

## Studies on Some Monosubstituted Diorganotin(IV) Dithiocarbamates

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Eleven new monosubstituted diorganotin(IV) dithiocarbamates of the general formula  $R_2Sn(X)dtc$  (where R = methyl-, butyl-, phenyl-, and benzyl-; X = -Cl, -I, -NCS, -N<sub>3</sub> or -NO<sub>2</sub>; dtc = diethyl dithiocarbamate and morpholine-N-carbodithioate) have been prepared and characterized. The TGA, molecular weight, dipole moment, mass, ir, uv, and <sup>1</sup>Hnmr spectral data are presented in support of a monomeric ester type structure of the compounds.

Several monochloro diorganotin dithiocarbamates have recently been prepared and characterized<sup>1</sup>.

On the basis of IR and PMR spectra, Honda and co-workers<sup>2</sup> suggested a bidentate character of the dithiocarbamate group in  $Me_2Sn(X)$  dimethyldithiocarbamates (where X = Cl, Br, and I); while Mossbauer studies<sup>3</sup> on several analogous  $R_2Sn(X)$  derivatives indicated a unidentate nature of the ligand. We have prepared and characterized eleven new monosubstituted diorganotin(IV) dithiocarbamates of the general formula  $R_2Sn(X)dtc$  (where R = methyl-, butyl-, phenyl-, and benzyl-; X = Cl, I, NCS, N<sub>3</sub> or NO<sub>2</sub>; dtc = diethyldithiocarbamate and morpholine-N-carbodithioate). The TGA molecular weight, mass, infrared, ultraviolet, proton nuclear magnetic resonance spectra and dipole moment data are consistent to a monomeric ester type structure having unidentate dithiocarbamate group.

### Experimental

Dimethyl-, di-n-butyl-, dibenzyltin dichloride and sodium diethyldithiocarbamate were procured from Alfa Inorganics, Inc., and used without further purification. Diphenyltin dichloride and ammonium morpholine-N-carbodithioate were prepared through the reported methods<sup>4,5</sup>. Solvents were purified through conventional methods and freshly distilled before use. The chlorosubstituted diorganotin(IV) dithiocarbamates were prepared by the following method.

A saturated solution of sodium or ammonium salt of dithiocarbamic acid (10 mmole) in 20 ml dry acetone or absolute methanol was added dropwise to a solution of diorganotin dichloride (20 mmole) in 15 ml of the same solvent. The reaction mixture after stirring for about an hour was filtered and the filtrate was evaporated to dryness. The crude solid thus obtained was extracted with benzene. The excess solvent from the solution was distilled off under reduced pressure and the residual product was

recrystallised from diethylether. It was finally dried under vacuum and analysed.

The compounds of the formula  $Ph_2Sn(X) dtc$  (where X = I, N<sub>3</sub>, NCS and NO<sub>2</sub>) were prepared by metathetical reaction between monochlorodiorganotin dithiocarbamates and the sodium or potassium salt of (X) in 1:1 molar ratio in acetone. The desired product was recrystallised from diethylether or benzene and dried under vacuum.

The thermogravimetric analysis was carried out at a heating rate of 5°C/min, using an instrument supplied by Fertilizer Corporation of India, Sindri (India). Molecular weights were determined cryoscopically in freezing benzene using a Beckmann thermometer of accuracy  $\pm 0.01^\circ$ . Conductance of  $10^{-3}M$  solution in nitrobenzene was measured with a Phillips conductivity assembly PR 9500. Infrared spectra were recorded in KBr in the region 4000-700  $cm^{-1}$  with Perkin Elmer 421 and a few compounds upto 250  $cm^{-1}$  using Perkin Elmer 521 in nujol mull between Cesium iodide plates. Electron spectra of  $10^{-3}M$  solution in chloroform were recorded in ultra violet region with Perkin Elmer 202 spectrometer, using 1 cm quartz cell. Mass spectrum of chlorodimethyltin(IV) morpholine-N-carbodithioate was recorded on a Hitachi RMU-6 instrument at 70 ev and 20 ev and an accelerating voltage of 8 kv with ionization chamber at 200°. Proton nuclear magnetic resonance spectrum was measured at room-temperature ( $\sim 25^\circ$ ) with a Varian A 60 D spectrometer at 60 MHz in deuterochloroform. Tetramethylsilane was used as an internal standard.

