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Discrete, Dimeric, and Polymeric Structures of Triphenyltin Esters of Chlorobenzoic Acids[1,2]

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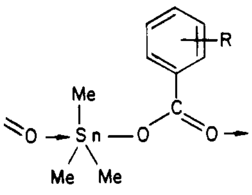
Received November 7, 1985

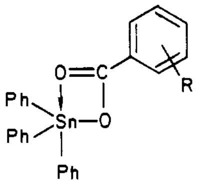
Reaction of bis(triphenyltin) oxide with *o*- and *p*-chlorobenzoic acids leads to the formation of the respective esters $Ph_3Sn(p\text{-}ClC_6H_4CO_2)$ (**1**) and $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (**2**). The hydrated etherate of **2**, $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2\cdot H_2O\cdot Et_2O$ (**3**), also is formed. X-ray crystallographic analysis reveals that **1** exists as a discrete, intramolecularly five-coordinated entity best described as a distorted tetrahedron with oxygen atoms bridging cis positions, whereas **2** has a one-dimensional polymeric formulation containing tin in a trigonal bipyramid with the axial positions occupied by oxygen atoms. The conformation around tin in **3** is similar to that in **2**, but a dimeric composition resulted, giving an end-stopped, hydrogen-bonded hydrate. Esters **2** and **3** are the first examples containing triphenyltin with oxygen donor ligands in this geometrical form. The variations in observed geometrical form in the solid state among **1**–**3** are attributed to steric and electronic effects of the *o*-chloro group in **2** and **3** tending to equalize the carboxyl group carbon–oxygen double-bond character. This results in more nearly equal oxygen–tin bond properties that favor the trans oxygen coordination found in the structures of **2** and **3**. Compound **1** crystallizes in the monoclinic space group $C2/c$ ($Z = 8$) with $a = 16.995$ (4) Å, $b = 11.403$ (4) Å, $c = 24.343$ (8) Å, and $\beta = 103.10$ (2)°. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$) with $a = 9.190$ (2) Å, $b = 11.407$ (4) Å, $c = 21.088$ (3) Å, and $\beta = 101.87$ (1)°. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$) with $a = 12.826$ (5) Å, $b = 17.759$ (3) Å, $c = 22.812$ (6) Å, and $\beta = 105.63$ (2) Å. The final conventional unweighted residuals were 0.035 (**1**), 0.032 (**2**), and 0.037 (**3**).

Introduction

Trimethyltin benzoates assume one-dimensional associated arrangements containing five-coordinated tin atoms, A.[3] In contrast, triphenyltin benzoates generally exist in a discrete five-coordinated form, B.[4,5] A delicate energy balance is present between these two forms although the greater electronegativity of the phenyl group over the methyl group has been cited[5] as a factor influencing the formation of the discrete form, as it gives the phenyl group greater access to an axial position of a trigonal bipyramid. Trimethyltin glycinate $Me_3Sn(O_2CCH_2NH_2)$ has the chain structure,[6] A, but the axial positions are occupied by only one of the carboxylate oxygen atoms and the less electronegative nitrogen atom. Hydrogen bonding, which enhances the donor property of the nitrogen atom at the expense of oxygen, probably accounts for the change in donor-atom coordination.[5]



A



B

The understanding of the interplay among various factors responsible for the preferential appearance of one of the five-coordinated representations, A and B, is important in assessing the biochemical action[7-10] of triorganotin derivatives. In this study, we report the reaction of triphenyltin oxide with chloro-substituted benzoic acids. The structures of the resultant esters were determined by X-ray crystallography. Structures in solution were assessed by infrared and ^{119}Sn NMR measurements. The new compounds isolated are $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (**2**) and $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2\cdot H_2O\cdot Et_2O$ (**3**). Observed changes in geometry between forms A and B are interpreted in terms of both hydrogen-bonding influences and the electron-withdrawing effect of the ring chlorine atom.

Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer Model R12A spectrometer at 60 MHz. Chemical shifts were measured in ppm relative to tetramethylsilane. Tin-119 NMR spectra were recorded on a Varian 300-MHz instrument operating at 111.862 MHz. Deuteriochloroform was used for the lock, with chemical shifts referenced to tetramethyltin. Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer using KBr cells. Solid spectra were recorded in Nujol and solution spectra in chloroform. Infrared and NMR concentrations were in the range of 2–5 wt %.

The preparation of the *p*-chloro derivative **1** follows the same procedure as that described below for the *o*-chloro derivative, **2**. This differs from the previous preparation of **1**, which used triphenyltin hydroxide as a starting material.[11] The melting point for **1** is 132–134 °C (lit.[11] mp 131–135 °C). ^1H NMR ($CDCl_3$): δ 8.06 (d), 7.80 (m), 7.47 (m), 7.40 (d). IR: solid (Nujol), 1630 cm^{-1} (ν_{COO}); solution ($CHCl_3$), 1630 cm^{-1} (ν_{COO}).

