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# ORGANOTIN CARBOXYLATES
# IV*. MÖSSBAUER AND INFRARED SPECTRA OF SOME TRIPHENYLTIN HALOACETATES, AND A TEST OF THE POINT-CHARGE MODEL

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## SUMMARY

Mössbauer and infrared spectroscopic techniques show that the compounds $Ph_3SnOCOR$ ($R=CH_3$, $CH_2I$, $CH_2Br$, $CH_2Cl$, $CHCl_2$, $CF_3$) are pentacoordinate polymers in the solid state with O–C–O bridges between the tin atoms. For $R=CCl_3$ a tetracoordinate monomeric species is obtained. The $^{119}Sn$ quadrupole splitting data allow a sensitive test of the predictive ability of the point-charge model, or any other additive model of quadrupole interactions.

## INTRODUCTION

In the previous papers of this series[1-3] we have been concerned primarily with two aspects of the structural and bonding characteristics of triorganotin carboxylates: (1) The conditions responsible for the occurrence of the two known solid state structural types, *i.e.* pentacoordinate polymers and tetracoordinate monomers; (2) The more subtle variations occasioned by changes in the "strength" of the parent carboxylic acid.

Numerous studies [1-9] have demonstrated that both trialkyl- and triaryltin carboxylates exist in the solid state as pentacoordinate polymers whenever steric considerations so allow. However, steric interaction between the alkyl or aryl groups bonded to tin and the "tail" of the carboxylate group can prevent such polymerization. For the triphenyltin derivatives, the change from one structural type to the other can occur with surprisingly small changes in the carboxylate group. Thus, $Ph_3SnO_2CCHMe_2$ and $Ph_3SnO_2CCH{=}CH_2$ are pentacoordinate polymers, whilst $Ph_3SnO_2CCMe_3$ and $Ph_3SnO_2CCMe{=}CH_2$ are tetracoordinate monomers in the solid state[3]. These changes in coordination number about the tin atom cause quite substantial changes in the carbonyl/carboxyl region of the infrared spectrum and in the Mössbauer quadrupole splitting (*QS*), with a small but significant change in isomer shift (*IS*)[3].

Our other main line of investigation[2] has been concerned with the differences observed in members of the series $Me_3SnO_2CCH_nX_{3-n}$ (X = halogen). All the compounds of this series appear to be polymeric solids, with bridging OCO groups, but

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* For Part III see ref. 3.

two definite trends are observed. Firstly, the carbonyl/carboxyl band separation increases monotonically with the Taft factor$\sigma^*$ for the $CH_nX_{3-n}$ function. Secondly, the $QS$ increases linearly with $\sigma^*$. A least-squares fit gives $QS=0.182\ \sigma^*+3.69$ with a standard deviation of only $2.1\times10^{-2}$.

It occurred to us that a study of the triphenyltin haloacetates might constitute a two-pronged attack encompassing both these areas of interest. In the first place such a study would enable us to make more subtle changes in the size of the $\alpha$-carbon substituents of the carboxylate group, and hopefully to define more precisely the steric requirements for polymerization. Secondly, if steric effects were *not* important in this series, we should observe the same trends in the infrared and Mössbauer spectra as shown by the trimethyltin compounds. As an added benefit, since a point-charge model[10-12] allows us to predict $QS$ values for these compounds, our results should constitute a test of the predictive value of this model for a range of compounds not previously considered.

During the course of this work, Poller and co-workers[9] have published additional confirmation of our conclusions[1,3] concerning the occurrence of polymeric and monomeric triphenyltin carboxylates. The polymeric compounds exhibited a measureable Mössbauer absorption at room temperature, whereas the monomeric ones did not. On these grounds Poller *et al.*[9] conclude that $Ph_3SnOCOCH_2Cl$ is a pentacoordinate polymer in the solid state. In the absence of steric interaction between the phenyl groups and the acid residue, there seems no reason to suppose that any of the triphenyltin haloacetates will depart from this structure.

