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# TRIPHENYLTIN SUBSTITUTED BENZOATES: A SPECTROSCOPIC STUDY OF STRUCTURE IN SOLUTION AND SOLID PHASES

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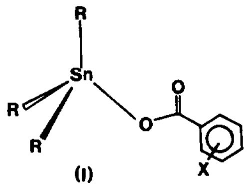
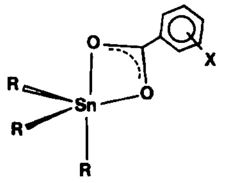
**Abstract**—$^{119}$Sn NMR and Mössbauer spectroscopic data have been recorded for 12 compounds of formula $Ph_3SnO_2CC_6H_4X$ (X = H, Me-2, $NH_2$-2, $NMe_2$-2, Cl-2, Cl-3, Cl-4, OH-2, OH-4, SMe-4 or OMe-2) and $Ph_3SnO_2CC_{10}H_7$-1. On the basis of these measurements all the compounds are assigned a coordination number of four at tin in solution, and, with the exception of the Cl-2 and OH-2 derivatives, retain this structure in the solid. Both of these latter compounds exhibit enhanced Mössbauer quadrupole splittings (3.71 and 2.97 mm $s^{-1}$), which are attributed to carboxylate- and hydroxyl-bridged structures, respectively. The variable-temperature Mössbauer spectra of two compounds (X = OMe-2 or OH-2) are discussed.

In recent years, triphenyltin compounds ($Ph_3SnX$) have achieved commercialization as toxicants in marine anti-fouling paints.[1–3] Fouling arises from the settlement, attachment and growth of marine animals and plants on submerged structures, and in general, plants are more resistant to this class of organotin biocide than other fouling species.[4–6] As part of an investigation intended to overcome this drawback and hence widen the spectrum of biocidal activity, we have synthesized a series of triphenyltin arylcarboxylates for raft testing.[7] In this report we consider the spectroscopic evidence for the structures of these compounds, determined in the solid state primarily by $^{119}$Sn Mössbauer spectroscopy, in non-aqueous solutions by $^{119}$Sn NMR, and linked by IR data in both phases.

Triorganotin derivatives of ring-substituted benzoic acids are rich with structural possibilities, centred around the triad of structures I–III. In addition to a tetrahedral geometry at tin arising from a monodentate carboxylate ligand, a bidentate ligand can either chelate (II) or bridge (III) tin atoms to result in variations on a trigonal bipyramidal geometry at the metal. In instances where the ring



(I)



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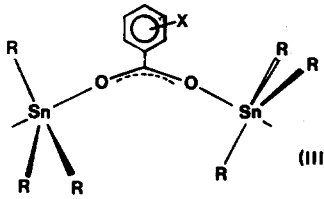

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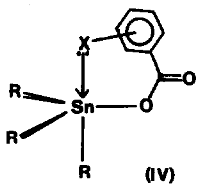

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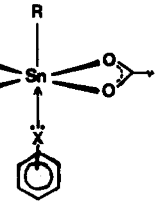

(V)

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substituent is non-passive in a coordination sense due to the presence of lone electron pairs or hydrogen bonding possibilities (e.g. X = $OCH_3$, $NH_2$ etc.), coordination between X and tin can occur at the expense of (IV), or in addition to (V), the bond from the acyl oxygen. In the solid state available examples are dominated by III,[8] with only one crystallographically authenticated claim being made for structure I, namely tricyclohexylstannyl 3-indolylacetate,[9] while data for $Ph_3SnO_2CC_6H_4X$ (X = $NH_2$-2, $NH_2$-4, $NMe_2$-2, OH-2, OMe-2 or SMe-4) have all been interpreted in terms of the five-coordinate structure II.[10,11] Distinctions between these architectures are important, since chelated structures, e.g. II, have been shown in some cases to lead to a significant decrease in biocidal activity.[12] Moreover, conflicting structural data have recently appeared in the literature relating to these systems,[10,11,13–15] which we now assess in the light of our own studies.