The dielectric constant data were collected at 25° at a radio frequency (MC/S) with the help of a dipole meter type RL09. Refractive index values were measured to a precision of  $\pm 0.0002$  with an Asco-Abbe refractometer, using sodium D-line as a source of light. The electric dipole moment data

were calculated from the following equation, outlined by Guggenheim<sup>6</sup>.

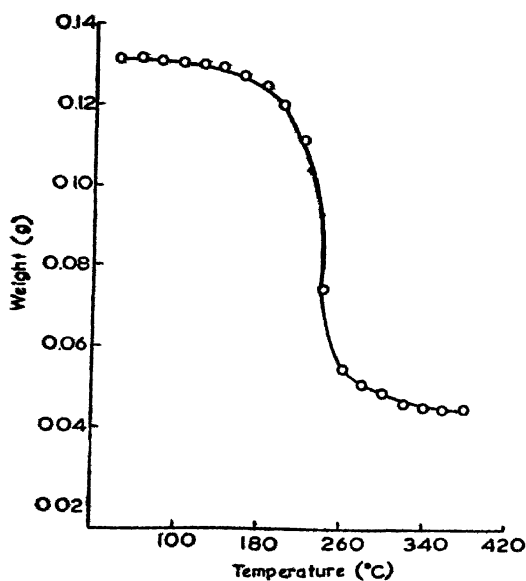
$$\mu^2 = \frac{9KT}{4\pi.N} \cdot \frac{3}{(\epsilon_1 + 2)} (n_1^2 + 2) \cdot \left( \frac{\Delta}{C} \right) \longleftrightarrow O$$

$$\Delta = (\epsilon_{12} - n_{12}^2) - (\epsilon_1 - n_1^2)$$

The symbols have their usual significance.

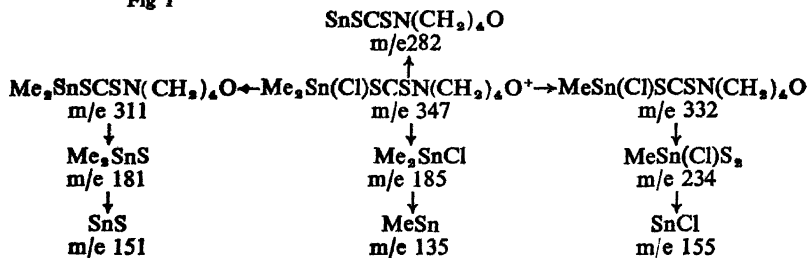
## Results and Discussion

All the compounds listed in Table 1 are white or light yellow crystalline solids, stable at room temperature and insensitive to atmospheric oxygen and moisture. These are soluble in common organic solvents. The thermogravimetric analysis of monochlorodiorganotin(IV) morpholine-N-carbodithioate indicates that the compound decomposes on heating to ~80°. The pyrolysis curve shown in fig.1 suggest that on further heating to ~360°, it finally changes to a non-volatile residue, identified as *tin metal*. The results agree with a earlier finding on tin (II) bisdimethyl- and diethyldithiocarbamates<sup>7</sup>.



Pyrolysis Curve of  $\text{Me}_2\text{Sn}(\text{Cl})\text{SCSN}(\text{CH}_3)_4\text{O}$

Fig 1



Scheme 1—Fragmentation pattern of  $\text{Me}_2\text{Sn}(\text{Cl})\text{SCSN}(\text{CH}_3)_4\text{O}$

Conductance values in nitrobenzene indicate nonelectrolytic behaviour of the compounds while molecular weight data suggest the monomeric character in benzene. The monomolecular nature of the newly synthesised compounds is further supported from a mass spectrum of  $\text{Me}_2\text{Sn}(\text{Cl})\text{SCSN}(\text{CH}_3)_4\text{O}$ . Species with m/e value greater than that of the parent ion were not observed. A typical fragmentation pattern of the compounds is shown in scheme 1.

In contrast to previous finding on analogous compound<sup>8</sup>, the most abundant peak in the spectrum is that of  $\text{SnSCSN}(\text{CH}_3)_4\text{O}$ .

