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MÖSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS

V*. TRIPHENYLTIN COMPOUNDS

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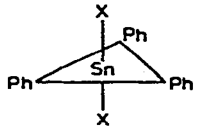
SUMMARY

The Mössbauer spectra of 37 triphenyltin compounds have been studied and the relationship between quadrupole splitting and structure analysed. Large quadrupole interactions of ~4.0–2.6 mm·sec^{-1} are associated with trigonal bipyramidal structures. It is concluded that triphenyltin nitrate has a structure with bridging nitrate groups. Evidence is presented that the oxinate group is chelating in triphenyltin oxinate.

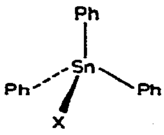
INTRODUCTION

The quadrupole splitting observed in the Mössbauer spectra of Ph_3SnX compounds varies from zero (when $X = SiPh_3$[1]) to 4.00 mm·sec^{-1} (when $X = OCOCF_3$[2]). In the present work the results of some Mössbauer measurements on triphenyltin compounds are reported and the relationship between quadrupole splitting and structure discussed.

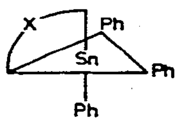
There are three possible structures for triphenyltin compounds [Fig. (I), (II) and (III)]. While a number of stereoisomers are possible for structures (I) and (III), the X-ray data available[3] suggest that R_3SnX compounds with bridging X groups adopt the configuration shown (I) with planar Ph groups. There are no X-ray data available at present for compounds of type (III) and, for example, although several studies of triphenyltin oxinate have been reported[4,5], there is uncertainty as to whether this compound has structure (II) or (III).



(I)



(II)



(III)

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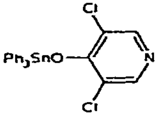
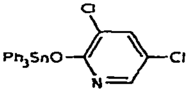
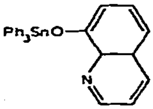
[*] For Part IV see ref. 30.

TABLE 1

MÖSSBAUER PARAMETERS OF TRIPHENYLTIN COMPOUNDS[a]

No.	*Compound*	δ	Δ	*Ref.*
1	$Ph_3SnOCOCF_3$	1.40	4.00	2
2	Ph_3SnNO_3	1.41	4.00	[b]
3	$Ph_3SnOCOCHCl_2$	1.42	3.86	[b]
4	Ph_3SnNCO	1.10	3.76	[b]
	Ph_3SnNCO	1.30	2.47	10
5	Ph_3SnNCS	1.45	3.63	[b]
	Ph_3SnNCS(in benzene)	1.39	2.63	[b]
	Ph_3SnNCS (in pyridine)	1.35	3.12	[b]
6	Ph_3SnF	1.25	3.52	6
7	$Ph_3SnOCOCH_2Cl$	1.30	3.46	11
8	$Ph_3SnOCO(CH_2)_{14}CH_3$	1.25	3.44	12
9	$Ph_3SnOCO(CH_2)_4CH_3$	1.32	3.43	12
10	$Ph_3SnOCOCH_3$	1.26	3.34	11
11	$Ph_3SnOCOCH_2CH_3$	1.28	3.31	11
12	$Ph_3SnCl \cdot Me_2SO$	1.26	3.25	13
13	$Ph_3SnCl \cdot Bu_2SO$	1.30	3.20	13
14		1.31	3.20	14
15	$Ph_3SnO(C_6H_4CHO\text{-}2)$	1.32	3.18	[b]
16	$[Ph_3SnCl]_2 \cdot Me_2N(CH_2)_2NMe_2$	1.38	3.18	[b]
17	$Ph_3SnCl \cdot$ 4,4'-Bipy	1.36	3.10	[b]
18	Ph_3SnOH	1.24	2.98	[b]
19	$Ph_3SnCl \cdot$ 4-phenylpyridine	1.40	2.90	[b]
20	$Ph_3SnS(C_5H_4N\text{-}4)$	1.37	2.61	14
21	Ph_3SnCl	1.41	2.61	[b]
	Ph_3SnCl(in pyridine)	1.34	3.15	[b]
22	Ph_3SnBr	1.37	2.48	6
23	$Ph_3SnO(C_6H_3Cl_2\text{-}2,6)$	1.36	2.46	14
	$Ph_3SnO(C_6H_3Cl_2\text{-}2,6)$ (in pyridine)	1.35	2.90	14
24		1.31	2.35	14
	Idem (in pyridine)	1.34	2.77	14
25	Ph_3SnI	1.22	2.31	[b]
26	$Ph_3SnOCOCMe_3$	1.22	2.30	11
27	$Ph_3SnOSnPh_3$	1.14	2.27	[b]
28	Ph_3SnOPh	1.34	2.27	[b]
29	$Ph_3SnOCOC(Me){=}CH_2$	1.21	2.26	12
30	$Ph_3SnO(C_{10}H_7\text{-}1)$	1.33	2.24	[b]
31	$Ph_3SnO(C_6H_4OMe\text{-}2)$	1.25	2.16	[b]
32	$Ph_3SnO(C_6H_3Cl_2\text{-}2,4)$	1.34	2.07	14
	$Ph_3SnO(C_6H_3Cl_2\text{-}2,4)$ (in pyridine)	1.58	2.87	14
33	$Ph_3SnO(C_6H_4NH_2\text{-}2)$	1.26	2.06	[b]
34	$Ph_3SnO(C_6H_4NO_2\text{-}4)$	1.40	2.02	15
35		1.07	1.75	[b]
36	Ph_3SnSPh	1.39	1.49	[b]
37	$Ph_3SnSSnPh$	1.20	1.46	[b]