## EXPERIMENTAL

### *Spectroscopic studies*

$^{119}Sn$ NMR spectra were recorded under nuclear Overhauser suppressed conditions, in 10-mm tubes on a JEOL FX60Q spectrometer, with field frequency lock to external $D_2O$. $^{119}Sn$ chemical shifts ($\delta$ $^{119}Sn$) are relative to $Me_4Sn$ and are accurate to $\pm 0.1$ ppm.

IR spectra were recorded in the region 4000–200 $cm^{-1}$ on a Perkin–Elmer 1330 spectrometer, either in $CCl_4$ or toluene solutions [0.2 g $(3.0\ cm)^{-3}$], or as KBr discs.

$^{119}Sn$ Mössbauer spectra were obtained using a constant acceleration, microprocessor controlled spectrometer (Cryophysics Ltd, Oxford, U.K.), with a 512 channel data store. A barium stannate source was used at room temperature and samples were packed in perspex discs and cooled to 80 K using a liquid nitrogen cryostat. Isomer shift data are relative to $SnO_2$ as reference; spectral data obtained at both collaborating institutions were identical within experimental error. Details of the variable-temperature experiment, including the method of data acquisition and manipulation are described elsewhere.[8] Samples containing 1 mg $^{119}Sn$ $cm^{-2}$ were used to minimize saturation effects and to comply as fully as possible with the criteria of a "thin sample", while maintaining the viability of the experiment, i.e. good-quality spectra accumulated in

Table 1. Analytical data[a] for $Ph_3SnX$

| | X | M.p. (lit.) (°C) | C | H | N | Sn | Cl |
|---|---|---|---|---|---|---|---|
| 1 | $O_2CC_6H_5$ | 85–87 (84–85.5[b])[c] | 63.6 (63.7) | 4.4 (4.3) | | 25.1 (25.3) | |
| 2 | $O_2CC_6H_4NH_2$-2 | 110–112 (108–109[d])[e] | 61.4 (61.7) | 4.5 (4.3) | 2.9 (2.9) | 23.9 (24.5) | |
| 3 | $O_2CC_6H_4NMe_2$-2 | 80–82 (79–80[f])[g] | 62.8 (63.0) | 5.2 (4.9) | 2.7 (2.7) | 23.2 (23.2) | |
| 4 | $O_2CC_6H_4Cl$-3 | 88–90[g] | 59.4 (59.4) | 3.9 (3.8) | | 23.7 (23.5) | 7.0 (7.0) |
| 5 | $O_2CC_6H_4Cl$-4 | 128–134 (131–135[h])[c] | 59.0 (59.4) | 3.7 (3.8) | | 23.5 (23.5) | 7.1 (7.0) |
| 6 | $O_2CC_6H_4OH$-2 | 122–124 (123–124[i])[c] | 60.8 (61.6) | 4.0 (4.1) | | 24.4 (24.4) | |
| 7 | $O_2CC_6H_4OH$-4 | 141–143 (117[j])[k] | 62.3 (61.6) | 4.2 (4.1) | | 24.5 (24.4) | |
| 8 | $O_2CC_6H_4OMe$-2 | 110–112 (107–108[i])[l] | 62.3 (62.3) | 4.5 (4.4) | | 23.6 (23.7) | |
| 9 | $O_2CC_6H_4Me$-2 | 68–70[e] | 63.9 (64.3) | 4.5 (4.5) | | 24.4 (24.5) | |
| 10 | $O_2CC_{10}H_7$-1 | 127–129[c] | 66.5 (66.8) | 4.3 (4.2) | | 22.4 (22.8) | |
| 11 | $O_2CC_6H_4SMe$-4[m] | 143–145 (141–143[i])[g] | 60.6 (60.4) | 4.4 (4.3) | | 23.4 (23.0) | |
| 12 | $O_2CC_6H_4Cl$-2 | 58–60[c] | 58.7 (59.4) | 3.8 (3.8) | | 23.5 (23.5) | 6.9 (7.0) |
| 13 | OC(Ph)CHCO(Ph) | 146–148 (135–136[n])[g] | 68.9 (69.0) | 4.6 (4.7) | | 20.6 (20.8) | |

[a] Calculated values in parentheses.