## Infrared spectra

The characteristic infrared absorption frequencies ( $\text{cm}^{-1}$ ) with their assignments are listed in Table-1. From a comparison of the spectra of selenium bis (dithiocarbamates) with zinc bis (diethyldithiocarbamate), it has been concluded that the two doublets at ~1500 and ~1000  $\text{cm}^{-1}$ , assignable to  $\nu(\text{C-N})$ ,  $\nu(\text{C-S})$  modes are associated with the monodentate dithiocarbamate group<sup>9-10</sup>, whereas single intense absorption for the two modes of vibration is attributed to the bidentate or chelated nature of the ligand<sup>8,11</sup>. In the present investigation, the spectra of all the compounds invariably exhibit two strong bands for  $\nu(\text{C-N})$  and  $\nu(\text{C-S})$  stretching modes, suggesting the presence of monodentate dithiocarbamate group in  $\text{R}_2\text{Sn}(\text{X})$  dithiocarbamates.

Besides the above two modes of vibration for the dithiocarbamate group, the spectra of mono substituted diorganotin(IV) dithiocarbamates show characteristic bands of the substituent functional groups (viz.  $\text{N}_3$ ,  $\text{NO}_2$  and  $\text{NCS}$ ). Absorptions at  $2060 \pm 10$ ,  $1315 \pm 5$  and  $653 \pm 1$   $\text{cm}^{-1}$  in the spectra of two azido substituted diphenyltin dithiocarbamates are assigned to  $(-\text{N}=\text{N}=\text{N}-)$  asymmetric, symmetric stretching and bending modes of vibration<sup>12,13</sup>. In the spectrum of mono nitratodiphenyltin diethyldithiocarbamates the bands at 1535 and 1490, 1247 and 825  $\text{cm}^{-1}$ , assignable to  $-\text{NO}_2$  asymmetric, symmetric stretching and out-of-plane deformation modes, suggest that it is covalently bonded in the compound<sup>14,15</sup>. It has been reported that in (iso) thiocyanate, the  $\nu(\text{C}\equiv\text{N})$ ,  $\nu(\text{C-S})$  stretchings and  $\nu(\text{NCS})$  bending modes lie in the range 2040-2080, 800-830, 460-490  $\text{cm}^{-1}$  respectively while in the (normal) thiocyanate, the correspon-

TABLE-I : ANALYTICAL DATA AND RELEVANT INFRARED ABSORPTION FREQUENCIES (cm<sup>-1</sup>) R<sub>4</sub>Sn (X) dte.

Sr. No.	Compounds	m.p. (°C)	Analysis Found (Calcd)		%H	IR absorption		ν(C-S)	ν(Sn-S)
			% Sn	% C		νC-N	νC-S		
1.	Ph <sub>3</sub> Sn(Cl)SCSN(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	142 (143.5)*	26.07 (26.09)	44.83 (44.68)	4.40 (4.38)	1512 vs 1505 vs	1020 vs 986 s	394 vs	
2.	Ph <sub>3</sub> Sn(I)SCSN(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	141	21.71 (21.76)	37.10 (37.22)	3.83 (3.65)	1518 vs 1508 vs	1018 vs 995 vs	390	
3.	Ph <sub>3</sub> Sn(N <sub>3</sub> )SCSN(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	81-83	25.31 (25.69)	44.05 (44.06)	4.42 (4.31)	1520 vs 1510 vs	1020 vs 999 vs		
4.	Ph <sub>3</sub> Sn(NCS)SCSN(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	109-111 (109-10)* <sup>18</sup>	24.78 (24.84)	44.90 (45.09)	4.14 (4.17)	1510 vs 1510 s, sh	1018 vs 1001 s, sh		
5.	Ph <sub>3</sub> Sn(NO <sub>2</sub> )SCSN(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	128	24.83 (24.63)	42.09 (42.21)	4.10 (4.14)	1478 vs 1471 vs	1020 vs 998 vs		
6.	Ph <sub>3</sub> Sn(Cl)SCSN(CH <sub>3</sub> ) <sub>2</sub> O	164-5	24.98 (25.31)	43.35 (43.40)	3.98 (3.22)	1484 vs 1469 s, sh	1010 vs 1000 vs		
7.	Ph <sub>3</sub> Sn(N <sub>3</sub> )SCSN(CH <sub>3</sub> ) <sub>2</sub> O	105-7	24.92 (24.95)	42.67 (42.77)	3.76 (3.77)	1460 vs 1450 vs	1015 vs 1010 vs	360 vs	
8.	Ph <sub>3</sub> Sn(NCS)SCSN(CH <sub>3</sub> ) <sub>2</sub> O	134-6	23.98 (24.14)	43.21 (43.81)	3.42 (3.65)	1500 vs 1488 s	1026 vs 994 vs	350 vs	
9.	Me <sub>3</sub> Sn(Cl)SCSN(CH <sub>3</sub> ) <sub>2</sub> O	142-2	34.12 (34.39)	24.43 (24.28)	4.44 (4.04)	1481 vs 1455 s, sh	1026 vs 1000 vs	360 vs	
10.	Br <sub>2</sub> Sn(Cl)SCSN(CH <sub>3</sub> ) <sub>2</sub> O	111-13	23.36 (23.87)	45.21 (45.68)	4.41 (4.42)	1490 vs 1477 vs	1029 vs 994 vs	370 vs	
11.	Bu <sub>3</sub> Sn(Cl)SCSN(CH <sub>3</sub> ) <sub>2</sub> O	133-4	27.43 (27.67)	35.93 (36.27)	5.87 (6.03)	1485 vs 1475 vs	1024 vs 998 vs		

