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SOME TRIORGANOTIN(IV) DITHIOCARBAMATES

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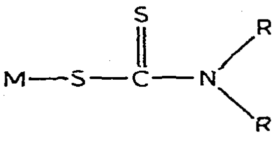
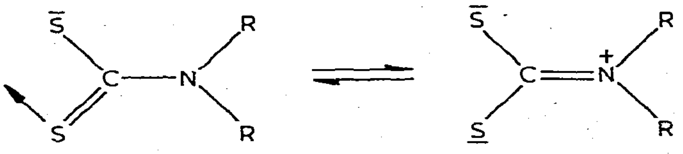
Summary

Several new triorganotin dithiocarbamates of the formula R_3SnDtc (R = phenyl, n-butyl and benzyl; Dtc = n-propyl, n-butyl, n-dibutyl-, benzyl-, 2-phenylethyl- and dibenzyl-dithiocarbamates or pyrrolidine-, piperidine- and morpholine-*N*-carbadithioate) have been prepared and characterized. The infrared, ^1H NMR and electronic spectra and the molecular weight data indicate that the compounds possess an ester type structure and that the dithiocarbamate moiety acts as a monodentate uninegative ligand.

Introduction

Unlike metal dithiocarbamates [1-5], a study of organotin(IV) [6], and tin(IV) *N,N*-disubstituted dithiocarbamates [7] reveals that the dithiocarbamate ring can act both as a monodentate (A) or as a bidentate and chelating (B, C) uni negative ligand.


(A)


(B) (C)

The bidentate behaviour of the dithiocarbamate moiety in R_2Sn^{IV} and RSn^{IV} *N,N*-disubstituted dithiocarbamates [8-12] is well established, while Bonati et al. [9] have suggested that in corresponding R_3Sn^{IV} compounds, no sure evidence is found for or against the chelation of the dithiocarbamate moiety.

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TABLE 1

ANALYTICAL DATA AND RELEVANT IR BANDS, (cm^{-1}) FOR TRIORGANOTIN(IV) DITHIOCARBAMATES

Compound	M.p. (°C)	Analysis found (calcd.) (%)			Mol. Wt. Found (calcd.)	ν(C—N)	ν(C—S)	ν(Sn—S)
		C	H	Sn				
$Ph_3SnSCSNH(CH_2)_2CH_3$ (I)	86 [b]	53.32	4.45	23.97	314	1530vs,	1022vs,	418vs,
		(54.54)	(4.75)	(24.58)	(484)	1475vs	1000vs	375vs
$Ph_3SCSNH(CH_2)_3CH_3$ (II)	131 [a, b]	55.16	4.66	23.90	392	1512s,	1021vs,	420s,
		(55.42)	(5.02)	(23.89)	(498)	1480s	999vs	380vs
$Ph_3SnSCSN[(CH_2)_3CH_3]_2$ (III)	114 [a, b]	58.52	6.23	21.90	540	1490w(br),	1019vs,	420s,
		(58.48)	(5.95)	(21.48)	(554)	1479s	998vs	388s
$Ph_3SnSCSNHC_6H_5$ (IV)	136 [a, b]	57.09	4.44	23.10	456	1494m,	1020vs,	419s,
		(57.91)	(4.05)	(22.97)	(518)	1478s	998vs	379vs
$Ph_3SnSCSNHCH_2C_6H_5$ (V)	124-125 [b] 126 [30]	57.50	4.28	22.06	470	1504vs,	1020vs,	410s,
		(58.65)	(4.32)	(22.36)	(532)	1478vs	998vs	380vs
$Ph_3SnSCSNH(CH_2)_2C_6H_5$ (VI)	93-94 [b]	59.14	4.61	21.79	450	1505vs,	1022vs,	
		(59.34)	(4.57)	(21.79)	(546)	1474vs	999vs	
$Ph_3SnSCSN(CH_2C_6H_5)_2$ (VII)	93-94 [b]	62.40	5.21	20.70	540	1495vs,	1012vs,	420s,
		(63.66)	(4.66)	(19.13)	(622)	1485w	998vs	378vs
$Ph_3SnSCSN(CH_2)_4$ (VIII)	137 [b]	56.16	4.76	23.06	362	1565vs,	1015vs,	418vs,
		(55.64)	(4.68)	(23.90)	(496)	1460s(br)	990vs	394vs
$Ph_3SnSCSN(CH_2)_5$ (IX)	150 [b]	57.22	4.32	23.40	497	1565vs,	1015vs,	414vs,
		(56.47)	(4.90)	(23.33)	(510)	1488vs	991vs	404vs
$Ph_3SnSCSN(CH_2)_2(CH_2OCH_2)$ (X)	165 [a, b]	53.15	4.32	22.70	436	1475(sh),	1020vs,	420vs,
		(53.90)	(4.48)	(23.24)	(512)	1460vs(br)	990vs	409vs
$(Ph_3SnSCSNH)_2CH_2CH_2^-$ (XI)	138-139 [b]	53.95	4.18	24.98	796	1495vs	1020vs	
		(52.74)	(3.95)	(26.15)	(910)	1470vs	998vs	
$BZ_3SnSCSNHC_6H_5$ (XII)	125-126 [a]	60.79	5.55	20.96	480	1525s	1045s	
		(60.00)	(4.82)	(21.25)	(560)	1495s	1020s	
$Bu_3SnSCSN(CH_2)_4$ (XIII)	b.p. 145°/7 mmHg	45.82	7.92	26.76	—	1475vs	1009vs	
		(46.78)	(8.02)	(27.28)	(436)	1440vs	954vs	