[b] R. C. Poller, *J. Inorg. Nucl. Chem.* 1962, **24**, 593.

[c] Recrystallized from petroleum ether.

[d] Reference 15.

[e] Recrystallized from ether–petroleum ether.

[f] Reference 10.

[g] Obtained analytically pure after reaction solvent removal.

[h] Reference 14.

[i] Reference 11.

[j] Reference 24.

[k] Recrystallized from benzene.

[l] Recrystallized from toluene–petroleum ether.

[m] Sulphur found: 6.1; calc.: 6.2%.

[n] Reference 17.

*ca* 12 h. For temperatures above 110 K, samples containing 1.5 mg $^{119}$Sn cm$^{-2}$ were required to maintain this condition. However, data from the two parts of each experiment coalesced into a single line which exhibited no systematic curvature, suggesting that vibrational anharmonicity within the lattice is also absent.

### *Synthesis*

Compounds **2**, **3**, **8**, **11** and **13** (Table 1) were prepared by an azeotropic dehydration reaction between stoichiometric amounts of triphenyltin hydroxide and either the appropriate arylcarboxylic acid or 1,3-diphenylpropane-1,3-dione, in refluxing toluene and using a Dean and Stark trap. Reflux times were typically 2 h. The remaining compounds in Table 1 were prepared by refluxing together reagents using acetone as the reaction solvent. Recrystallization solvents, m.ps and analytical data for all the compounds studied are given in Table 1.

## DISCUSSION

### *Solution-state structure*

$^{119}$Sn NMR data for a range of triphenylstannyl esters of substituted benzoic acids (**1**–**12**) are given in Table 2. The data are measured in non-coordinating solvents, and show no concentration dependence for the chemical shift. This shift is a sensitive indicator of coordination number at tin, shifts moving to low frequency with increasing number of bonds to the metal. The relevant reference data for this discussion are $(Ph_3Sn)_2O$ (−83.6 ppm) and

$Ph_3SnOC(Ph)CHCO(Ph)$ (−221.2 ppm)

which are unambiguously four-[16] and five-coordinate (**II**),[17] respectively, in the solid state and it is unlikely in either case that this situation will alter upon dissolution. The chemical shifts for **1**–**12** lie in the range −96.2 to −124.5 ppm and can confidently be assigned to a four-coordinate metal atom (**I**). Our data corroborate previous work, which has associated a chemical-shift range of −40 to −120 ppm for $Ph_3SnX$ compounds of coordination number four.[13,14]

These structural inferences can be extrapolated to the solid state, by consideration of $\nu_{asym}$(C=O), as measured in KBr discs or $CCl_4$ solutions (Table 2). Assignment of these bands cannot however be made with total confidence due to the presence of absorptions associated with stretching vibrations of the benzene ring, which occur in the same region of the spectrum. For **1**–**11**, the data are essentially independent of phase, and hence imply that the carboxylate moiety is unidentate in the solid state

Table 2. $^{119}$Sn NMR (ppm)[a] and IR (cm$^{-1}$)[b] spectroscopic data for $Ph_3SnX$

| | | | $\nu_{asym}$(C=O) | |
|---|---|---|---|---|
| | X | $\delta$ $^{119}$Sn[c] | Solid | Solution[c] |
| **1** | $O_2CC_6H_5$ | −114.3 | 1622 | 1618 |
| **2** | $O_2CC_6H_4NH_2$-2 | −119.5 | 1615 | 1622 |
| **3** | $O_2CC_6H_4NMe_2$-2 | −124.5 | 1613 | 1613 |
| **4** | $O_2CC_6H_4Cl$-3 | −105.9 | 1627 | 1638 |
| **5** | $O_2CC_6H_4Cl$-4 | −108.2 | 1638 | 1638 |
| **6** | $O_2CC_6H_4OH$-2 | −96.2 | 1629 | 1630 |
| **7** | $O_2CC_6H_4OH$-4 | −114.5[d] | 1605 | 1605[d] |
| **8** | $O_2CC_6H_4OMe$-2 | −121.9 | 1629 | 1628 |
| **9** | $O_2CC_6H_4Me$-2 | −119.9 | 1625 | 1628 |
| **10** | $O_2CC_{10}H_7$-1 | −116.2 | 1622 | 1628 |
| **11** | $O_2CC_6H_4SMe$-4 | −115.6 | 1628 | 1636 |
| **12** | $O_2CC_6H_4Cl$-2 | −106.3 | 1540 | 1640 |
| **13** | OC(Ph)CHCO(Ph) | −221.2[e] | | |
| **14** | OH | −83.3 | | |
| **15** | $OSnPh_3$ | −83.6 | | |

