The Mössbauer Recoil-free Fraction and Structure. Part 3.[1] Triorganotin Arylazobenzoates †

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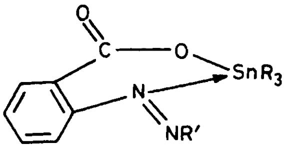
The structures of five triorganotin arylazobenzoates, $SnR_3[O_2CC_6H_4(N_2R')\text{-}o]$, have been investigated by tin-119 Mössbauer spectroscopy, and in one case by *X*-ray crystallography. Crystals of the compound, (4), with R = Ph and R′ = 2-hydroxy-5-methylphenyl are monoclinic, space group *C*2/*c*, with a = 32.525(6), b = 9.475(5), c = 19.957(5) Å, β = 103.034(5)°, and Z = 8. The structure was solved by Patterson and Fourier methods using the intensities of 4 192 independent, non-zero reflections to a final *R* value of 0.0524, and comprises independent, non-interacting molecules. The carboxylato-group chelates the tin atom [Sn–O 2.070(5) and 2.463(7) Å] resulting in a distorted *cis*-SnC_3O_2 five co-ordinated geometry at tin. Tin-119 Mössbauer spectral data indicate that two derivatives (R = Ph, R′ = 4-dimethylaminophenyl and 2-hydroxynaphthyl), have very similar structures to (4), but those of others (R = Ph, R′ = 4-hydroxynaphthyl and R = C_6H_{11}, R′ = 2-hydroxy-5-methylphenyl) are different. The data suggest a molecular structure for the 4-hydroxynaphthyl compound in which the tin is chelated by one carboxyl oxygen atom and a nitrogen atom with a *meridional*-SnC_3ON geometry, and a weakly carboxylato-bridged chain structure for the cyclohexyl compound.

The series of triorganotin derivatives of arylazobenzoic acids prepared and investigated spectroscopically by Majee and Banerjee [2,3] offer interesting structural possibilities. Their u.v. spectra recorded in non-polar solvents exhibit large bathochromic shifts indicative of N→Sn co-ordination and structure (1; R′ = aryl), but which is absent in co-ordinating solvents as the weak N→Sn bond is replaced by a donor solvent molecule (solv) as in (2). Further, when the aryl group contains a donor group in the *ortho* position, the arylazobenzoato-group was postulated to function as a terdentate ligand, giving rise to structure (3). Because such a structure would constitute the first example of a six-co-ordinated triorganotin compound, we have investigated the structure of triphenyltin *o*-(2-hydroxy-5-methylphenylazo)benzoate, (4), by *X*-ray crystallography. In addition, this and four other triorganotin arylazobenzoates, triphenyltin *o*-(4-dimethylaminophenylazo)benzoate, (5), triphenyltin *o*-(2-hydroxynaphthylazo)benzoate, (6), triphenyltin *o*-(4-hydroxynaphthylazo)benzoate, (7), and tricyclohexyltin *o*-(2-hydroxy-5-methylphenylazo)benzoate, (8), have been studied by tin-119 Mössbauer spectroscopy.



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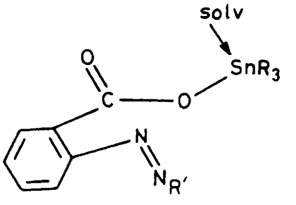

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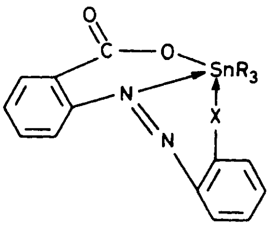

(3)

X = OH or NH_2

Experimental

The synthesis of the complexes has been reported previously.[2]

The Crystal and Molecular Structure of Compound (4).—Bright orange crystals of the material were obtained by recrystallisation from ethanol. One of dimensions 0.3 × 0.4 × 0.4 mm was mounted on a fine glass fibre and used for both the initial photography and the subsequent intensity-data collection.

Crystal data. $C_{32}H_{36}N_2O_3Sn$, M = 605.28, Monoclinic, space group *C*2/*c*, a = 32.525(6), b = 9.475(5), c = 19.957(5) Å, β = 103.034(5)°, U = 5 992.36 Å^3, Z = 8, $F(000)$ = 2 448, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 36.61 cm^{-1}.

The intensities of 4 192 independent, non-zero reflections were measured for $\theta < 25°$ using a Hilger and Watts Y290 automatic four-circle diffractometer. The intensity data were corrected for Lorentz and polarisation effects, but not for absorption due to the low μ value.