## EXPERIMENTAL

### *Triphenyltin haloacetates*

Because some difficulties have been reported[9] (and also observed by us) in the preparation of triphenyltin derivatives of haloacetic acids, details of our procedures are given here. For some of these compounds, alternate routes have been published[9,13]

(*a*). *$Ph_3SnOCOCH_2I$.* Stoichiometric quantities of triphenyltin chloride and sodium iodoacetate were heated under reflux in methanol. The product was recrystallized from carbon tetrachloride, washed with water, suction filtered and dried *in vacuo*.

(*b*). *$Ph_3SnOCOCH_2Br$.* Triphenyltin hydroxide and bromoacetic acid (10% excess) were dissolved in ethanol and stirred at room temperature for 2 h. The solvent was removed by evaporation at room temperature and the product dried in air.

(*c*). *$Ph_3SnOCOR$ ($R=CH_2Cl$, $CHCl_2$, $CCl_3$).* Stoichiometric amounts of triphenyltin hydroxide and the appropriate acid were stirred in anhydrous methanol at room temperature for 4 h, the solvent removed under reduced pressure and the product dried *in vacuo*. In the case of the trichloroacetate derivative this procedure yielded the adduct $Ph_3SnOCOCCl_3\cdot MeOH$. Pumping on the sample for several hours failed to remove methanol. Recrystallization from carbon tetrachloride afforded pure triphenyltin trichloroacetate.

(*d*). *$Ph_3SnOCOCF_3$.* Triphenyltin hydroxide and trifluoroacetic acid (1/1 mole ratio) were dissolved in absolute ethanol, and the reaction mixture was stirred for 16 h at room temperature. The solvent was evaporated under reduced pressure, and the product further dried in air.

Analytical data (analyses by P. Borda of this Department) and melting points of all these compounds are given in Table 1.

TABLE 1

ANALYTICAL DATA AND MELTING POINTS FOR TRIPHENYLTIN HALOACETATES

| Compound | C(%) | | H(%) | | X(%) | | M.p.(°C) |
|---|---|---|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found | Calcd. | Found | |
| $Ph_3SnOCOCH_2I$ | 44.91 | 45.17 | 3.20 | 3.10 | 23.72 | 23.75 | 133–137 |
| $Ph_3SnOCOCH_2Br$ | 49.23 | 49.35 | 3.51 | 3.31 | 16.38 | 16.10 | 146–149 |
| $Ph_3SnOCOCH_2Cl$ | 54.16 | 54.38 | 3.72 | 3.66 | 7.99 | 8.21 | 154–156 |
| $Ph_3SnOCOCHCl_2$ | 50.26 | 50.08 | 3.37 | 3.20 | 14.83 | 14.60 | 174–177 |
| $Ph_3SnOCOCF_3$ | 51.84 | 51.71 | 3.24 | 3.27 | 12.31 | 12.08 | 121–123 |
| $Ph_3SnOCOCCl_3$ | 46.88 | 47.09 | 2.95 | 2.94 | 20.76 | 20.58 | 86–89 |
| $Ph_3SnOCOCCl_3 \cdot MeOH$ | 46.29 | 46.09 | 3.49 | 3.40 | 19.56 | 19.80 | 104–107 |

*Mössbauer and infrared spectra*

The Mössbauer spectrometer and attendant experimental details have been described elsewhere[3,14]. A 5mCi $BaSnO_3$ source was employed. The spectra were fitted to Lorentzian lineshapes, this being the only constraint imposed.

Infrared data were collected on a Perkin–Elmer 457 instrument. Solid state spectra were obtained using Nujol or halocarbon oil mulls between CsI plates. Solution spectra were run in carbon tetrachloride with matched KBr cells.