[a] Relative to $Me_4Sn$.

[b] ±3 cm$^{-1}$.

[c] $CCl_4$ solution unless indicated otherwise.

[d] Toluene solution.

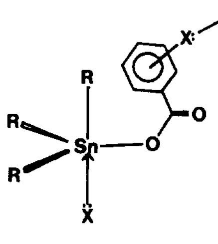
[e] The previously reported value of −82.2 ppm (S. J. Blunden and P. J. Smith, *J. Organomet. Chem.* 1982, **226**, 157) is incorrect and is believed to have been due to either $Ph_3SnOH$ or $(Ph_3Sn)_2O$.

also. This rules out **II**, **III** and **V** as viable structures in this latter phase, and calls into question the interpretation of the X-ray crystallographic data for $Ph_3SnO_2CC_6H_4X$ (X = $NH_2$-2, $NMe_2$-2, OH-2, OMe-2 or SMe-4)[10,11] which the authors discuss in terms of a five-coordinate structure (**II**). Structures involving additional coordination via $X: \rightarrow Sn$ cannot be entirely eliminated. Structures of type **IV** can be discounted since chelation should persist in solution, but an alternative five-coordinate species incorporating intermolecular $X: \rightarrow Sn$ coordination (**VI**) is still possible.

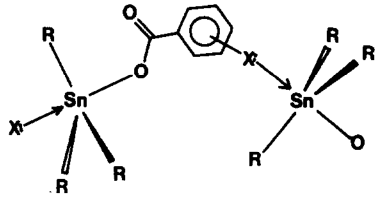
In contrast, IR data for the Cl-2 derivative (**12**) varies markedly between solution and the solid state, and follows the established pattern for a carboxylate-bridged structure (**III**) in the solid, with breaking of the intermolecular bond upon dissolution. The $^{119}Sn$ NMR data under the conditions of dilution employed in the study indicate that the tin is, as expected from the IR data, four-coordinate in solution ($\delta$ $^{119}Sn$ $-106.3$ ppm). In principle, the $^{119}Sn$ chemical shift of compounds with this structure should show a concentration dependence, with shifts moving to low frequency (more negative values) as concentration (and hence the degree of association) increases. This was not observed in this study, and at the concentration levels used [0.2–0.8 g 3.0 cm)$^{-3}$] the variation in shift was negligible ($-106.3$ to $-107.1$ ppm). We conclude that at these concentrations complete dissociation of the polymer into discrete molecules had always occurred.

### *Solid-state structure*

Indirect evidence for the solid-state structure of organotin compounds can be derived from Mössbauer spectroscopy. In this context, the most useful parameter is the quadrupole splitting (QS), for which parameter a given range is associated with a particular coordination number and geometry at tin: 1.00–2.40 mm $s^{-1}$ (**I**), 1.70–2.40 mm $s^{-1}$ (**II**) and 3.00–4.00 mm $s^{-1}$ (**III**).[18] From the foregoing discussion of $^{119}Sn$ NMR and IR data, two structures are possible for **1**–**11** in the solid state, namely **I** and **VI**. While this latter variation could give rise to a *cis*-$OXSnR_3$ geometry (**VIa**), intermolecular bonding invariably results in the *trans*-$OXSnR_3$ structure (**VIb**)[19,20] and should show Mössbauer parameters similar to structure **III**, i.e. QS ~ 3.00–4.00 mm $s^{-1}$. Mössbauer data for the triphenyltin carboxylates studied are given in Table 3. Compounds **1**–**5** and **7**–**10** all have QS in the range 2.30–2.55 mm $s^{-1}$, and of the two alternative structures indicated are only consistent with **I**. However, it should be noted that these QS data could also be interpreted in terms of chelated structures **II** and **IV**, *and only with the help of ancillary spectroscopic data (IR and* $^{119}$*Sn NMR) can a valid distinction between these alternatives be made.* Indeed, QS data for five-coordinated **13** (2.25 mm $s^{-1}$) overlap with the above, and cannot be differentiated on the basis of Mössbauer data alone.