[a] Method a see Experimental. [b] Method b see experimental.

The present communication reports the synthesis, characterisation and thermal decomposition of some new triorganotin(IV) dithiocarbamates (R_3SnDtc) (R = phenyl, n-butyl, and benzyl; Dtc = n-propyl-, n-butyl-, n-dibutyl-, benzyl-, 2-phenylethyl- or dibenzyl-dithiocarbamates or pyrrolidine-, piperidine and morpholine-*N*-carbadithioate). A study of the conductance, dipole moment, infrared proton magnetic resonance and electronic spectra suggests, for the first time, an ester type structure of the compounds.

Results and discussions

The newly synthesised triorganotin(IV) dithiocarbamates have been prepared in high yield through one of the following reactions:

$$R_3SnCl + NaSCSNR_2' \rightarrow R_3SnSCSNR_2' + NaCl \tag{1}$$

$$R_3SnOH + CS_2 + R_2'NH \rightarrow R_3SnSCSNR_2' + H_2O \tag{2}$$

[$(R_3Sn)_2O$ may also be used in place of R_3SnOH]

Bonati et al. [9] reported that reaction 1, using *N*-monosubstituted dithiocarbamates at room temperature yields bis(triorganotin) sulphide, hydrogen sulphide and the corresponding amine isothiocyanate. We, however, succeeded in synthesising triorganotin(IV) monosubstituted dithiocarbamates (II—IV and XII; Table 1) at ~ —20°C through this reaction. The compounds have been characterised by elemental analysis, molecular weight and conductance data.

All compounds, except tributyltin(IV) pyrrolidine-*N*-carbodithioate, which is a liquid, are well defined white crystalline solids with sharp melting points. They are soluble in chloroform, benzene and carbon tetrachloride but are sparingly soluble in petroleum ether and diethyl ether. Molecular weights in freezing benzene presented in Table 1 indicate their monomeric character in solution, while the conductance data in nitrobenzene show that the compounds are non-electrolytes.