Preparation of (*o*-Chlorobenzoato)triphenyltin, $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (2). Bis(triphenyltin) oxide (1.01 g, 1.41 mmol) was dissolved in dry benzene (150 mL), and *o*-chlorobenzoic acid (2.81 mmol) was added to it. The reaction mixture was heated under reflux for 4 h, with a Dean–Stark evaporator used to distill off water azeotropically. Removal of benzene from the reaction mixture under vacuum yielded an oil, which was dissolved in a chlorobenzene/hexane mixture (1:1) and cooled, affording colorless crystals of **2**: mp 79–82 °C; yield 70%. ^1H NMR: centers of multiplets at 8.0 and 7.6 ppm. ^{119}Sn NMR ($CDCl_3/Me_4Sn$): δ −107.9. IR: solid (Nujol), 1570 cm^{-1} (ν_{COO}); solution ($CHCl_3$), 1630 cm^{-1} (ν_{COO}). Anal. Calcd for $C_{25}H_{19}O_2ClSn$: C, 59.39; H, 3.79. Found: C, 59.62; H, 3.90.

Recrystallization of the *o*-chloro derivative in a slightly wet ether/hexane mixture yielded crystals of $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2\cdot H_2O\cdot Et_2O$ (**3**); mp 96–98 °C.

Crystallography. All X-ray crystallographic studies were performed with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) =$

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[1] Pentacoordinated Molecules. 65. Previous paper in the series: Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 607.

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Table I. Atomic Coordinates in Crystalline $Ph_3Sn(p\text{-}ClC_6H_4CO_2)$ (**1**)[a]

atom type[b]	coordinates 10^4x	10^4y	10^4z
Sn	627.6 (2)	4447.8 (3)	3925.7 (2)
Cl	4096 (1)	5325 (2)	7095 (1)
O1	1373 (2)	4382 (3)	4714 (2)
O2	1957 (3)	5919 (4)	4436 (2)
C1	1917 (3)	5209 (5)	4802 (3)
C2	2460 (3)	5231 (5)	5369 (2)
C3	2382 (3)	4392 (5)	5772 (2)
C4	2883 (4)	4433 (6)	6308 (3)
C5	3456 (4)	5298 (6)	6429 (3)
C6	3551 (4)	6145 (6)	6036 (3)
C7	3045 (3)	6097 (5)	5501 (3)
CA1	−86 (3)	2977 (5)	4038 (2)
CA2	−887 (3)	3120 (5)	4048 (2)
CA3	−1350 (4)	2174 (6)	4139 (3)
CA4	−1026 (4)	1089 (7)	4214 (4)
CA5	−217 (5)	920 (6)	4222 (4)
CA6	255 (4)	1856 (6)	4130 (3)
CB1	1261 (3)	4155 (7)	3272 (2)
CB2	1059 (4)	3192 (6)	2930 (3)
CB3	1435 (5)	3014 (7)	2480 (3)
CB4	2015 (4)	3808 (8)	2393 (3)
CB5	2209 (4)	4758 (8)	2730 (3)
CB6	1838 (4)	4947 (7)	3178 (3)
CC1	−70 (3)	6001 (5)	3844 (2)
CC2	−500 (4)	6308 (6)	3304 (3)
CC3	−998 (5)	7303 (7)	3237 (3)
CC4	−1080 (5)	7950 (6)	3693 (4)
CC5	−658 (5)	7645 (6)	4228 (3)
CC6	−147 (4)	6668 (6)	4303 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

0.71359 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[12]

Crystals were mounted inside thin-walled glass capillaries, which were sealed. For **1** and **2** this procedure was precautionary. For **3**, it was necessary since the crystals, which are deliquescent, degrade rapidly under ambient conditions.

Data were collected by using the θ–2θ scan mode for $2° \leq 2\theta_{MoK\alpha} \leq 43°$ for **1** and **3** and $2° \leq 2\theta_{MoK\alpha} \leq 50°$ for **2**. No corrections were made for absorption. The structures were solved by using a combination of Patterson and difference-Fourier techniques and were refined by using full-matrix least-squares technique.[13]

X-ray Crystallographic Studies for $Ph_3Sn(p\text{-}ClC_6H_4CO_2)$ (1). Crystals of **1** grown from benzene solution are colorless rhombohedrons. The crystal used for data collection had dimensions of 0.23 × 0.28 × 0.35 mm.

Crystal Data: $C_{25}H_{19}O_2SnCl$ (**1**), monoclinic space group $C2/c$ [C_{2h}^6–No. 15],[14] $a = 16.995$ (4) Å, $b = 11.403$ (4) Å, $c = 24.343$ (8) Å, $\beta = 103.10$ (2)°, $Z = 8$, $\mu_{MoK\alpha} = 1.253$ mm^{-1}. A total of 2634 independent reflections ($+h,+k,\pm l$) were measured.