(VIa)



(VI b)

QS data for **6** (2.97 mm $s^{-1}$) and **12** (3.71 mm $s^{-1}$) must be considered separately from those above. The solid-state structure for **6** reveals an intramolecular $C{=}O \cdots Sn$ separation of 3.071(2) Å, and an intermolecular $HO \cdots Sn$ interaction at 3.035(2) Å.[11] Since intermolecular interactions such as the latter will be absent in dilute solutions, $^{119}Sn$ NMR data indicate that the $C{=}O \cdots Sn$ intramolecular distance of 3.071(2) Å is fortuitous, and does not represent a bonding interaction (*vide supra*). The enhanced QS value in the solid state relative to other four-coordinated analogues can thus be attributed to the intermolecular $HO \cdots Sn$ bond, which results in coordination expansion at tin to five, and formation of a *trans*-$O_2SnR_3$ geometry (**VIb**). A parallel bonding situation is evident in the two analogous arylazobenzoates (**16** and **17**).[21] The structure of **16** shows (at best) weak intramolecular $C{=}O \cdots Sn$ coordination to produce a type **II** structure (QS = 2.36 mm $s^{-1}$) in which the 2-OH group is involved in intramolecular hydrogen bonding. Intramolecular bonding of this latter type is precluded on steric grounds in the 4-OH derivative (**17**) (QS = 3.06 mm $s^{-1}$) and thus the hydroxyl group in all likelihood assumes an intermolecular, bridging role akin to **6**.

The 2-chloro derivative (**12**), whose $^{119}Sn$ NMR and IR data collectively point toward a carboxylate-bridged structure (**III**), shows the highest QS recorded in this study (3.71 mm $s^{-1}$), and is totally consistent with such a *trans*-$O_2SnR_3$ environment

Table 3. $^{119}$Sn Mössbauer data for $Ph_3SnX$

| | X | IS[a] | QS[a] | $\Gamma_1$[b] | $\Gamma_2$[b] |
|---|---|---|---|---|---|
| 1 | $O_2CC_6H_5$ | 1.24 | 2.55 | 0.97 | 0.93 |
| 4 | $O_2CC_6H_4Cl$-3 | 1.27 | 2.42 | 0.95 | 0.96 |
| 5 | $O_2CC_6H_4Cl$-4 | 1.24 | 2.36 | 0.96 | 0.93 |
| 6 | $O_2CC_6H_4OH$-2 | 1.34 | 2.97 | 1.01 | 1.01 |
| 7 | $O_2CC_6H_4OH$-4 | 1.31 | 2.55 | 1.02 | 1.02 |
| 8 | $O_2CC_6H_4OMe$-2 | 1.25 | 2.30 | 1.03 | 1.03 |
| 9 | $O_2CC_6H_4Me$-2 | 1.25 | 2.42 | 0.92 | 0.92 |
| 10 | $O_2CC_{10}H_7$-1 | 1.23 | 2.33 | 0.98 | 0.95 |
| 11 | $O_2CC_6H_4SMe$-4 | 1.27 | 2.42 | 1.02 | 1.01 |
| 12 | $O_2CC_6H_4Cl$-2 | 1.34 | 3.71 | 1.07 | 0.93 |
| 13 | OC(Ph)CHCO(Ph) | 1.13 | 2.25 | | |
| 16 | $O_2CC_6H_4(N_2C_6H_3OH$-2, Me-5)-2[c] | 1.28 | 2.36 | | |
| 17 | $O_2CC_6H_4(N_2C_{10}H_6$-1, OH-4)-2[c] | 1.35 | 3.06 | | |

[a] $\pm 0.04$ mm $s^{-1}$.