Solution and refinement of the structure were carried out by conventional three-dimensional Patterson and Fourier syntheses with anisotropic, full-matrix least-squares refinement. After inclusion of calculated hydrogen-atom positions, convergence was achieved at an *R* value of 0.0524. All calculations were performed with the CRYSTALS suite of programs.[4] Scattering factors used were those for neutral atoms.[5]

Final fractional atomic co-ordinates are listed in Table 1, intramolecular bond distances and angles in Table 2.

Tin-119 *Mössbauer Spectra.*—Our Mössbauer equipment has been described previously.[6] Samples were finely ground to eliminate preferential orientation effects prior to loading in the

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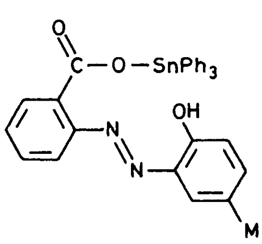
† *Supplementary data available* (No. SUP 23441, 44 pp.): Mössbauer data at 77—175 K; thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



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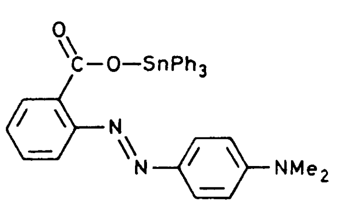

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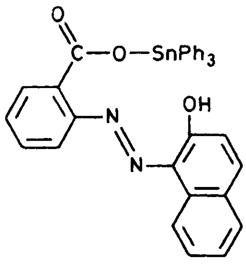

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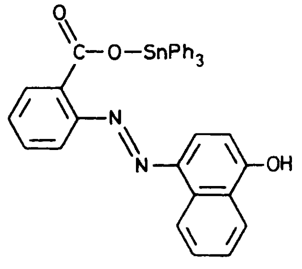

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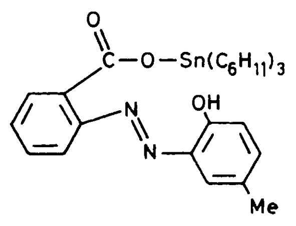

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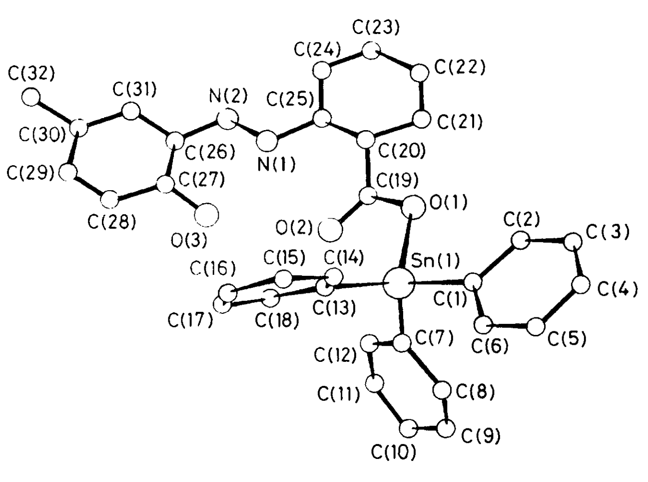


Figure 1. Molecular structure of compound (4) showing the atomic numbering

variable-temperature cryostat (Oxford Instruments Ltd.). Spectra were recorded at various temperatures in the range 77—175 K, accumulating a minimum of 10^6 counts per channel, and subsequently fitted to Lorentzian line shapes by usual least-squares methods.

Results

Structure of Compound (4).—Crystals of the compound comprise discrete molecular units, in which the carboxylato-group functions as an anisobidentate chelating ligand [Sn–O 2.070(5), Sn · · · O 2.463(7) Å], thus rendering the tin atom five-co-ordinated (Figure 1). As can be seen from the unit-cell projection (Figure 2), no intermolecular carboxylato-bridging occurs. The geometry at the tin atom is intermediate between tetrahedral and *cis*-trigonal bipyramidal, in which the carboxylato-ligand spans equatorial and axial sites [*cf.* other examples of this stereochemistry: $SnMe_3(ONPhCOPh)$,[7] $SnPh_3(ONPhCOPh)$,[8] and $SnPh_3(OCPhCHCPhO)$ [9]]. The observed distortions of the bond distances and angles involving tin are consistent with this view. The tin–carbon bond in the second axial site *trans* to the co-ordinate Sn · · · O bond is marginally longer [2.139(6) Å], whilst the sum of the equatorial angles at tin is 340.7°. The angle between the axial carbon and equatorial oxygen atoms [O(1)–Sn(1)–C(1)] is only 95.5(2)°, although the two other axial–equatorial bond angles involving C(1) are greater [111.0(2) and 107.5(2)°], with the equatorial C–Sn–C angle being increased to 117.0(2)° due to the proximity of the carbonyl oxygen atom [O(2)].