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[a] Measurements were made with the pure compounds, unless otherwise stated. Units of δ and Δ are mm · sec^{-1}, isomer shifts refer to tin(IV) oxide. In our measurements line widths observed were 0.80–0.92 mm · sec^{-1}. [b] Present work.

DISCUSSION

Parish and Platt[6] have reported point change calculations for compounds of types (I) and (II) which enable partial quadrupole splittings (PQS) to be assigned to each group bonded to tin. These calculations assume that the ligand contributions are additive. Using the work of Collins and Travis[7], the point change equation for structure (III) can also be generated. Adopting the usual conventions and a suitable choice of axes, then $\Delta \propto V_{zz} \cdot (1+\eta^2/3)^{\frac{1}{2}}$, where $\eta = (V_{xx} - V_{yy})/V_{zz}$. Assuming the Sn–X bonds are equivalent, then;

$$\Delta \propto (\tfrac{3}{2}[\mathrm{R}]-2[\mathrm{X}]) \cdot \left\{1 + \frac{3(-\frac{1}{2}[\mathrm{R}])^2}{(\frac{3}{2}[\mathrm{R}]-2[\mathrm{X}])^2}\right\}^{\frac{1}{2}},$$

which reduces to;

$$\Delta \propto (3[\mathrm{R}]^2 - 6[\mathrm{R}] \cdot [\mathrm{X}] + 4[\mathrm{X}]^2)^{\frac{1}{2}}.$$

Thus the point change equations for the three structures discussed are:

$$\Delta(\mathrm{I}) \propto -3[\mathrm{R}] + 4[\mathrm{X}] \qquad (i)$$

$$\Delta(\mathrm{II}) \propto -2[\mathrm{R}] + 2[\mathrm{X}] \qquad (ii)$$

$$\Delta(\mathrm{III}) \propto (3[\mathrm{R}]^2 - 6[\mathrm{R}] \cdot [\mathrm{X}] + 4[\mathrm{X}]^2)^{\frac{1}{2}} \qquad (iii)$$

Since [R] is negative and [X] is positive, then it is possible to predict that Δ(I) > Δ-(II). Care should be exercised when calculating the quadrupole splittings from the ligand contributions as these may vary in compounds having differing coordination numbers at tin.

The Mössbauer spectra of 37 triphenyltin compounds are given in Table 1; some of these results are reported for the first time, a few previously reported Mössbauer parameters have been redetermined and some literature values are also included. Two accounts of the Mössbauer spectra of R_3SnX compounds appeared while the present work was in preparation and these reports complement the present study. One concentrated particularly on compounds containing tin–metal bonds[1] so this class of compound is not discussed here, and the other was mainly confined to triphenyltin halides and dithiocarbamates[8].