The 29 independent non-hydrogen atoms were refined anisotropically, while the 19 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement factors[15] were $R = 0.035$ and $R_W = 0.046$ for the 2135 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (2). Crystals of **2** grown from chlorobenzene are colorless rhombohedrons. The crystal used for data collection had dimensions of 0.25 × 0.25 × 0.25 mm.

Table II. Selected Bond Lengths (Å) and Angles (deg) in $Ph_3Sn(p\text{-}ClC_6H_4CO_2)$ (**1**)[a]

type[b]	length	type	length
Sn–O1	2.048 (4)	Sn–CC1	2.115 (6)
Sn–O2	2.861 (4)	O1–C1	1.304 (7)
Sn–CA1	2.123 (5)	O2–C1	1.216 (7)
Sn–CB1	2.139 (6)	C1–C2	1.477 (8)
type	**angle**	**type**	**angle**
O1–Sn–O2	49.8 (1)	O1–C1–O2	121.1 (6)
O1–Sn–CA1	95.7 (2)	O1–C1–C2	115.7 (5)
O1–Sn–CB1	112.5 (2)	O2–C1–C2	123.2 (5)
O1–Sn–CC1	109.4 (2)	C1–C2–C3	120.4 (5)
O2–Sn–CA1	145.6 (2)	C1–C2–C7	119.4 (5)
O2–Sn–CB1	86.2 (2)	Sn–CA1–CA2	120.3 (4)
O2–Sn–CC1	85.4 (2)	Sn–CA1–CA6	121.0 (4)
CA1–Sn–CB1	111.8 (2)	Sn–CB1–CB2	118.5 (4)
CA1–Sn–CC1	110.5 (2)	Sn–CB1–CB6	121.0 (5)
CB1–Sn–CC1	115.3 (2)	Sn–CC1–CC2	117.4 (5)
Sn–O1–C1	113.0 (4)	Sn–CC1–CC6	122.7 (4)
Sn–O2–C1	76.1 (4)		

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

Table III. Atomic Coordinates in Crystalline $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (**2**)[a]

atom type[b]	coordinates 10^4x	10^4y	10^4z
Sn	2012.1 (3)	2143.2 (2)	2625.1 (1)
Cl	2156 (1)	199 (1)	4380 (1)
O1	897 (3)	575 (2)	2903 (1)
O2	1858 (3)	−1053 (2)	2579 (1)
C1	1161 (4)	−510 (3)	2937 (2)
C2	517 (4)	−1157 (3)	3439 (2)
C3	877 (5)	−893 (4)	4095 (2)
C4	258 (6)	−1488 (5)	4545 (3)
C5	−812 (7)	−2337 (6)	4331 (3)
C6	−1243 (6)	−2599 (5)	3678 (4)
C7	−558 (6)	−2023 (4)	3226 (3)
CA1	865 (4)	2003 (3)	1637 (2)
CA2	648 (5)	2979 (4)	1235 (2)
CA3	−92 (6)	2868 (5)	594 (3)
CA4	−624 (6)	1786 (6)	354 (2)
CA5	−445 (6)	825 (5)	749 (2)
CA6	291 (5)	933 (4)	1389 (2)
CB1	969 (5)	3112 (3)	3274 (2)
CB2	1705 (5)	3961 (4)	3680 (2)
CB3	985 (7)	4583 (5)	4096 (2)
CB4	−469 (8)	4367 (5)	4099 (3)
CB5	−1223 (7)	3523 (6)	3704 (4)
CB6	−512 (6)	2892 (4)	3288 (3)
CC1	4164 (4)	1471 (4)	3044 (2)
CC2	4947 (5)	738 (4)	2708 (2)
CC3	6315 (6)	291 (4)	3005 (3)
CC4	6905 (5)	557 (5)	3649 (3)
CC5	6143 (5)	1265 (5)	3982 (2)
CC6	4771 (5)	1736 (5)	3681 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Crystal Data: $C_{25}H_{19}O_2SnCl$ (**2**), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^5–No. 14][16]), $a = 9.190$ (2) Å, $b = 11.407$ (4) Å, $c = 21.088$ (3) Å, $\beta = 101.87$ (1)°, $Z = 4$, $\mu_{MoK\alpha} = 1.330$ mm^{-1}. A total of 3791 independent reflections ($+h,+k,\pm l$) were measured. The structure was refined in the same manner as was described for **1**. The final agreement factors[15] were $R = 0.032$ and $R_W = 0.044$ for the 3145 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2\cdot H_2O\cdot Et_2O$ (3). Crystals grown from Et_2O/hexane are colorless, deliquescent laths. A fragment cut to dimensions of 0.28 × 0.30 × 0.38 mm was used for data collection.