The values of the structural parameters for the arylazobenzoato-group are not unusual. The two C–O bond distances of the carbonyl group are as expected unequal [1.224(8) and 1.296(8) Å], with the longer C–O distance being associated

Table 1. Final fractional atomic co-ordinates for compound (4) (estimated standard deviations in parentheses)

Atom	*X/a*	*Y/b*	*Z/c*
Sn(1)	0.113 41(1)	0.037 14(5)	0.040 81(2)
C(1)	0.123 3(2)	−0.086 5(7)	0.132 6(3)
C(2)	0.158 3(2)	−0.169 9(8)	0.154 9(4)
C(3)	0.163 4(3)	−0.244 0(10)	0.216 6(4)
C(4)	0.133 7(3)	−0.235 0(10)	0.254 9(4)
C(5)	0.098 4(3)	−0.154 0(10)	0.233 4(4)
C(6)	0.093 6(3)	−0.077 6(9)	0.171 9(4)
C(7)	0.067 9(2)	−0.054 1(7)	−0.039 3(3)
C(8)	0.039 5(3)	−0.149 8(9)	−0.022 7(4)
C(9)	0.008 3(3)	−0.211 0(10)	−0.074 5(6)
C(10)	0.005 9(3)	−0.178 0(10)	−0.141 6(5)
C(11)	0.033 1(4)	−0.084 0(10)	−0.159 1(5)
C(12)	0.064 6(3)	−0.022 0(10)	−0.108 5(4)
C(13)	0.104 5(2)	0.248 3(7)	0.067 7(3)
C(14)	0.089 5(2)	0.349 7(8)	0.018 4(4)
C(15)	0.080 7(3)	0.484 9(9)	0.038 1(5)
C(16)	0.087 8(3)	0.518 4(9)	0.106 6(6)
C(17)	0.103 3(3)	0.421 9(9)	0.155 8(5)
C(18)	0.111 9(2)	0.285 3(8)	0.137 7(4)
C(19)	0.176 6(2)	0.078 9(7)	−0.028 0(3)
C(20)	0.218 1(2)	0.073 4(7)	−0.048 1(3)
C(21)	0.242 6(2)	−0.049 5(7)	−0.032 7(3)
C(22)	0.280 9(2)	−0.059 7(8)	−0.051 1(4)
C(23)	0.296 0(2)	0.050 7(8)	−0.083 6(4)
C(24)	0.272 8(2)	0.172 3(8)	−0.098 9(3)
C(25)	0.233 5(2)	0.184 2(7)	−0.082 3(3)
C(26)	0.198 3(2)	0.526 3(7)	−0.141 1(3)
C(27)	0.160 9(2)	0.552 1(7)	−0.119 6(4)
C(28)	0.141 4(3)	0.683 2(9)	−0.133 1(4)
C(29)	0.158 2(3)	0.784 7(8)	−0.167 7(4)
C(30)	0.195 4(2)	0.760 9(8)	−0.101 1(3)
C(31)	0.214 6(2)	0.633 9(7)	−0.177 0(3)
C(32)	0.212 7(3)	0.875 0(9)	−0.229 0(4)
O(1)	0.173 9(2)	0.000 1(5)	−0.023 9(2)
O(2)	0.146 8(1)	0.152 5(5)	−0.056 3(2)
O(3)	0.142 1(2)	0.455 2(6)	−0.087 3(3)
N(1)	0.209 0(2)	0.310 2(6)	−0.093 9(2)
N(2)	0.222 0(2)	0.402 3(6)	−0.130 5(3)

Table 2. Intramolecular bond lengths (Å) and angles (°) for compound (4) (estimated standard deviations in parentheses)