[b] Full width at half height.

[c] Reference 21.

about tin in the solid. From the relative magnitudes of the QS for **6** and **12**, we also conclude that the intermolecular $C{=}O\cdots Sn$ bond is shorter than 3.0 Å.

Finally, we have attempted to distinguish coordination polymers such as **6** from discrete monomers, e.g. **8**, using variable-temperature $^{119}$Sn Mössbauer spectroscopy. Data recorded over the temperature ($T$) range 78–145 K for compounds **6** and **8** are shown in Fig. 1. We have previously correlated the lattice structure of phenyltin compounds with the temperature coefficient of the natural logarithm of the recoil-free-fraction ($a$):

$$a = -\frac{d[\ln f(T)]}{dT} = -\frac{d[\ln A(T)]}{dT},$$

$$a = -\frac{d[-6E_R T/k\theta M^2]}{dT},$$

where $A$ is the area under the Mössbauer resonance, $E_R$ the Mössbauer recoil energy and $\theta_M$ a characteristic temperature for the lattice, equivalent to the Debye temperature.[22] Under these systematics, in plots of ln $A$ vs $T$ the shallowest slopes are exhibited by linear or zig-zag polymers ($10^2a = 0.9$–$1.5$ $K^{-1}$) while monomeric lattices have $10^2a$ in excess of 1.20 $K^{-1}$, except in cases of extremely efficient packing where a more rigid lattice, akin to that of a polymer, results.[23] On the other hand, flexible polymers of an "S" or helical construction afford the tin a vibrational freedom enjoyed in non-associated lattices and steeper slopes ($10^2a \sim 1.70$ $K^{-1}$) are observed in ln $A$ vs $T$ plots.

The values of $10^2a$ for compounds **6** (1.36 $K^{-1}$) and **8** (1.46 $K^{-1}$) are very similar and consistent with discrete molecules within the lattice. Furthermore, this similarity in behaviour is also in accord with an approximately equal effective vibrating mass for the two cases, in consonance with the near equality in their molecular weights. Comparison can be drawn with $Ph_4Sn$ ($10^2a = 1.37$ $K^{-1}$)[22] and a series of chelated triphenyltin carboxylates, $Ph_3SnO_2CC_6H_4(N_2R\text{-}o)$ ($10^2a = 1.53$–$1.71$ $K^{-1}$).[21]

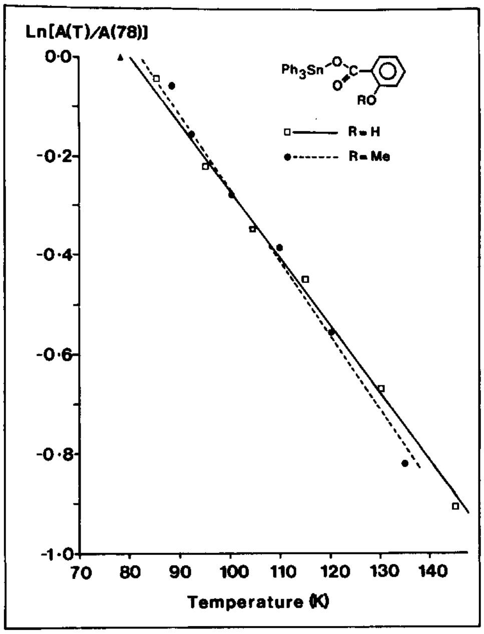


Fig. 1. Plot of $\log_e$ (normalized area) vs temperature for **8** and **6**. The slopes of the lines are $1.46\times10^{-2}$ $K^{-1}$ ($r = 0.993$, seven points) and $1.36\times10^{-2}$ $K^{-1}$ ($r = 0.997$, eight points), respectively. The point ▲ (78, 0.00) is common to both plots.