## RESULTS AND DISCUSSION

Poller *et al.*[9] have prepared triphenyltin chloroacetate by refluxing triphenyltin hydroxide and the acid in anhydrous benzene, and removing the solvent under reduced pressure. Their attempts to make the corresponding trichloro- and trifluoroacetate (and pivalate) by this route produced instead the phenylstannonic carboxylates $PhSn(O)OCOCX_3$ ($X = F, Cl, CH_3$). These authors[9] postulate a two-step mechanism involving phenyl–tin bond cleavage followed by hydrolysis of the intervening phenyltin tricarboxylate.

$$Ph_3SnOCOR + 2\,RCOOH \rightarrow PhSn(OCOR)_3 + 2\,C_6H_6$$

$$PhSn(OCOR)_3 + H_2O \rightarrow PhSn(O)OCOR + 2\,RCOOH$$

We have also found that reaction of triphenyltin hydroxide with strong carboxylic acids can lead to the phenylstannonic derivatives (identified by analysis and their characteristic IR and Mössbauer spectra[1]). Full details will be published in due course, but we should mention that the reactions appear to be sensitive to both temperature and solvent. Procedures involving heating of the reaction mixture tend to favour phenyl–tin bond cleavage, as does carrying out the reaction in a non-coordinating solvent such as benzene or carbon tetrachloride. Such bond cleavage appears to be inhibited if either methanol or ethanol is employed as solvent and the reaction proceeds at ambient temperature. Thus, $Ph_3SnOCOCF_3$ is obtained from the reaction of triphenyltin hydroxide and trifluoroacetic acid in absolute ethanol at 25°. The trichloroacetate derivative is isolated from a methanolic reaction mixture as the adduct, $Ph_3SnOCOCCl_3 \cdot MeOH$, whence it can be obtained in pure form by recrystallization from carbon tetrachloride. Pure $Ph_3SnOCOCCl_3$, like the corresponding pivalate, is tetracoordinate in the solid state, whereas $Ph_3SnOCOCF_3$ is pentacoordinate (*vide infra*). Thus it appears that a coordinating solvent tends to stabilize the $Ph_3Sn$ moiety, presumably through formation of a pentacoordinate species, and that a tetracoordinate intermediate is more vulnerable to attack by the acid and resultant phenyl–tin cleavage.

Mössbauer isomer shifts, quadrupole splittings and linewidths for the triphenyltin derivatives are given in Table 2, and infrared data in Table 3.

TABLE 2

MÖSSBAUER ISOMER SHIFTS QUADRUPOLE SPLITTINGS AND LINEWIDTHS FOR TRIPHENYLTIN HALOACETATES AT 80°K

| Compound | $IS^{a,b}$ (mm/s) | $QS_{obs}^{a}$ (mm/s) | $QS_{pred}^{c}$ (mm/s) | $\Gamma_1^{d}$ (mm/s) | $\Gamma_2^{d}$ (mm/s) |
|---|---|---|---|---|---|
| $Ph_3SnOCOH_3$ | 1.28 | 3.36 | 3.35 | 0.77 | 0.77 |
| | $1.26^e$ | $3.34^e$ | | $0.75^e$ | $0.80^e$ |
| $Ph_3SnOCOCH_2I$ | 1.31 | 3.59 | 3.52 | 0.71 | 0.75 |
| $Ph_3SnOCOCH_2Br$ | 1.32 | 3.51 | 3.56 | 0.90 | 0.96 |
| $Ph_3SnOCOCH_2Cl$ | 1.32 | 3.53 | 3.56 | 1.00 | 1.00 |
| | $1.30^e$ | $3.46^e$ | | $0.75^e$ | $0.80^e$ |
| $Ph_3SnOCOCHCl_2$ | 1.35 | 3.81 | 3.76 | 0.97 | 0.92 |
| $Ph_3SnOCOCF_3$ | 1.40 | 4.00 | 3.88 | 0.92 | 0.97 |
| $Ph_3SnOCOCCl_3$ | 1.30 | 2.97 | 3.84 | 0.87 | 1.04 |
| $Ph_3SnOCOCCl_3 \cdot MeOH$ | 1.33 | 3.50 | | 0.87 | 0.94 |

[a] ±0.03 mm/s. [b] Relative to $SnO_2$. [c] Calculated from eqn. (8) as described in the text. [d] ±0.05 mm/s. [e] Ref. 9.