Sn(1)–C(1)	2.139(6)	C(7)–C(8)	1.384(10)	C(18)–C(13)	1.408(10)	N(1)–N(2)	1.269(7)
Sn(1)–C(7)	1.120(7)	C(8)–C(9)	1.402(12)	O(1)–C(19)	1.296(8)	N(2)–C(26)	1.394(9)
Sn(1)–C(13)	2.114(6)	C(9)–C(10)	1.360(14)	O(2)–C(19)	1.224(8)	C(26)–C(27)	1.400(10)
Sn(1)–O(1)	2.070(5)	C(10)–C(11)	1.352(14)	C(19)–C(20)	1.495(9)	C(27)–C(28)	1.394(11)
Sn(1)–O(2)	2.463(7)	C(11)–C(12)	1.399(12)	C(20)–C(21)	1.406(9)	C(28)–C(29)	1.369(11)
C(1)–C(2)	1.375(10)	C(12)–C(7)	1.395(11)	C(21)–C(22)	1.379(10)	C(29)–C(30)	1.408(11)
C(2)–C(3)	1.395(10)	C(13)–C(14)	1.382(10)	C(22)–C(23)	1.3737(10)	C(30)–C(31)	1.356(10)
C(3)–C(4)	1.365(12)	C(14)–C(15)	1.389(11)	C(23)–C(24)	1.3710)	C(31)–C(26)	1.416(11)
C(4)–C(5)	1.364(13)	C(15)–C(16)	1.371(14)	C(24)–C(25)	1.398(9)	C(27)–O(3)	1.345(9)
C(5)–C(6)	1.401(11)	C(16)–C(17)	1.353(14)	C(25)–C(20)	1.403(9)	C(30)–C(32)	1.501(10)
C(6)–C(1)	1.377(10)	C(17)–C(18)	1.390(11)	C(25)–N(1)	1.424(8)		
O(1)–Sn(1)–C(1)	95.5(2)	O(1)–C(19)–C(20)	115.1(6)	C(14)–C(15)–C(16)	119.8(8)	N(2)–C(26)–C(31)	115.2(6)
O(1)–Sn(1)–C(7)	110.0(2)	O(1)–C(19)–O(2)	120.4(6)	C(15)–C(16)–C(17)	121.2(8)	C(31)–C(26)–C(27)	118.7(6)
O(1)–Sn(1)–C(13)	113.7(2)	C(20)–C(19)–O(2)	124.4(6)	C(16)–C(17)–C(18)	120.4(8)	C(26)–C(27)–C(28)	119.0(7)
C(1)–Sn(1)–C(7)	111.0(2)	Sn(1)–C(7)–C(8)	119.1(5)	C(17)–C(18)–C(13)	119.3(7)	C(27)–C(28)–C(29)	120.5(7)
C(7)–Sn(1)–C(13)	117.0(2)	Sn(1)–C(7)–C(12)	122.6(5)	C(19)–C(20)–C(21)	118.1(6)	C(28)–C(29)–C(30)	121.7(7)
C(13)–Sn(1)–C(1)	107.5(2)	C(12)–C(7)–C(8)	118.3(7)	C(19)–C(20)–C(25)	123.1(6)	C(29)–C(30)–C(31)	117.6(7)
Sn(1)–C(1)–C(2)	122.3(5)	C(7)–C(8)–C(9)	120.5(8)	C(25)–C(20)–C(21)	118.7(6)	C(30)–C(31)–C(26)	122.4(7)
Sn(1)–C(1)–C(6)	118.5(5)	C(8)–C(9)–C(10)	119.9(9)	C(20)–C(21)–C(22)	120.0(6)	C(24)–C(25)–N(1)	122.5(6)
C(6)–C(1)–C(2)	119.1(6)	C(9)–C(10)–C(11)	120.8(8)	C(21)–C(22)–C(23)	120.7(6)	C(20)–C(25)–N(1)	117.3(5)
C(1)–C(2)–C(3)	120.1(7)	C(10)–C(11)–C(12)	120.3(9)	C(22)–C(23)–C(24)	120.5(6)	C(26)–C(27)–O(3)	123.2(6)
C(2)–C(3)–C(4)	120.1(8)	C(11)–C(12)–C(7)	120.2(8)	C(23)–C(24)–C(25)	120.0(6)	C(28)–C(27)–O(3)	117.7(7)
C(3)–C(4)–C(5)	120.8(7)	Sn(1)–C(13)–C(14)	121.8(5)	C(24)–C(25)–C(20)	120.0(6)	C(29)–C(30)–C(32)	119.9(7)
C(4)–C(5)–C(6)	119.0(8)	Sn(1)–C(13)–C(18)	119.0(5)	C(25)–N(1)–N(2)	115.1(5)	C(31)–C(30)–C(32)	122.4(7)
C(5)–C(6)–C(1)	120.9(7)	C(18)–C(13)–C(14)	119.1(6)	N(1)–N(2)–C(26)	115.1(5)		
Sn(1)–O(1)–C(19)	105.5(4)	C(13)–C(14)–C(15)	120.2(8)	N(2)–C(26)–C(27)	126.0(6)		