Crystal Data: $(C_{25}H_{19}O_2SnCl)_2\cdot H_2O\cdot C_4H_{10}O$ (**3**), monoclinic space group $P2_1/c$ [C_{2h}^5–No. 14],[16] $a = 12.826$ (5) Å, $b = 17.759$ (3) Å, $c = 22.812$ (6) Å, $\beta = 105.63$ (2)°, $Z = 4$, $\mu_{MoK\alpha} = 1.166$ mm^{-1}. A total of 5713 independent reflections ($+h,+k,\pm l$) were measured. The 64 independent non-hydrogen atoms were refined anisotropically. Thirty phenyl hydrogen atoms were treated in the same manner as described for **1**. Coordinates for the hydrogen atoms of the water molecule were obtained from a difference-Fourier synthesis. These coordinates were refined in

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(12) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(13) The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98. For real and imaginary dispersion corrections for Sn, Cl, and O, see: *Ibid.*; pp 149–150.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 101.

(15) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

(16) Reference 14; p 99.

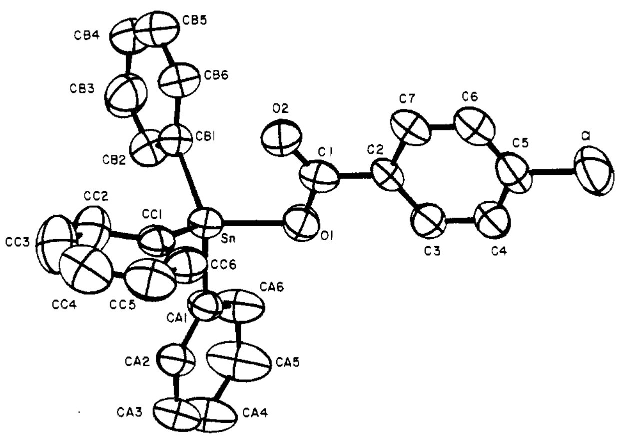


Figure 1. ORTEP plot of $Ph_3Sn(p\text{-}ClC_6H_4CO_2)$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

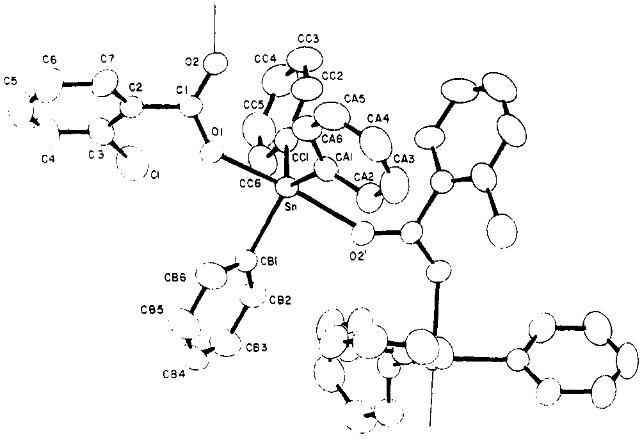


Figure 2. ORTEP plot of $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (**2**) with thermal ellipsoids at the 50% probability level. A 2_1 screw-related molecule is shown (primed atoms symmetry-transformed by $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$) to illustrate the full coordination of the Sn atom. Hydrogen atoms are omitted for purposes of clarity.

combination with fixed isotropic thermal parameters. The remaining hydrogen atoms were omitted from the refinement. The final agreement factors[15] were $R = 0.037$ and $R_W = 0.058$ for the 4719 reflections having $I \geq 2\sigma_I$.

Results

The atom-labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I, while selected bond lengths and angles are given in Table II. The corresponding material for **2** is given in Figure 2 and in Tables III and IV, while the corresponding material for **3** is given in Figure 3 and in Tables V and VI. Anisotropic thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from least-squares mean planes are provided as supplementary material.

Discussion

The triphenyltin ester of *p*-chlorobenzoic acid **1** exists in the solid state in the discrete, intramolecularly coordinated structure B (see Introduction), having oxygen atoms coordinated cis to one another, similar to the structures found for previous examples of triphenyltin derivatives.[4,5] Surprisingly, the X-ray analyses of the triphenyltin esters of *o*-chlorobenzoic acid (**2** and **3**) show that they reside in the geometrical form A, possessing trans axial coordination of oxygen ligands, the first examples of oxygen-containing triphenyltin esters in this structural form. The ^{119}Sn Mössbauer data presented in the accompanying paper for **1**–**3**[3a] are entirely consistent with the structures obtained here from X-ray analysis.