The newly synthesised compounds are insensitive to atmospheric oxygen and moisture and are thermally stable at room temperature but decompose on heating above their melting points. The thermogravimetric analysis of triphenyltin dibutyldithiocarbamate indicates that like organoantimony(III) dithiocarbamates [13], its decomposition starts at ~120°C into carbon disulphide, bis(triphenyltin) sulphide and bis(dibutyl)thiourea. The mass at 260°C corresponds to an equimolar mixture of bis(triphenyltin) sulphide and bis(dibutyl)thiourea. On further heating to 460°C it is completely changed to SnS_2 as shown below:

$$Ph_3SnSCSN[(CH_2)_3CH_3]_2 \xrightarrow[\Delta - CS_2]{120\text{-}260^\circ C} [Ph_3Sn]_2S + [Bu_2N]_2C{=}S \xrightarrow{\Delta \text{ upto } 460^\circ C}$$

$$SnS_2 \text{ (residue)}$$

Spectra

The IR, UV, ^1H NMR and dipole moment data are given in support of the suggested structure.

Infrared spectra

The infrared absorption frequencies of diagnostic values of triorganotin(IV) dithiocarbamates are listed in Table 1. In the spectra of metal dithiocarbamates, it has been previously shown that when the $R_2NC\overline{S}_2$ group acts as a bidentate ligand single ν(C—N) and ν(C—S) absorptions are observed [9,14], whereas the presence of a monodentate $R_2NC(S)S^-$ group gives rise to a doublet for the two modes of vibration [3,15,16]. In the spectra of the newly synthesised compounds reported in this investigation ν(C—N) and ν(C—S) absorptions appear as doublets around 1500 and 1000 cm^{-1}, respectively, the latter is obviously due to the presence of two non-equivalent C—S bonds [17]. The invariable splitting of the two modes of vibration is thus a strong evidence for the presence of a monodentate dithiocarbamate group.

In the far infrared region of the spectra, two strong absorptions at 417 ± 3 cm^{-1} and 397 ± 12 cm^{-1} which are absent in the spectrum of sodium diethyldithiocarbamate, are assigned to Sn—S stretching modes of vibration [18,19]. A strong absorption at ~450 cm^{-1} may be a coupled vibration due to the skeletal mode of the dithiocarbamate group and out-of-plane ring deformation [10,20].

¹H NMR spectra

The proton magnetic resonance absorptions of the compounds and their assignments listed in Table 2 show two groups of signals: multiplets due to the phenyl or butyl protons attached to the tin atom and splitted signals due to NR_2 protons. All compounds gave two triplets of NR_2 signals except XIII, where a multiplet is observed at τ 8.64 instead of a triplet. The spectra and their integration are consistent with the proposed stoichiometry of the compounds. The splitting in NR_2 protons is due to restricted rotation about the C—N bond which makes the two alkyl or aryl groups magnetically non-equivalent [21]. This may be taken as additional evidence for the presence of a monodentate dithiocarbamate group in triorganotin(IV) dithiocarbamates [10,13].

TABLE 2

^{1}H NMR SPECTRA OF TRIORGANOTIN(IV) DITHIOCARBAMATE IN $CDCl_3$, AT 30°C [a]

Compounds	Assignment	τ (ppm) [b]
VIII	Sn—Bu	9.20—7.97 (m), 9.45
	$N(CH_2)_2$	6.20 (t, *J* 7 Hz)
	$(CH_2)_2$	6.79 (t, *J* 7 Hz)
X	Sn—Ph	2.54 (m), (2.87—2.22)
	$N(CH_2)_2$	6.39 (t, *J* 5 Hz)
	(CH_2OCH_2)	5.97 (t, *J* 5 Hz)
XIII	Sn—Ph	2.51 (m), (2.79—2.22)
	$N(CH_2)_2$	6.22 (t, *J* 7 Hz)
	$(CH_2CH_2CH_3)_2$	8.64 (m), (9.24—8.04)

[a] Shift at 60 MHz relative to tetramethylsilane as internal reference. [b] Centre of signals.