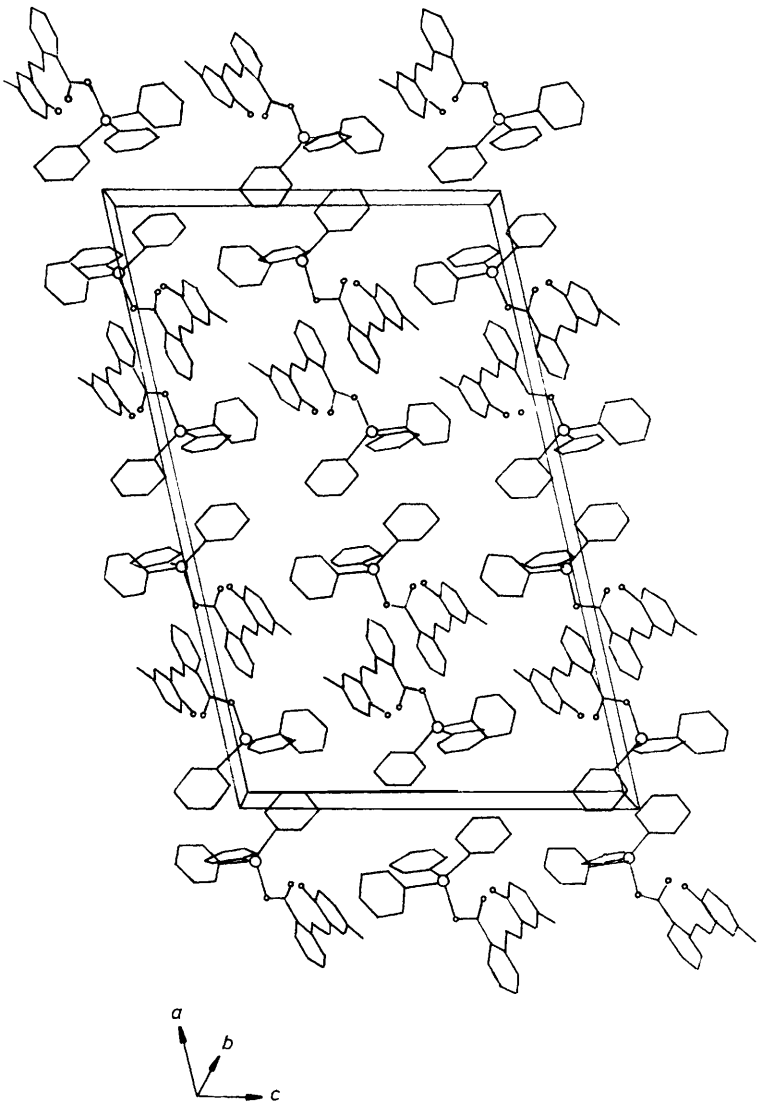


Figure 2. Projection of the unit cell of compound (4)

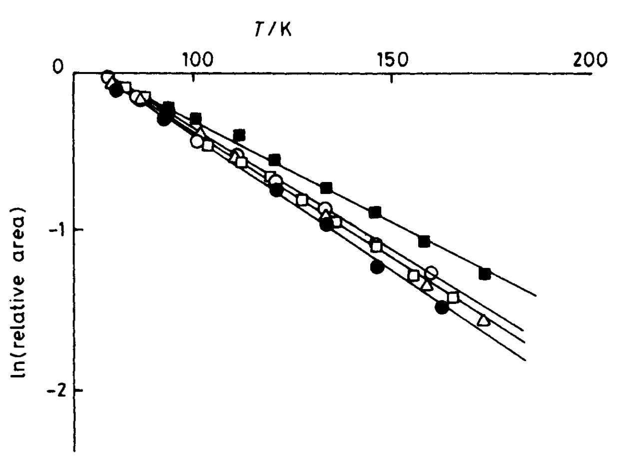


Figure 3. Plots of ln (relative area) *versus* temperature for compounds (4) (○), (5) (□), (6) (△) (7) (●), and (8) (■)

with the shorter Sn–O bond, and *vice versa*. The arylazobenzoato-unit exhibits a *trans* geometry at the N=N bond, with the ligand apparently held in a quite rigid conformation by a trifurcated hydrogen bond involving the aryl hydroxyl group [O(3)], a nitrogen atom [N(1)] of the azo-group, and the carbonyl oxygen atom [O(2)], resulting in O(3)–O(2) 2.94(1), O(3)–N(1) 2.58(1) Å, and O(2)–N(1) 2.62(1) Å.

Tin-119-*Mössbauer Data*.—Tin-119 Mössbauer data were recorded at temperatures in the range 77—175 K for the five triorganotin arylazobenzoates and plots of ln (relative area) *versus* temperature are shown in Figure 3. Isomer shifts, quadrupole splittings, and recoil-free-fraction temperature coefficients are summarised in Table 3. All spectra consist of a quadrupole-split doublet which exhibits a low intensity asymmetry, the lower velocity line being the more intense.