Compounds having structure (I)

The crystal and molecular structures of the compounds Me_3SnF[3b], Me_3SnCN[3a], Me_3SnNCS[3c], $(Me_3Sn)_2N_2C$[3f], Me_3SnOH[3c], Me_3SnCl[3g], $Me_3SnOCOMe$[9] and $Me_3SnOCOCF_3$[9] have been determined and all indicate pentacoordinate Me_3SnX molecules with bridging X groups and essentially planar Me_3Sn systems. Hence, starting with the PQS value of [Cl] 0.63[6] it is possible to obtain PQS values for [Me], [OCOMe], [$OCOCF_3$], [NCS], [F] and [OH] using eqn. (*i*). The results for these calculations are shown in Table 2, the value for [Me] being −0.27 (taken from the value Δ = 3.32 mm·sec^{-1} for $Me_3SnCl_2^-$[15]).

Assuming that the triphenyltin compounds are isostructural, the values of the quadrupole splittings for these compounds can be calculated from the [X] values given in Table 2. Triphenyltin fluoride is used to calculate [Ph] −0.19. The calculated quadrupole splittings are compared with the observed values in Table 3. The agree-

TABLE 2

CALCULATION OF PARTIAL QUADRUPOLE SPLITTING VALUES [X] FOR GROUPS ATTACHED TO TIN

Compound(Me_3SnX)	Δ ($mm \cdot sec^{-1}$)	[X]
Me_3SnCl	3.41[6]	0.63
Me_3SnF	3.77[6]	0.74
Me_3SnNCS	3.77[15]	0.74
$Me_3SnOCOMe$	3.68[16]	0.72
$Me_3SnOCOCF_3$	4.22[16]	0.85
Me_3SnOH	2.91[17]	0.53

TABLE 3

CALCULATED AND OBSERVED VALUES OF QUADRUPOLE SPLITTINGS FOR TRIPHENYLTIN COMPOUNDS

Compound	Δ *found*[a] (*calcd.*) ($mm \cdot sec^{-1}$)
Ph_3SnCl	2.61(3.09)
Ph_3SnNCS	3.63(3.53)
$Ph_3SnOCOMe$	3.34(3.45)
$Ph_3SnOCOCF_3$	4.00(3.97)
Ph_3SnOH	2.98(2.69)

[a] These values are taken from Table 1.

ment is excellent for the isothiocyanate, acetate and trifluoroacetate indicating that these compounds have structure (I) with bridging X groups. The chloride and hydroxide are regarded as borderline cases having structures between (I) and (II). Thus, although recent X-ray studies[18] indicate that Ph_3SnCl is tetrahedral at room temperature, there is evidence[19] that the compound has structure (I) at low temperatures. The value of $\Delta \sim 2.6$ mm·sec^{-1} may be taken as indicating the approximate lower limit of Δ for Ph_3SnX compounds with structure (I).

It is possible to calculate the quadrupole splitting for any triphenyltin compound from that of the corresponding trimethyltin compound. Since $\Delta(Me) - \Delta(Ph) = 3[Ph] - 3\,[Me]$ only the values of [Ph] and [Me] need be known. Thus $\Delta(Ph) = \Delta(Me) - 0.24$ and predicted quadrupole splittings are compared with observed values for a random selection of compounds having $\Delta > 2.6$ mm·sec^{-1} in Table 4. There is good agreement between calculated and observed values of the quadrupole splitting suggesting that all of the compounds in Table 4 have structure (I). It is thus possible, with reasonable certainty, to assign structure (I) to compounds 1–20 (Table 1).