Table IV. Selected Bond Lengths (Å) and Angles (deg) in $Ph_3Sn(o\text{-}ClC_6H_4CO_2)$ (**2**)[a]

type[b]	length	type	length
Sn–O1	2.201 (3)	Sn–CC1	2.136 (4)
Sn→O2′	2.384 (3)	O1–C1	1.261 (4)
Sn→O2	3.649 (3)	O2–C1	1.250 (4)
Sn–CA1	2.138 (4)	C1–C2	1.506 (5)
Sn–CB1	2.134 (4)	C3–Cl	1.734 (5)
type	**angle**	**type**	**angle**
O1–Sn–O2′	173.76 (9)	Sn–O1–C1	135.9 (3)
O1–Sn–CA1	92.0 (1)	Sn–O2–C1	60.8 (2)
O1–Sn–CB1	87.4 (1)	O1–C1–O2	124.6 (4)
O1–Sn–CC1	92.3 (1)	O1–C1–C2	115.0 (3)
O2′–Sn–CA1	92.0 (1)	O2–C1–C2	120.4 (3)
O2′–Sn–CB1	86.5 (1)	C1–C2–C3	123.1 (4)
O2′–Sn–CC1	89.1 (1)	C1–C2–C7	118.2 (4)
CA1–Sn–CB1	117.8 (1)	C2–C3–Cl	120.5 (3)
CA1–Sn–CC1	127.2 (1)	C4–C3–Cl	117.4 (3)
CB1–Sn–CC1	114.8 (2)	Sn–CA1–CA2	121.0 (3)
O2–Sn–O1	34.6 (1)	Sn–CA1–CA6	120.4 (3)
O2–Sn–O2′	150.88 (4)	Sn–CB1–CB2	122.4 (3)
O2–Sn–CA1	83.7 (1)	Sn–CB1–CB6	119.4 (3)
O2–Sn–CB1	71.3 (1)	Sn–CC1–CC2	122.6 (3)
O2–Sn–CC1	120.9 (1)	Sn–CC1–CC6	118.6 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

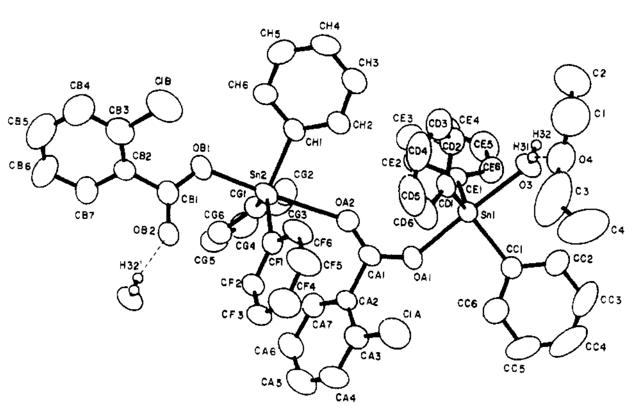
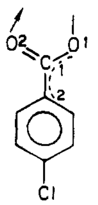
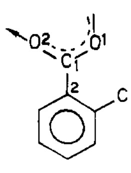


Figure 3. ORTEP plot of $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2{\cdot}H_2O{\cdot}Et_2O$, *3*, with thermal ellipsoids at the 50% probability level. A translationally related (primed atoms symmetry-transformed by $1 - x, y, z$) water molecule is included to illustrate the hydrogen bonding. The remaining hydrogen atoms are omitted for purposes of clarity.

As detailed in the following section, the presence of chlorine in the ortho position induces nonplanarity within the benzoate group between the CO_2 unit and the attached phenyl group. Consistent with relative bond lengths in **1** and **2**, this steric interaction, between the *o*-chlorine atom in **2** and the neighboring O1 atom of the carboxyl group, appears partly responsible for the near equality in the C–O bond lengths of the carboxyl group. This may be caused by a different electronic structure in **1** with respect to **2**, illustrated as a change from C to D, i.e. the above-mentioned nonplanarity in D causing a reduction in the C1–C2 bond order compared to that of C. The C1–C2 bond length in **1** is 1.477 Å. In **2** and **3**, this distance increases to 1.506 and 1.509 Å, respectively.



C



D

However, the ortho steric effect is not the sole factor influencing the formation of the polymeric form A. In this regard the benzoate ester $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ has the discrete structural form B.[4] Here, appreciable nonplanarity resides in the benzoate portion

Table V. Atomic Coordination in Crystalline $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2\cdot H_2O\cdot Et_2O$ (**3**)[a]