Discussion

Observed structures for triorganotin carboxylates fall into two categories: (*i*) the trimethyl-, trivinyl-, and tribenzyl-tin carboxylates, $SnMe_3(O_2CCX_3)$ (X = H or F),[10] $Sn(CH=CH_2)_3$-

Table 3. Mössbauer data for triorganotin derivatives of arylazobenzoic acids

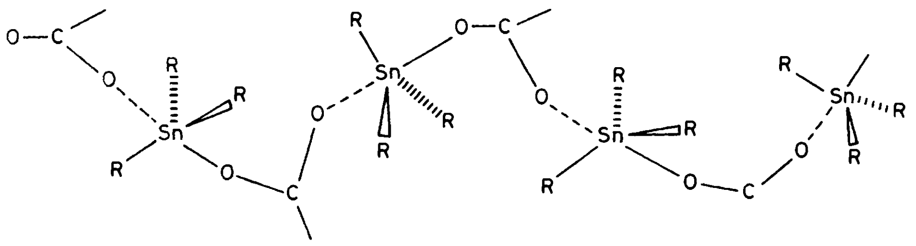
Compound	Isomer shift *	Quadrupole splitting *	*a* †
(5)	1.296	2.383	−1.590
(4)	1.285	2.356	−1.528
(6)	1.297	2.312	−1.596
(7)	1.347	3.059	−1.710
(8)	1.455	3.349	−1.299

* In mm s^{-1}. † $K^{-1} \times 10^2$.

(O_2CR) [R = CCl_3 [11] or $C_5H_4Fe(C_5H_5)$ [12]], and $Sn(CH_2Ph)_3(O_2CMe)$,[13] all of which possess the one-dimensional polymeric structure (I), with the carboxylato-groups strongly bridging in the usual *syn,anti* fashion planar triorganotin residues; and (*ii*) the two tricyclohexyltin carboxylates, $Sn(C_6H_{11})_3(O_2CCX_3)$ (X = H [14] or F [15]), which, although these have been (mis)represented as examples of monomeric triorganotin carboxylates with unidentate carboxylato-ligands and four-co-ordinated tin, are better considered as similar, although weakly *syn,anti*-bridged, one-dimensional polymers (II).

The structure of compound (4) is, therefore, the first characterised example of a truly monomeric triorganotin carboxylate. It is interesting to note that, in spite of the bulky phenyl groups attached to tin and the very large steric demands of the arylazobenzoato-group which prevent intermolecular bridging, the carboxyl group prefers to function as a chelating ligand giving the five-co-ordinated structure (III), rather than as a unidentate ligand. An example of the four-co-ordinated structure (IV) still awaits characterisation.

Tin–oxygen bond-distance data for triorganotin carboxylates and other relevant compounds are compared in Table 4. Although marginally the lowest such observed, the covalent Sn–O bond distance in compound (4) [2.070(5) Å] is comparable to the values observed for other triorganotin carboxylates, which fall in the range 2.08—2.21(1) Å. Those compounds possessing strongly bridged structures, however, generally exhibit distances towards the higher end of this range. The intramolecular co-ordinate $Sn \cdots O$ distance [2.463(7) Å], whilst being somewhat longer than for other examples with a *cis*-five-co-ordinated geometry, is significantly shorter than the corresponding distances in $Sn(C_6H_{11})_3(O_2CMe)$ [2.95(4) Å] [14] and $Sn(C_6H_{11})_3(O_2CCF_3)$ (3.11 Å) [15] {*cf.* the value observed in trimethyltin glycinate [3.23(2) Å] [16] in which the carboxylato-group is unidentate}, and is within the range observed for the intermolecular $Sn \cdots O$ bridging distance in the strongly bridged structures [2.391(4)—2.65(2) Å]. The intermolecular $Sn \cdots O$ bridging distances in the two tricyclohexyltin carboxylates are very long (3.84 and 3.70 Å for the acetate and trifluoroacetate, respectively). Nevertheless, these cause considerable distortion of the SnC_3 framework towards planarity (sum of the CSnC angles = 349° for the acetate and 352° for the trifluoroacetate).



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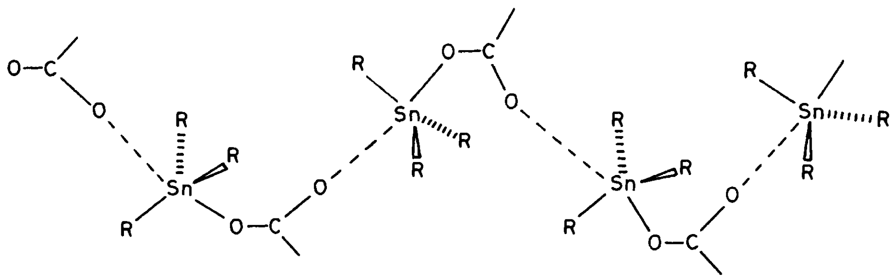