TABLE 3

CARBON–OXYGEN STRETCHING FREQUENCIES IN TRIPHENYLTIN HALOACETATES ($cm^{-1}$)

| Compound | Solid state | | $CCl_4$ solution | |
|---|---|---|---|---|
| | $\nu_a$(OCO) | $\nu_s$(OCO) | $\nu$(C=O) | $\nu$(C–O) |
| $Ph_3SnOCOCH_3$ | 1548 | 1420 | 1640 | 1370 |
| $Ph_3SnOCOCH_2I$ | 1548 | 1380 | 1650 | 1324 |
| $Ph_3SnOCOCH_2Br$ | 1568 | 1409 | 1686 | 1353 |
| $Ph_3SnOCOCH_2Cl$ | 1576 | 1411 | 1662 | 1345 |
| $Ph_3SnOCOCHCl_2$ | 1595 | 1402 | 1683 | 1330 |
| $Ph_3SnOCOCF_3$ | 1650 | 1447 | 1722 | 1400 |
| $Ph_3SnOCOCCl_3$ | 1700 | 1305 | 1700 | 1292 |
| $Ph_3SnOCOCCl_3 \cdot MeOH$ | 1665 | 1334 | 1702 | 1294 |

Except in the case of $Ph_3SnOCOCCl_3$, both the *QS* and solid state OCO stretching frequencies show qualitatively the anticipated trends, *i.e.*, an increase in *QS* and OCO band separation with increasing strength of the parent acid. The *QS* values are typical of those usually associated with oxygen-bridged triorganotin polymers[1-3,9,12,15]. There is also a quite substantial shift in OCO frequencies between solid state and dilute solution (~5% w/v) which can be attributed[1-4,16] to a polymer-monor transition on dissolution. These observations allow us to conclude that (except for the trichloroacetate) the triphenyltin haloacetates are isostructural with the homologous trimethyltin compounds.

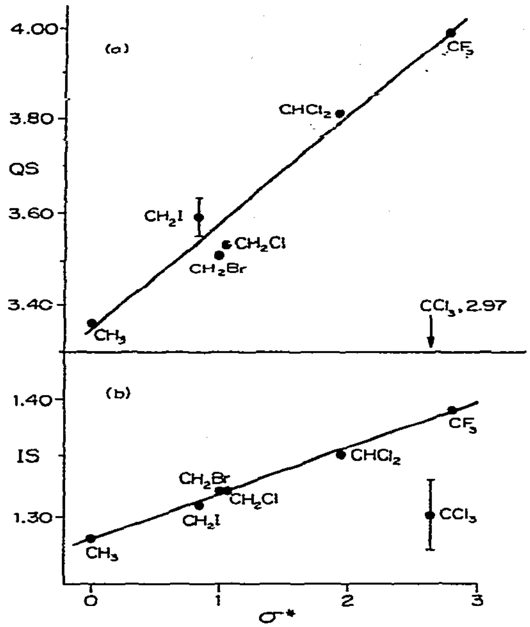

Fig. 1. Dependence of (a) quadrupole splittings (*QS*) and (b) isomer shift (*IS*) on Taft inductive factor $\sigma^*$ of the R′ group[21] for triphenyltin haloacetates, $Ph_3SnOCOR'$. The R′ groups are indicated on the figure.

