C15)	111.7	A(C24-C23-H48)	109.5	R(C18-S19)	1.741
A(S11-As55-S19)	98.6	A(C23-C24-H52)	110.6	R(C18-N20)	1.397
A(C13-N12-C15)	111.8	A(C23-C24-H53)	109.5	R(S19-As55)	2.194
A(N12-C13-C14)	112.8	A(C23-C24-H54)	111.0	R(N20-C21)	1.478
A(N12-C13-H35)	107.5	A(H47-C23-H48)	107.4	R(N20-C23)	1.478
A(N12-C13-H36)	112.0	A(H52-C24-H53)	108.5	R(C21-C22)	1.546
A(N12-C15-C16)	111.6	A(H52-C24-H54)	108.6	R(C21-H45)	1.090
A(N12-C15-H37)	108.9	A(H53-C24-H54)	108.5	R(C21-H46)	1.092

**Molecular geometry**

The optimized structure of Tris(diethyldithiocarbamato) arsenic(III) complex are shown in the following fig(4). The corresponding minimum energy obtained by HF/sto-3g\* method were fall on - 5308.7987974. From the optimized geometry the optimized structural parameters are tabulated on table (2).

**UV spectra**

The UV spectrum of the title complex is shown in figure (2). The spectrum of the title complex gives an intense peak at 236.5 nm. This is followed by very less intense peaks with maximum at 253.0 and 266.0 nm. These result good agreement with computational calculation

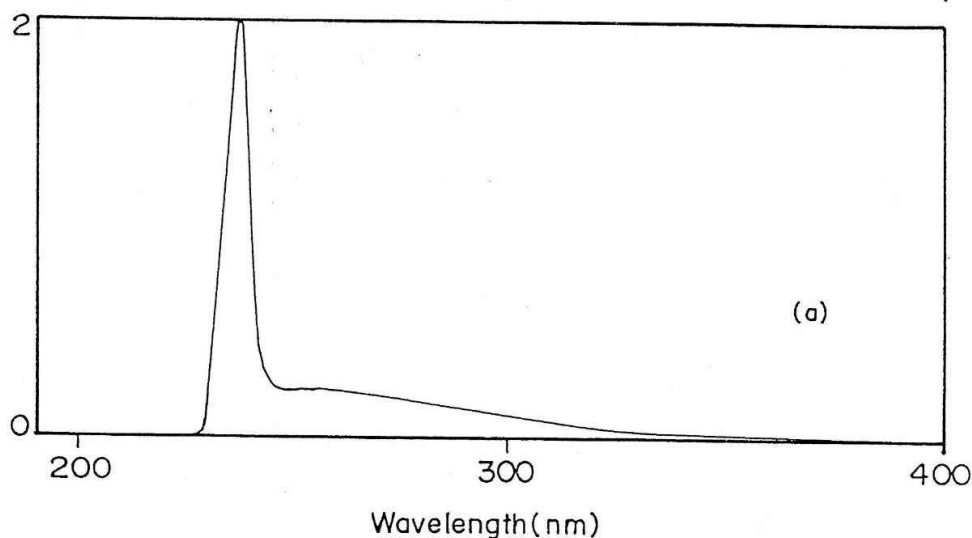


Figure 2. UV spectrum of Tris (diethyldithiocarbamato)arsenic(III)

**Thermal properties**

Tris (diethyldithiocarbamato) arsenic (III) is a brown colour complex and its melting point 151°C. On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions: heat capacity ( $C_{p,m}^0$ ), entropy ( $S_m^0$ ) and enthalpy ( $H_m^0$ ) were calculated using perl script THERMO.PL [14] and are listed in Table 3. As observed from Table 8, the values of  $C_{p,m}^0$ ,  $S_m^0$  and  $H_m^0$  all increase with the increase of temperature from 100 to 1000 K, which is attributed to the enhancement of the molecular vibration as the temperature increases.

Table 3: Thermal properties of Tris (diethyldithiocarbamato) arsenic (III)

T (K)	S (J/mol.K) [ $S_m^0$ ]	Cp (J/mol.K) [ $C_{p,m}^0$ ]	ddH (kJ/mol) [ $H_m^0$ ]
100.00	503.75	239.78	14.20
200.00	711.79	366.14	44.94
298.15	876.13	461.83	85.65
300.00	878.99	463.58	86.50
400.00	1025.20	557.02	137.55
500.00	1159.15	645.53	197.74
600.00	1283.99	724.62	266.34
700.00	1400.98	793.26	342.32
800.00	1510.87	852.55	424.68
900.00	1614.33	904.02	512.57
1000.00	1711.96	949.02	605.27

**CONCLUSION**

In this study, we have performed an experimental and quantum chemical study on Tris(diethyldithiocarbamato) arsenic(III) complex. Theoretical spectral frequencies FT-IR and UV are obtained. The theoretical data are in good agreement with experimental data of FT-IR. The charge transfer from lone pair of atom to its antibonding orbital is more. The HOMO LUMO energy strongly supports the presence of intramolecular energy transfer with the molecule.

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