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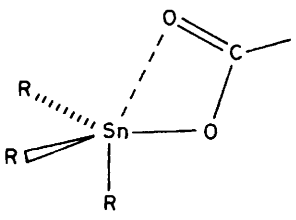

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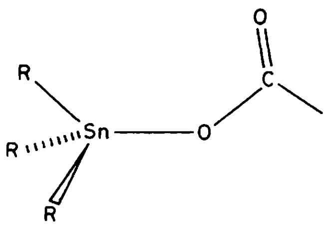


(IV)

Table 4. Tin–oxygen bond data (Å) for triorganotin carboxylates and related compounds

Compound	Sn–O	Sn···O intramolecular	Sn···O intermolecular	Ref.
(4)	2.070(5)	2.463(7)	—	This work
$SnPh_3(ONPhCOPh)$	2.091(5)	2.308(4)	—	8
$SnMe_3(ONPhCOPh)$				7
molecule 1	2.064(6)	2.392(6)	—	
2	2.152(6)	2.263(6)	—	
$SnPh_3(OCPhCHPhO)$	2.094(7)	2.276(7)	—	9
$Sn(C_6H_{11})_3(O_2CMe)$	2.12(3)	2.95(4)	3.84	14
$Sn(C_6H_{11})_3(O_2CCF_3)$	2.08	3.11	3.70	15
$SnMe_3(O_2CMe)$	2.205(3)	—	2.391(4)	10
$SnMe_3(O_2CCF_3)$	2.177(14)	—	2.458(15)	10
$Sn(CH=CH_2)_3(O_2CCCl_3)$	2.17(2)	—	2.49(1)	11
$Sn(CH=CH_2)_3[O_2CC_5H_4Fe(C_5H_5)]$	2.12(1)	—	2.42(1)	12
$Sn(CH_2Ph)(O_2CMe)$	2.14(2)	—	2.65(2)	13
$SnMe_3(glyO)$ *	2.21(1)	3.23(2)	—	16

* glyO = Glycinate.

In light of the known structure of compound (4) the structures of the other four triorganotin arvlazobenzoates can be assessed from an analysis of the tin-119 Mössbauer isomer shift, quadrupole splitting, and recoil-free-fraction temperature coefficient. The latter parameter is defined in the ' thin-absorber ' approximation as in equation (i) where $A(T)$, $f(T)$,

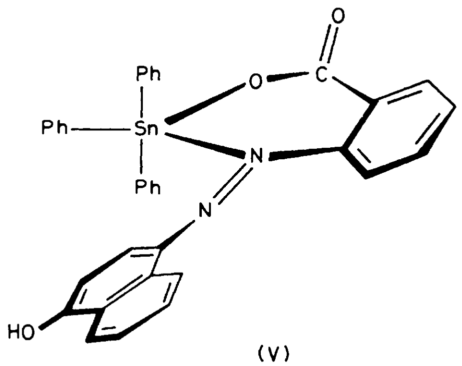
$$a = \frac{d[A(T)]}{dT} = \frac{d[f(T)]}{dT} = \frac{d\{\exp[-\langle x_{iso}(T)^2\rangle]\}}{dT} = \frac{d[\exp(-6E_RT/k\theta_D{}^2)]}{dT} \quad \text{(i)}$$

and $\langle x_{iso}(T)^2\rangle$ are, respectively, the resonance area, recoil-free fraction, and mean-square amplitude of displacement of the Mössbauer nuclide at temperature T; E_R is the recoil energy, and θ_D the Debye temperature obtained from the linear plots of ln$A(T)$ *versus* T in the temperature range 77—175 K (Figure 3). We have previously shown that this parameter is a useful guide to the lattice structure of tin compounds.[17] For compounds possessing a structure comprising non-interacting molecules, a has a value of *ca.* -1.8×10^{-2} K^{-1}. However, the presence of intermolecular bonding interactions increases a. Thus, the value for $SnMe_3(O_3SPh)\cdot H_2O$, in which adjacent molecules are hydrogen-bonded into one-dimensional chains, is reduced to -1.7×10^{-2} K^{-1}, whilst the values for $SnMe_3(O_2CC_5H_4N\text{-}2)\cdot H_2O$ and $SnMe_2(ONHCOMe)_2$, which have more complex hydrogen-bonding networks, are -1.27×10^{-2} and -0.92×10^{-2} K^{-1} respectively. The strongly bridged one-dimensional chain structure of $SnMe_3(ONC_6H_{10})$ exhibits a value of -0.97×10^{-2} K^{-1}.