ding absorptions occur at 2080-2120, 690-720 and 410-440  $\text{cm}^{-1}$ .<sup>16-19</sup> In the spectra of the two thiocyanate dithiocarbamates, these absorptions have been identified at  $2053 \pm 8$ ,  $821 \pm 1$ , and  $470 \pm 5 \text{ cm}^{-1}$ , which agree well with the presence of a N-bonded thiocyanate group in the compound<sup>20</sup>.

In the far infrared region of the spectra, a band at  $372 \pm 22 \text{ cm}^{-1}$  is assigned to  $\nu(\text{Sn-S})$  mode<sup>21,22</sup>. A shift in  $\nu(\text{Sn-S})$  stretching mode towards lower wave number on substituting diethyldithiocarbamate with morpholine-N-carbodithioate may be attributed to the rigid heterocyclic system of the latter, which show lesser tendency to release electrons<sup>22</sup> and as a consequence, the Sn-S bond has a lower bond order. Among the compounds examined, the chloro diphenyltin(IV) diethyldithiocarbamate is expected to be the most stable as it indicates a strong Sn-S bond. The Sn-Cl stretching mode, expected to lie around  $400 \text{ cm}^{-1}$  could not be identified with certainty due to overcrowded nature of the spectra in this region.

Absorptions at 575 and  $460 \text{ cm}^{-1}$  in the spectrum of monochlorodibenzyltin morpholine-N-carbodithioate and at 565 and  $520 \text{ cm}^{-1}$  in the corresponding methyl derivatives are assigned to  $\nu_{\text{asym}}(\text{Sn-alkyl})$  and  $\nu_{\text{sym}}(\text{Sn-alkyl})$  modes of vibration<sup>24,25</sup>. In the spectra of two azido and (iso) thiocyanate diphenyltin derivatives, a band at  $\approx 290 \text{ cm}^{-1}$  is attributed to  $(\text{Sn-aryl})$  asymmetric stretching mode<sup>26</sup>. The corresponding  $\nu_{\text{sym}}(\text{Sn-aryl})$  could not be identified since it lies beyond the recorded range of the spectra. The strong absorptions at  $\approx 450 \text{ cm}^{-1}$  in the spectra of the compounds may be attributed to a coupled vibration of skeletal modes of vibration of the dithiocarbamate<sup>2</sup> and an out-of-plane ring deformation<sup>26</sup>.

#### Electronic spectra :

The electronic spectra of the compounds namely,  $\text{Ph}_2\text{Sn}(\text{Cl})$  diethyl dithiocarbamate and  $\text{Ph}_2\text{Sn}(\text{N}_3)$  morpholine-N-carbodithioate show two absorptions