As shown in Fig. 1, a plot of *QS* against $\sigma^*$ is linear, a least squares treatment (omitting the trichloroacetate) giving $QS = 0.231\ \sigma^* + 3.34$ mm/s, with a standard deviation of $4.5 \times 10^{-2}$. For the trimethyltin derivatives we suggested[2] that this trend arose from an increasing asymmetry of the two Sn–O bonds with increasing $\sigma^*$ of the haloacetate group, and that the $Me_3Sn$ fragment should remain virtually unaffected. Preliminary X-ray structural data[17] for $Me_3SnOCOCH_3$ and $Me_3SnOCOCF_3$ seem to support this suggestion. In the acetate the two Sn–O distances are 2.20 and 2.39 Å, while in the trifluoroacetate the corresponding bond lengths are 2.18 and 2.48 Å. The average Sn–C distance is 2.13 Å in both compounds.

Both infrared and Mössbauer data indicate a different type of structure for $Ph_3SnOCOCCl_3$. The carbonyl/carboxyl bands are almost identical for the solid and and dilute solution, and the *QS* is far below the value (~3.9 mm/s) anticipated for a pentacoordinated structure. These data are consistent[1-3] with a monomeric, tetracoordinated species in the solid state, although the *QS* is somewhat larger than those found for non-halogenated monomeric triphenyltin carboxylates (*e.g.*, for $Ph_3SnOCOCMe_3$, $QS = 2.40$ mm/s)[3]. This is in line with the general trends observed in the pentacoordinated species, where the *QS* for $Ph_3SnOCOCHCl_2$ (3.81 mm/s) is significantly greater than that for $Ph_3SnOCOCHMe_2$ (3.32 mm/s)[3].

Platt[18] has discussed recently the magnitude of the *QS* to be expected for tetracoordinated tin compounds, and has suggested that such derivatives will generally not show *QS* values greater than ~2.8 mm/s. In view of the present results it may be necessary to revise this limit upwards. For $Ph_3SnOCOCCl_3$, the virtual identity of the OCO band positions in the solid and in dilute solution imply little, if any, intermolecular association in the solid state.

A further indication of the monomeric nature of $Ph_3SnOCOCCl_3$ is the observation that a stable 1/1 adduct, $Ph_3SnOCOCCl_3 \cdot MeOH$ is initially isolated from the methanolic reaction mixture. This compound has a *QS* of 3.50 mm/s (Table 2), consistent with a pentacoordinate structure. The solid state IR results also suggest that only one of the carboxylate oxygens is bonded to tin, and as expected, the OCO bands in $CCl_4$ solution are closely similar to those of the neat trichloroacetate. No such adducts were isolated for other members of the series; indeed, a number of these were prepared in methanolic solution, wherefrom the compounds were obtained in pure form.

It is interesting that the isomer shift data for these compounds also appear to increase linearly with the Taft factor for the $CH_{3-n}X_n$ group (Fig. 1), the sole exception again being the trichloroacetate derivative. It should be noted, however, that the difference in *IS* between the first and last members of the series is less than twice the sum of the estimated errors of the measurements, so we do not wish to place undue emphasis on this apparent trend. Indeed, for the corresponding trimethyltin compounds[2] there was no discernable influence of $\sigma^*$ upon *IS*, the standard deviation of a least-squares fit being significantly greater than the spread of values about the median. If the present trend is not fortuitous, it presumably arises from an increasing withdrawal of *p*-electron density into the bonding orbital directed towards the carboxylate oxygens ($p_z$) as the electronegativity of the $CH_{3-n}X_n$ group increases. This would tend to deshield the *s*-electron density at the tin nucleus, raising the *IS*. However, it is clear that at best such an effect is very small.