atom type[b]	coordinates			atom type[b]	coordinates		
	10^4x	10^4y	10^4z		10^4x	10^4y	10^4z
Sn1	4304.7 (4)	1020.7 (3)	2456.7 (2)	CD5	2931 (7)	3166 (6)	2873 (5)
Sn2	−557.1 (4)	1413.0 (3)	1371.1 (2)	CD6	3223 (6)	2402 (5)	2861 (4)
ClA	2261 (2)	973 (2)	3858 (1)	CE1	4125 (5)	419 (4)	1631 (3)
ClB	−2903 (2)	3393 (1)	443 (1)	CE2	3157 (6)	404 (4)	1180 (3)
OA1	2873 (3)	582 (3)	2667 (2)	CE3	3080 (7)	8 (5)	637 (3)
OA2	1381 (4)	915 (3)	1954 (2)	CE4	3940 (8)	−356 (5)	541 (4)
O3	5886 (4)	1533 (3)	2299 (3)	CE5	4893 (7)	−363 (4)	980 (4)
OB1	−2097 (4)	1846 (3)	860 (2)	CE6	5003 (6)	22 (4)	1526 (3)
OB2	−3027 (4)	1331 (3)	1450 (2)	CF1	−533 (5)	1753 (4)	2269 (3)
CA1	1841 (5)	618 (4)	2443 (3)	CF2	−1086 (6)	1369 (4)	2629 (3)
CA2	1191 (5)	226 (4)	2817 (3)	CF3	−1000 (6)	1624 (5)	3214 (3)
CA3	1343 (6)	323 (4)	3444 (3)	CF4	−366 (8)	2255 (6)	3435 (4)
CA4	723 (7)	−63 (5)	3763 (4)	CF5	181 (8)	2625 (6)	3084 (4)
CA5	−60 (8)	−578 (6)	3445 (5)	CF6	112 (7)	2363 (5)	2501 (4)
CA6	−236 (6)	−671 (5)	2826 (4)	CG1	−821 (5)	291 (4)	1035 (3)
CA7	384 (6)	−277 (4)	2509 (4)	CG2	−58 (6)	−55 (5)	803 (3)
CB1	−2970 (5)	1750 (4)	1023 (3)	CG3	−211 (7)	−805 (5)	576 (4)
CB2	−3974 (5)	2115 (4)	636 (3)	CG4	−1119 (7)	−1196 (4)	591 (4)
CB3	−4024 (7)	2803 (5)	341 (4)	CG5	−1875 (7)	−853 (4)	825 (3)
CB4	−4990 (9)	3097 (6)	−48 (4)	CG6	−1737 (6)	−122 (4)	1053 (3)
CB5	−5940 (9)	2648 (6)	−112 (4)	CH1	235 (5)	2159 (4)	893 (3)
CB6	−5925 (7)	1983 (6)	208 (4)	CH2	1321 (6)	2316 (5)	1073 (3)
CB7	−4940 (6)	1713 (4)	573 (3)	CH3	1781 (7)	2830 (5)	754 (4)
CC1	5269 (5)	517 (4)	3269 (3)	CH4	1154 (7)	3203 (5)	257 (4)
CC2	6398 (7)	526 (5)	3428 (4)	CH5	68 (7)	3067 (5)	83 (4)
CC3	7008 (8)	196 (6)	3958 (5)	CH6	−397 (6)	2549 (5)	393 (3)
CC4	6510 (10)	−153 (6)	4343 (4)	O4	6674 (5)	2840 (4)	2916 (3)
CC5	5401 (9)	−192 (6)	4201 (4)	C1	6982 (10)	3505 (6)	2643 (6)
CC6	4803 (7)	140 (5)	3664 (4)	C2	7107 (9)	3339 (6)	2049 (5)
CD1	3807 (5)	2168 (4)	2459 (3)	C3	6379 (11)	2919 (10)	3510 (6)
CD2	4044 (6)	2700 (4)	2073 (4)	C4	7063 (15)	2794 (11)	4008 (6)
CD3	3740 (7)	3443 (5)	2077 (5)	H31	5997 (65)	1959 (47)	2379 (36)
CD4	3179 (8)	3669 (5)	2476 (5)	H32	6132 (65)	1471 (44)	2008 (37)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

of the structure attributable to the steric size of the o-Me_2N group.

In the context of a wider range of structures for triorganotin esters of aromatic acid derivatives,[3-5] planarity within the aromatic acid portion of the molecule persists in the absence of ortho substituents. However, in some cases, even when ortho substituents are present for triphenyltin derivatives in the geometrical form B, e.g. derivatives containing either the salicylate or the naphthoate group, planarity in the carboxylate portion persists.[3]

As an additional factor, the electron-withdrawing effect of the o-chlorine atom in **2** tends to favor structure D by both reducing the C1–C2 multiple-bond character and increasing the acidity of the tin atom. The operation of the ortho steric effect coupled with the presence of an electron-withdrawing ring substituent is consistent with the observed equalization of the Sn–O bond lengths in the trans representation A. The latter tendency toward bond equalization in the A form compared to the tendency of Sn–O bond lengths in the B form to be different generally is observed.[3-5]

In the case of the ortho-substituted ester $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ the electron-donating effect of the dimethylamino group would tend to stabilize the formulation C relative to D. Evidence that the electron-withdrawing effect does not operate independently is found in the observed discrete structural form for the p-chloro derivative **1**, which indicates that the electron-withdrawing effect alone appears insufficient to tip the balance in favor of the trans polymeric form A.[17]

Further, the hydrated end-stopped dimeric structure found for the o-chloro derivative **3** supports the above rationalization for the appearance of the polymeric form A for **2** in terms of both an ortho steric factor and a ring-substituent electron-withdrawing term in that packing forces are unlikely to be similar in both **2** and **3**. Hence, packing forces do not act as an important influence in stabilizing form A in these cases.