It is not necessary to discuss the structures of compounds 1–20 in detail as, for example, the general principles of $R_3SnOCOR'$ structures have been discussed[22] and recent papers[11,12,23] have confirmed that most $Ph_3SnOCOR$ compounds have structure (I). Further evidence that triphenyltin isothiocyanate is a bridged compound is, firstly, that the compound showed a Mössbauer effect at room temperature,

TABLE 4

CALCULATION OF THE QUADRUPOLE SPLITTINGS OF TRIPHENYLTIN COMPOUNDS USING THE RELATIONSHIP $\Delta(\text{Ph}) = \Delta(\text{Me}) - 0.24$

Compound	*Δ found (mm·sec⁻¹)* *R=Me*	*Δ found (calcd.) (mm·sec⁻¹)* *R=Ph*
$R_3SnOCOH$	3.56[15]	3.58[12](3.32)
R_3SnN_3	3.23[20]	3.19[20](2.99)
$R_3SnN\text{–}CH{=}N\text{–}C_6H_4$	2.89[21]	2.59[21](2.65)
$R_3SnN\text{–}N{=}N\text{–}C_6H_4$	3.18[20]	2.98[20](2.94)
$R_3SnN\text{–}N{=}CH\text{–}N{=}CH$	2.96[20]	2.76[20](2.72)
$R_3SnOCOCHCl_2$	4.08[16]	3.86[a](3.84)
R_3SnNO_3	4.14[17]	4.00[a](3.90)

[a] These values are taken from Table 1.

indicating a polymeric structure. Secondly, when the spectrum of a frozen benzene solution of the compound was measured the quadrupole splitting decreased to 2.63 mm·sec^{-1} consistent with dissociation of the polymer in solution. In frozen pyridine solution Δ increased to 3.12 mm·sec^{-1} consistent with coordination of pyridine tending to cause an increase in the coordination number of tin from 4 to 5. Similar conclusions regarding the structure of Ph_3SnNCS have been reached by other workers[8]. The absence of association in triphenyltin chloride at room temperature has already been referred to and this is the reason for the relatively large increase in Δ which occurs when triphenyltin chloride is converted to a 5-coordinate adduct (compounds 12, 13, 16, 17, 19 and 21). Compare the much smaller increase when the 5-coordinate Me_3SnCl (Δ=3.41 mm·sec^{-1}(ref. 15)) is converted to the 5-coordinate Me_3SnCl·pyridine (Δ=3.44 mm·sec^{-1} (ref.15)).

The quadrupole splitting of the isocyanate (compound 4) is consistent with a 5-coordinate tin atom and bridging NCO groups. This conclusion differs from that reported by Leung and Herber[10] who proposed a 4-coordinate structure although discrepancy in the melting points reported[10] could mean that different compounds are involved.

A number of studies of triphenyltin nitrate have been reported[24–26] and there has been speculation[25] as to whether the infrared spectra indicate bridging, or monodentate, nitrate groups. The compound used in our work was prepared by the method of Shapiro and Becker[24,26] and was stable in air[26].

The infrared spectrum (1515 s, 1506 s (sh), 1492 s, 1410 m, 1288 s, 1271 s, 979 m, 801 m, 451 s (sh), 278 m-s, 266 m cm^{-1}) confirmed that this material was identical with the anhydrous compound obtained by Clark and Goel[25]. The Mössbauer spectrum (compound 2, Table 1) clearly indicates that the compound contains a bridging nitrate group, the quadrupole splitting being one of the largest observed for triphenyltin compounds. We were unable to measure an effect at room temperature, suggesting that the compound is a cyclic oligomer rather than a polymer.

Compounds having structures (II) and (III)

Triphenyltin compounds having quadrupole splittings below 2.6 mm·sec^{-1} (compounds 22–37, Table 1) may have structures (II) or (III) as can be seen by inserting appropriate values for [R] and [X] in eqns. (*ii*) and (*iii*). The various classes of compounds are therefore discussed separately.

The diminishing donor properties of the halogen in Ph_3SnBr (Δ=2.48 mm·sec^{-1}) and Ph_3SnI (Δ=2.31 mm·sec^{-}) are paralleled by decreasing Δ values and tetrahedral structures seem likely.

The Mössbauer spectrum of $Ph_3SnOSnPh_3$ shows that all the tin atoms are equivalent. Structure (I) is rejected because of the magnitude of Δ and structure (III) must be rejected for steric reasons. It is therefore suggested that the oxide (compound 27) and by similar reasoning $Ph_3SnSSnPh_3$ (compound 37) have tetrahedral coordination at the tin atoms.

Organotin derivatives of carboxylic acids carrying substituents on the α-carbon atom (compounds 26 and 29) have atypical, low, values of the quadrupole splitting and it has been suggested that these have structure (II)[12,23].