TABLE 3

ELECTRONIC SPECTRA OF TRIORGANOTIN(IV) DITHIOCARBAMATES

Compound	λ_{max} (nm)	log. ϵ
IV	252	4.30
	293	2.34
V	247	3.13
	267	2.47
X	257	4.07
	294	2.34
VIII	250	4.17
	280	2.92

Electronic spectra

Table 3 shows wavelengths of maximum absorptions in the ultraviolet region and the corresponding molar absorptivities (log ϵ) for the dithiocarbamates studied. The compounds exhibit two bands at ~250 nm and ~280 nm. Although the exact assignment to these bands is not certain, it seems to be agreed [22,23], that the two absorptions are due to the intra-ligand transitions [24]. Recently it has been suggested that the high energy band (ca. 250 nm) is connected with a transition located in the CS_2 group of the ligand [25]. The presence of unsplitted bands at ~250 nm in the spectra of our compounds is in favour of monodentate uninegative dithiocarbamate groups [26].

The electric dipole moment of triorganotin(IV) dithiocarbamates has been calculated by Guggenheim's method [27], and the data ($\mu \sim 2.21$—3.32 D) indicate the presence of monodentate dithiocarbamate groups in the compounds. A detailed study of dipole moments of different types of organotin(IV) dithiocarbamates is in progress and will be published subsequently. Anti-microbial activity of these compounds in vitro is being investigated and preliminary results indicate excellent possibilities of these compounds to act as important biocides.

The results indicate that in contrast to several metal, R_2Sn^{IV} and RSn^{IV} dithiocarbamates, the triorganotin(IV) dithiocarbamates possess an ester type structure. The observations are in agreement with the proposed structure for $Me_3SnSCSNMe_2$ on the basis of an X-ray crystallographic study [28].

Experimental

Ammonium salts of *N,N'*-phenyl; n-butyl-, di-n butyl-dithiocarbamic acids and ammonium morpholine *N*-carbodithioate were prepared by the reported method [29]. Ph_3SnOH, $(Bu_3Sn)_2O$ and Bz_3SnCl obtained from Alfa Inorganics were used without further purification. Amines were distilled before use and the constant boiling middle fraction was employed for the reactions. Solvents used were purified by conventional methods. Representative methods for the preparation of the compounds are listed in Table 1.

(a) Triphenyltin(IV) n-butyl dithiocarbamate

A solution of ammonium n-butyl dithiocarbamate (10 mmol) in 20 ml dry acetone was added to a solution of triphenyltin chloride (10 mmol) in the same solvent at ~ —20°C. The reaction mixture was stirred for about an hour and filtered. The filtrate after distilling off the excess solvent yielded a white crystalline solid which was recrystallized from diethyl ether and dried in vacuum.

(b) Tributyltin(IV) pyrrolidine-N-carbodithioate:
A solution of pyrrolidine (20 mmol) in 5 ml chloroform was slowly added to a solution of bis(tributyltin) oxide or tributyltin hydroxide (10 mmol) and carbon disulphide (20 mmol) in 15 ml chloroform at ~ —20°C with constant stirring. The reaction mixture was further stirred for about four hours. Excess solvent was then distilled off under reduced pressure and the resultant yellow liquid was extracted from diethyl ether to yield a yellow, viscous liquid which distilled at 145°/7 mmHg.

The other compounds were prepared through the method reported by Kupchik et al. [30] for triphenyltin *N*-benzyl dithiocarbamate.

Infrared spectra were recorded in Nujol mulls between CSI plates in the region 4000—300 cm^{-1} using a Perkin—Elmer 521 spectrophotometer. Proton magnetic resonance spectra were measured at room temperature (~30°C) with a Varian A60D spectrometer in deutrochloroform. Electronic spectra in the concentration range $0.04—0.16 \times 10^{-3}$ *M* were recorded with a Perkin—Elmer 202 spectrometer using 1 cm quartz cell in chloroform.

Conductance of 10^{-3} *M* solutions in nitrobenzene was measured using a Philips conductivity assembly PR 9500. Molecular weights were determined cryoscopically in benzene using a Beckman thermometer of accuracy ±0.01°.

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