The data for the two derivatives (5) and (6) are almost identical to those of (4) indicating their structural similarity. Quadrupole-splitting values for these three derivatives are also very similar to those of $\overline{\mathrm{SnPh_3(ONPhCO}}\mathrm{Ph)}$ (2.32 mm s^{-1})[8] and $\overline{\mathrm{SnPh_3(OCPhCHCPhO}}\mathrm{)}$ (2.25 mm s^{-1}),[9] which are known to possess *cis*-five-co-ordinated structures somewhat less distorted from ideal geometry, corroborating the chelating, rather than unidentate, bonding nature of the carboxylato-group in these derivatives. The value of the temperature coefficient, a, for compounds (4)—(6), however, is higher (*ca.* -1.55×10^{-2} K^{-1}) than that (-1.85×10^{-2} K^{-1}) measured for $SnPh_3(ONPhCOPh)$, a monomeric solid. Since *inter*molecular interaction, proposed previously [17] as the principal contribution to the raising of the value of a, is absent in compound (4), and also by inference in (5) and (6), it would appear that the higher values of a in this case are due to crystal-packing effects restricting motion of the molecule in the crystal. A similar rationalisation has been advanced to account for the higher values of the (*OO*-dialkyl dithiophosphato)triphenyltin esters, $SnPh_3[SP(=S)(OR)_2]$ [$a = -1.43 \times 10^{-2}$ (R = Et) and -1.40×10^{-2} K^{-1} (R = Pr^i)],[18] and tetraphenyltin ($a = -1.659 \times 10^{-2}$ K^{-1}),[19] which is known to possess a molecular crystal lattice.[20] In the present case, the planarity of the arylazobenzoato-ligand enables the molecules to pack efficiently in an interleaving fashion in the crystal. In contrast, molecules of $SnPh_3(ONPhCOPh)$ are more spherical in nature, and are well spaced in the crystal.[8]

The Mössbauer parameters for compound (8) are obviously quite different, indicating a gross change from the structure of its triphenyltin homologue. The increase in isomer shift is as expected for a change from an electron-withdrawing phenyl group to an electron-donating cyclohexyl group. The quadrupole splitting for compound (8) (3.349 mm s^{-1}) is much higher, whilst the value of a increases to -1.299×10^{-2} K^{-1}, both of which are consistent with the weakly bridged chain structure (II) exhibited by both tricyclohexyltin acetate [14] and trifluoroacetate,[15] which have quadrupole splittings of 3.33 and 3.78 mm s^{-1}, respectively.[15] The value of a for compound (8) is comparable with those of the weakly bridged chain structures proposed for triethyl- and tripropyl-tin cyclohexanone oximate (-1.16×10^{-2} and -1.43×10^{-2} K^{-1}, respectively),[17] but is higher than that observed for the trimethyltin homologue (-0.97×10^{-2} K^{-1}) [17] and trimethyltin glycinate (-1.15×10^{-2} K^{-1}),[16] both of which are strongly bridged one-dimensional structures.

The quadrupole splitting and a values for compound (7) represent somewhat of a paradox. The increase in quadrupole splitting to 3.059 mm s^{-1} could similarly indicate a distortion towards a *trans*-SnC_3O_2 geometry at tin, implicit in which is the occurrence of some weak *inter*molecular interactions. However, the decrease of a to -1.710×10^{-2} K^{-1} is inconsistent with this argument, and suggests a molecular solid which is more loosely packed than the other three triphenyltin arylazobenzoates. An alternative rationalisation of these Mössbauer data is that in this case the arylazobenzoato-ligand chelates the tin atom not as an O,O-chelating carboxyl ligand as in compound (4) giving a distorted *cis*-SnC_3O_2 geometry, but rather as an O,N-chelate where the larger



(V)

ligand 'bite' requirement [the O(2)-N(1) distance in (4) is 2.62(1) Å; *cf.* the O(1)-O(2) distance of 2.33 Å] allows a preference in these circumstances for the *meridional*-SnC_3ON geometry (V), for which a quadrupole splitting much greater than 2.3 mm s^{-1} would be expected.[21] If indeed this is adopted by compound (7) it is not readily apparent why it should be preferred, and suggests that rather subtle factors affect the structure. No examples of triorganotin compounds possessing the *mer*-SnC_3X_2 geometry have as yet been characterised by structural techniques. Nevertheless, this geometry has been proposed for the cationic species $[SnPh_3(OPO)]^+$ (OPO = $OPh_2\widehat{P\;P}Ph_2O$ or $OPh_2\widehat{P\;P}Ph_2O$) which exhibit quadrupole splittings of 3.52 and 3.56 mm s^{-1}, respectively.[21]

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