Structural Details. The molecular geometry for the p-chlorobenzoate **1** is very similar to that for other triphenyltin benzoates we have studied,[4,5] which have an intramolecular bond from the carbonyl oxygen atom to the tin atom and no such intermolecular interaction. The atoms Sn, CA1, O1, O2, Cl and C1–C7 are coplanar to within ±0.034 Å, with CB1 and CC1 on opposite sides of this plane (1.715 and 1.871 Å, respectively). The geometry about the tin atom is best described as distorted tetrahedral, where the fifth ligand atom, O2, approaches the face of the tetrahedron defined by O1, CB1, and CC1. There are no other Sn–E contacts up to a distance of 4.0 Å.

The angles around the Sn atom, excepting O2, range from 95.7 (2) to 115.3 (2)°, where the former deviation from the tetrahedral angle of 109.5° is the angle O1–Sn–CA1, due to the approach of O2 opposite CA1, and the latter is the angle CB1–Sn–CC1, which is apparently opened up by the approach of O2. It is possible to view the distortions in the geometry as being in the direction of a trigonal bipyramid (TBP) with O2 and CA1 in axial positions (O2–Sn–CA1 = 145.6 (2)°).

For the o-chlorobenzoates **2** and **3**, the geometry about tin is essentially trigonal bipyramidal, with the three phenyl groups occupying equatorial positions, the ester oxygen atom, O1, occupying one of the axial sites, and an oxygen atom from another molecule occupying the second axial position. While this geometry is usual for the trimethyltin carboxylates,[18] this is the only example of a triphenyltin benzoate that has the form A geometry.[19] Since the packing and, in fact, the ligand oxygen atoms are different in **2** and **3**, it is likely that the form A TBP geometry is the preferred geometry about tin for triphenyltin o-chlorobenzoate.

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(17) Preliminary X-ray work on the o-NO_2-substituted ester, $Ph_3Sn[o\text{-}(NO_2)C_6H_4CO_2]$, indicates a trans form A in agreement with this rationalization.

(18) Reference 4 and references cited therein.

(19) Molloy, K. C.; Purcell, T. G.; Quill, K.; Nowell, I. *J. Organomet. Chem.* **1984**, *267*, 237. A similar geometrical arrangement is present in triphenyltin acetate, although a sixth intramolecular Sn–O "bond", arising from the bridging acyl oxygen atom (Sn–O = 3.206 (3) Å) is somewhat conducive in forming this geometry as seen from the C–Sn–C angles of the phenyl groups.

Table VI. Selected Bond Lengths (Å) and Angles (deg) in $[Ph_3Sn(o\text{-}ClC_6H_4CO_2)]_2 \cdot H_2O \cdot Et_2O$ (**3**)[a]

type	length	type	length
Sn1–O3	2.335 (5)	Sn2–OA2	2.636 (5)
Sn1–OA1	2.162 (4)	Sn2–OB1	2.147 (5)
Sn1–CC1	2.127 (7)	Sn2–CF1	2.125 (6)
Sn1–CD1	2.128 (7)	Sn2–CG1	2.122 (6)
Sn1–CE1	2.121 (7)	Sn2–CH1	2.134 (7)
Sn1–OA2	3.620 (5)	Sn2–OB2	3.223 (5)
CA1–OA1	1.287 (7)	CB1–OB1	1.281 (8)
CA1–OA2	1.231 (7)	CB1–OB2	1.240 (8)
CA1–CA2	1.509 (9)	CB1–CB2	1.499 (9)
O3–H31	0.78 (8)	O3–H32	0.82 (8)
H31---O4	2.03 (8)	H32′---OB2	1.89 (8)
O3---O4	2.755 (8)	O3′---OB2	2.694 (7)

type	angle	type	angle
O3–Sn1–OA1	175.9 (2)	OA2–Sn2–OB1	176.9 (2)
O3–Sn1–CC1	88.3 (2)	OA2–Sn2–CH1	87.2 (2)
O3–Sn1–CD1	84.5 (2)	OA2–Sn2–CF1	80.8 (2)
O3–Sn1–CE1	87.2 (2)	OA2–Sn2–CG1	84.7 (2)
OA1–Sn1–CC1	89.2 (2)	OB1–Sn2–CH1	89.8 (2)
OA1–Sn1–CD1	93.9 (2)	OB1–Sn2–CF1	101.2 (2)
OA1–Sn1–CE1	96.9 (2)	OB1–Sn2–CG1	95.9 (2)
CC1–Sn1–CE1	117.5 (2)	CH1–Sn2–CF1	115.5 (3)
CC1–Sn1–CD1	120.3 (2)	CH1–Sn2–CG1	116.5 (2)
CD1–Sn1–CE1	121.3 (2)	CF1–Sn2–CG1	124.9 (3)
Sn1–OA1–CA1	137.6 (4)	Sn2–OB1–CB1	122.9 (5)
OA1–CA1–OA2	125.0 (6)	OB1–CB1–OB2	123.1 (6)
OA1–CA1–CA2	114.7 (6)	OB1–CB1–CB2	116.9 (6)
OA2–CA1–CA2	120.2 (6)	OB2–CB1–CB2	119.8 (6)
CA1–OA2–Sn2	139.3 (4)	CB1–OB2–H32′	128 (2)
Sn1–O3–H31	117 (6)	O3′–H32′---OB2	169 (8)
Sn1–O3–H32	128 (6)	O3–H31---O4	155 (8)
H31–O3–H32	104 (7)		