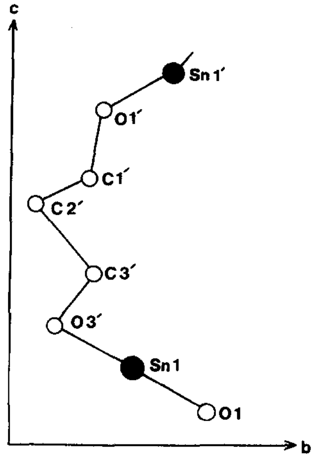


Fig. 2. Polymer propagation in **6**, shown as a projection of part of the cell contents onto the *bc* plane. Only atoms linking metal centres are included for clarity. Data taken from Ref. 11.

In contrast, carboxylate-bridged triorganotins adopt polymers of "stretched-S" construction and are typified by $Ph_3SnO_2CCH_3$ ($10^2a = 1.91\ K^{-1}$).[8]

The variable-temperature Mössbauer experiment is clearly insensitive to the intermolecular Sn · · · OH interaction in **6**, which weakly associates adjacent molecules. This is, perhaps, not surprising. The Sn · · · O bond is long (3.035 Å)[11] and hence weak. In addition, and equally importantly, the spatial arrangement of the bridging unit —OC · $C_6H_4O$— (Fig. 2) lies off the Sn–Sn′ vector, producing a polymer which, like $Ph_3SnO_2CCH_3$, is of flattened helix or "S"-form, and hence plays no role in inhibiting the vibrational motion of the Mössbauer atom. The nature of the Sn · · · OH interaction in **6** thus manifests itself more clearly in perturbations of the electric field gradient about tin, and hence in the QS, rather than in the lattice dynamics of the metal atom.

## CONCLUSIONS

Of the triphenyltin arylcarboxylic acid derivatives studied, most (**1–5** and **7–11**) form four-coordinated structures about tin in both the solid and in solution. Derivatives of 2-OH and 2-Cl benzoic acids are also four-coordinate at tin in dilute solutions, but expand the coordination number to five in the solid, via intermolecular OH · · · Sn and C═O · · · Sn linkages, respectively.

These results are in general agreement with other spectroscopic studies on these and related systems[13,14,24] but in the cases of $NH_2$-2, $NMe_2$-2, OH-2 and OMe-2 benzoic acid derivatives conflict with the interpretation of X-ray crystallographic data[10,11] in which emphasis is placed upon a weakly bidentate carboxylate group and a five-coordinate geometry about tin. While cases such as these, which are at the interface of two coordination geometries, will always be subjective in their analysis, our work highlights the importance of spectroscopic methods in making these assessments. Moreover, the crystallographic data must be reviewed in terms of both distances and angles about tin *in toto* and not selectively, and our appraisal of the data under these terms reveals a far less clear-cut picture than that presented by the original authors. For example, in the case of $Ph_3SnO_2CC_6H_4NMe_2$-2, while the intramolecular Sn—O bond lengths (2.115 and 2.564 Å) suggest chelation by the carboxylate group, the angular changes are not totally in accord, viz. angles within the "equatorial" plane (which should change from 109°28′ towards 120°) are 122.1, 112.6 and 104.9°, while between the "axial" α-carbon of the phenyl ring and ligating atoms in the "equatorial" girdle about tin (which should change from 109°28′ towards 90°) the angles are 92.9, 108.4, and 114.8°. Many (but in fairness not all!) of these angular variations are simply in accord with the expected rehybridization within a tetrahedral framework, which concentrates *p*-character in the bond to the more electronegative oxygen, hence naturally closing from 109°28′ angles involving oxygen while opening those which only involve carbon. In short, interpretation of this data in terms of a coordination number of five at tin is tenuous, and underlines our recommendations for the need of ancillary spectroscopic data in such circumstances.

We are currently trying to identify those factors which influence the choice of chelated vs bridged structures in systems of this type and will report our findings in a subsequent paper.

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