maxima at  $254 \pm 1$  and  $287 \pm 3 \text{ cm}^{-1}$  of molar absorptivities( $\epsilon$ ) approximately log 4 and 3 respectively in the ultraviolet region. Jorgensen<sup>27,28</sup> considered these absorptions to be connected with the intraligand transition. In the spectra of the compounds examined, a band at  $254 \text{ cm}^{-1}$  is suggested to be associated with the  $(\pi-\pi^*)$  transition mainly in the  $\text{C}=\text{S}$  group<sup>29</sup>. Recently from a study of the electronic spectra of arsenic tris-(dithiocarbamates), it is reported that if dithiocarbamate group is co-ordinated to central metal atom with the two inequivalent (C-S) bonds per ligand, the high energy absorption ( $\text{Ca} \approx 254 \text{ nm}$ ) has also two bands<sup>30</sup>. The presence of single intense absorption in this region in the spectra of the two compounds under investigation, strongly supports that the dithiocarbamate group is monodentate in  $\text{R}_2\text{Sn}(\text{X})$  derivatives.

#### <sup>1</sup>HNMR spectra :

The proton nuclear magnetic resonance spectrum of  $\text{Ph}_2\text{Sn}(\text{N}_3)\text{SCSNET}_2$  shows two groups of signal : a multiplet due to phenyl proton directly bonded to tin ( $\text{Sn-Ph} = 2.04$ - $2.40$  and a splitted signal due to  $\text{NR}_2$  protons ( $\text{N-CH}_2$ )<sub>2</sub> =  $6.22$  (q,  $J = 7\text{Hz}$ ) ; ( $\text{CH}_2$ )<sub>2</sub> =  $8.67$ , (t,  $J = 7\text{Hz}$ ). The spectrum and its integration is consistent with the proposed stoichiometry of the compound. The splitting in the  $\text{NR}_2$  protons in the spectrum is attributed to the restricted rotation about the C-N bond which makes the two alkyl groups inequivalent<sup>31</sup>. This may be taken as an additional evidence for the presence of monodentate dithiocarbamate group in monosubstituted diorganotin(IV) dithiocarbamates<sup>11,32</sup>.

#### Dipole moment :

The results of dipole moment measurements are summarised in Table-2. The presence of bidentate dithiocarbamate group in monosubstituted diorganotin(IV) dithiocarbamates expected to give dipole moment value comparable to penta co-ordinated organotin(IV) compounds. Contrary to this, but the data listed in Table-2 agree with that of alkyl

TABLE-2 : DIPOLE MOMENT DATA OF  $\text{R}_2\text{Sn}(\text{IV}) (\text{X})$  DATA

	Concentration mole/cc $\times 10^{-3}$	dielectric constant. ( $\epsilon/\lambda$ )	refractive indices (n)	$\Delta$	( $\Delta/\text{C}$ ) C $\rightarrow$ O	Dipole moment D.
1	2.00	2.2921	1.5008	0.0379	2.89	3.89
	7.26	2.3057	1.5014	0.0509		
	12.52	2.3259	1.5018	0.0696		
	17.78	2.3566	1.5024	0.0994		
4	2.00	2.2885	1.4982	0.0439	7.05	6.08
	8.00	2.3376	1.4987	0.0915		
	14.00	2.3773	1.4991	0.1300		
	20.00	2.4195	1.4997	0.1704		
6	2.00	2.2750	1.4969	0.0343	3.78	4.45
	7.12	2.2958	1.4975	0.0533		
	12.26	2.3192	1.4980	0.0752		
	17.98	2.3415	1.4987	0.0954		
9	4.34	2.2755	1.4975	0.0330	2.68	3.74
	11.32	2.2947	1.4982	0.0507		
	18.30	2.3270	1.4988	0.0706		
	25.27	2.3367	1.4991	0.0890		
10	2.00	2.2698	1.4965	0.0303	3.03	3.98
	6.83	2.2869	1.4972	0.0453		
	11.67	2.3067	1.4978	0.0633		
	16.43	2.3218	1.4982	0.0772		

esters of dithiocarbamic acid<sup>22</sup> and tetra co-ordinated diorganotin(IV) dichloride<sup>24</sup> indicating the presence of unidentate dithiocarbamate ligand. The exceptionally large dipole moment value of (iso) thiocyanate diphenyltin diethyldithiocarbamate as compared to that of chlorosubstituted derivative may be attributed to the greater Sn-NCS polarity<sup>25</sup>.

The spectral and dipole moment data discussed above suggest that monosubstituted diorganotin(IV) dithiocarbamates possess an ester type structure similar to triorganotin(IV) dithiocarbamates<sup>26</sup>.

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