All the remaining compounds in Table 1 (*i.e.* Nos. 23, 24, 28, 30–36) are phenoxides or thiophenoxides and have either structures (II) or (III). There is no well authenticated example of structure (III) and it seems likely that most of the compounds have tetrahedral structures. However, while there is no basis for unequivocal choice, we suggest that triphenyltin oxinate probably has the chelated structure (III). Thus, when the oxinate (compound 35) and the 1-naphthoxide (compound 30) are compared, it would be predicted that the introduction of the ring nitrogen atom would increase the quadrupole splitting whereas the reverse is observed. This is consistent with a change in structure from (II) for the naphthoxide to (III) for the oxinate. Dimethyltin dioxinate is known to have a *cis* octahedral structure[27] and the PQS value for a chelating oxine group is [oxinate] 0.72. Substituting in equation (*iii*) gives Δ (calcd.) = 1.74 mm·sec^{-1} to be compared with an observed value of 1.75 mm·sec^{-1}, again indicating structure (III) for triphenyltin oxinate.

EXPERIMENTAL

The Mössbauer spectrometer and the technique used to measure the spectra of solid compounds have been described elsewhere[28]. Solutions (~0.3 *M*) were enclosed in cells made from polythene film. All Mössbauer measurements were made at 80 K and the spectra were calibrated with β-tin and tin(IV) oxide. The results were computed on the University of London Atlas computer, using a programme supplied by Dr. T. C. Gibb, which was modified to suit our requirements.

Preparation of compounds

Triphenyltin phenoxides. A solution containing equimolar proportions of triphenyltin hydroxide and the phenol in dry benzene was boiled under reflux for 2 h. The water formed in the reaction was removed by azeotropic distillation and collected in a Dean and Stark separator. After evaporation of the benzene, the product was crystallised where possible. Triphenyltin oxinate and triphenyltin 2-formylphenoxide were also prepared by reaction between triphenyltin chloride and the phenol followed by neutralization of the hydrochloric acid formed with triethylamine.

Analytical and other details of the new compounds are given in Table 5, known compounds were shown to have melting points in agreement with those previously reported.

Adduct of triphenyltin chloride with tetramethylethylene-1,2-diamine. Tetramethylethylenediamine (0.70 g) was added to a warm solution of triphenyltin chloride (2.30 g) in benzene (20 ml). On standing, an almost quantitative yield of $[Ph_3SnCl]_2 \cdot Me_2NCH_2CH_2NMe_2$ was obtained as white crystals. The analytical specimen had m.p. 120–123° after recrystallisation from benzene (see Table 5).

TABLE 5

ANALYSES OF TRIPHENYLTIN COMPOUNDS

Compound	*M.p. (°C)*	*Analysis found (calcd.) (%)*			
		C	*H*	*N*	*Sn*
Ph_3SnOPh	90–91°	65.2	4.6		
		(65.0)	(4.6)		
$Ph_3SnOC_6H_4CHO$-2	167–169°	63.7	4.2		25.1
		(63.7)	(4.3)		(25.2)
$Ph_3SnOC_6H_4NH_2$-2	gum	62.6	4.8	2.95	25.4
		(62.9)	(4.6)	(3.1)	(25.9)
$Ph_3SnOC_6H_4OMe$-2	115–117°	63.5	5.0		24.9
		(63.5)	(4.7)		(25.1)
$Ph_3SnOC_{10}H_7$-1	gum	69.2	4.5		23.8
		(68.2)	(4.5)		(24.1)
$[Ph_3SnCl]_2 \cdot Me_2NCH_2CH_2NMe_2$	120–123°	57.2	5.2	3.2	
		(56.9)	(5.2)	(3.2)	

Triphenyltin nitrate. This was prepared by the method of Shapiro and Becker[24] from triphenyltin chloride and silver nitrate at −80°. However, unlike the compound reported by these workers, the compound prepared here was air-stable, its infrared spectrum and m.p. of 182–184° (lit.[29] m.p. 181–182°) confirmed the formation of triphenyltin nitrate. (Found: Sn, 28.65. $C_{18}H_{15}O_3NSn$ calcd.: Sn, 28.8%.)

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