### POINT-CHARGE PREDICTIONS

The *QS* is given by

$$QS = \tfrac{1}{2}eQ \cdot V_{zz} \cdot (1+\eta^2/3)^{\frac{1}{2}}, \tag{1}$$

where $eQ$ is the nuclear quadrupole moment, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and the $V_{ii}$ are the diagonal *efg* tensor elements, conventionally chosen such that $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$. In the point-charge model, the ligands L are treated as localised concentrations of electronic charge $q_L$ situated at a distance $r_L$ from the central metal atom. The contribution [L] of a particular ligand to the *efg* is given by[10,11,19]:

$$[L] = < q_L \cdot r_L^{-3} > \tag{2}$$

For a molecule of the type $R_3SnX_2$ having $D_{3h}$ symmetry, one readily obtains[11,12]:

$$QS = 4[X] - 3[R], \tag{3}$$

where we have redefined the parameters [L] to incorporate the factor $eQ/2$. Results for a number of other structural types have also been published[11,12,19]. We shall refer to the [L] as partial quadrupole splitting (*PQS*) parameters[20].

Very recently, Parish and Platt[11b] have estimated $PQS$ values for a number of substituents. Starting from the $SnCl_5^-$ ion, for which $QS=[Cl]$, they were able to obtain [R] and [X] (R = alkyl, aryl; X = F, Br, I) from data on alkyl- and aryltin halide compounds. The value for [Me] so found and our data for the trimethyltin haloacetates[2], would allow us to derive $PQS$ values for the various haloacetate groups, which could then be used to predict $QS$ values for the triphenyltin derivatives. However, such a procedure is not really necessary. For any series of compounds $R_3Sn(X_i)_2$ of $D_{3h}$ symmetry, we have

$$(QS)_i = 4[X_i] - 3[R], \tag{4}$$

and for an isostructural homologous series $R'_3Sn(X_i)_2$,

$$(QS)'_i = 4[X_i] - 3[R'] = (QS)_i + 3([R] - [R']) \tag{5}$$

Thus, only a knowledge of the *difference* [R] − [R′] is required in the computation. The actual values of [R], [R′] and $[X_i]$ are quite immaterial here, and the inclusion of an additive scaling factor would not affect ones predictions.

Furthermore, let us suppose that a given series of compounds yields $QS$ values which show a linear dependence upon some physical variable $\zeta$ (which might be Taft factor, group electronegativity, p*Ka*, etc.), *i.e.*, $QS = m\cdot\zeta + b$. Then it follows as a corollary to eqn. (5) that for any isostructural homologous series, $(QS)' = m\cdot\zeta + b'$. Thus series should yield parallel straight lines.

Although our discussion has been couched in terms of a point-charge formalism, the conclusions apply equally to any theoretical model of quadrupole interactions containing the assumption of additivity or transferable equivalents of charge, that is, to any model which enables one to calculate $PQS$ values.

The $PQS$ values of Parish and Platt[11b] for Me and Ph, together with our data for the trimethyltin haloacetates[2] yields the predicted $QS$ values for the phenyl derivatives shown in the fourth column of Table 2. For the pentacoordinate compounds, agreement between calculated and observed values appears to be quite satisfactory. Thus, although we may not have employed the "correct" values of [Me] and [Ph] for the compounds under study, at least their difference is approximately correct.

However, a much more stringent test of the additivity assumption can be made by comparing predicted and observed gradients of the $QS$ *vs.* $\sigma^*$ correlation for the phenyltin compounds:

Predicted: $QS = 0.182\,\sigma^* + 3.36$

Observed: $QS = 0.231\,\sigma^* + 3.34$

We see that the observed gradient is some 20% greater than that predicted. Presumably, this reflects the inadequacy of the assumption that the $PQS$ value for a given ligand is totally independent of the nature of the other ligands attached to the central metal atom. More surprising, perhaps, than the discrepancy itself is the fact that the gradient for the phenyl derivatives is greater than that for the methyl homologs. Owing to the somewhat smaller electronegativity difference between X and R for the phenyl compounds, we might have expected the phenyl groups to have a slight "levelling" effect and to diminish the dependence of $QS$ upon $\sigma^*$. Such appears not to be the case.

In conclusion, it seems that an additive model of quadrupole interactions is capable of fair predictive accuracy when applied to homologous series as was done here. On the other hand, high precision for such a model should not be expected.

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