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

For **2**, intermolecular bonds between carbonyl–oxygen atoms and tin atoms of 2_1-screw-related molecules (O2′ → Sn) result in the formation of associated chains having a zigzag tin–carboxylate backbone to which the aryl groups are appended. For **3**, a similar interaction (OA2 → Sn2) between the two independent tin chlorobenzoate molecules of the asymmetric unit results in the formation of a dimeric unit. These dimeric units are joined together by water molecules that are translationally related along $\vec{a}$: the water molecule that provides the second axial ligand of Sn1 (O3 → Sn1) is also hydrogen-bonded to OB2 (H32′···OB2 = 1.89 (8) Å), forming chains of dimeric units connected by water molecules. The ether molecules are appended to these chains due to a hydrogen bond to the water molecules (H31···O4 = 2.03 (8) Å).

A characteristic set of features of the tin carboxylates is the near coplanarity of the tin atom and the three atoms of the carboxyl group and the positioning of the carbonyl oxygen atom "cis" to the tin atom. These features are not "automatic" since rotational freedom should exist both about the Sn–O_{ester} bond and about the formally single C–O_{ester} bond.

In the case of species like **1**, which have only an intramolecular dative bond to the Sn atom, such an arrangement is concomitant with the formation of this bond: this "cis" arrangement is necessary if the bond is to exist at all, and the coplanarity of the four atoms minimizes the distance between the tin atom and the carbonyl oxygen atom. For **1**, the atoms Sn, O1, C1 and O2 are coplanar to within ±0.003 Å and the distance O2 → Sn = 2.861 (4) Å as compared to the van der Waals sum of 3.70 Å. For intermolecularly bonded trigonal-bipyramidal species like **2** and **3**, the persistence of these factors results in a residual and much weaker interaction, resulting in a Sn–O2 distance of 3.649 (3) Å for **2** and Sn1–OA2 and Sn2–OB2 distances for the dimeric formulation of **3** of 3.620 (5) and 3.223 (5) Å, respectively. Although the former two Sn–O distances are hardly different from the van der Waals sum of 3.70 Å, the latter value for **3** is comparable to that found in triphenyltin acetate.[19] In all of these cases the bridging carbonyl oxygen atom is "cis" to its intramolecular tin atom.

A structural feature that distinguishes (*o*-chlorobenzoato)triphenyltin (**2**) from (*p*-chlorobenzoato)triphenyltin (**1**), which has the discrete geometrical form **B** rather than **A**, is the rotation of the carboxyl group out of the plane of the *o*-chlorophenyl group. The latter apparently mitigates crowding between the chlorine atom and O1. In **2**, the dihedral angle between the plane of the carboxyl group and the plane of the *o*-chlorophenyl group is 60.6° while the distance between Cl and O1 is 3.121 (3) Å as compared to the van der Waals sum of 3.2 Å. In **3**, the corresponding values are 49.8° and 3.098 (5) Å for chlorobenzoate group A and 34.1° and 2.991 (6) Å for chlorobenzoate group B. In **1**, near planarity is indicated by a dihedral angle of 2.1° between the aforementioned groups.

Solid- and Solution-State Structures. The weakness of the forces holding the triphenyltin benzoates **2** and **3** in the geometrical form A in the solid state is apparent from solution infrared data. As found with previous studies[3-5] on the triphenyltin derivatives, the C═O stretching frequency is unchanged on going from Nujol to a solution sample for the B form. Typically, the $\nu_{COO(asym)}$ absorption is in the range 1615–1630 cm^{-1}, indicative of retention of structure. This range represents a lowering in the carboxyl stretch upon coordination from that in the free acids.[20] Here the range centers at ~1670 cm^{-1} for compounds of this type. For **1** having the B form, a value for the ν_{COO} stretch of 1630 cm^{-1} in Nujol and in $CHCl_3$ was obtained, indicating retention of this geometry in solution. However, for **2**, ν_{COO} in Nujol was shifted to 1570 cm^{-1} but was at 1630 cm^{-1} in $CHCl_3$. These results indicate that the polymeric A form in the solid found by X-ray analysis was disrupted in solution to give the discrete intramolecularly coordinated B form. In order for this to occur for **2**, sufficient energy must be supplied to cleave the intermolecular Sn–O2′ bond. However, energy is gained as the intramolecular Sn–O2 bond increases in strength as the structure rearranges to form B, a somewhat tetrahedral arrangement of the Ph_3Sn–O1 system.

The ^{119}Sn NMR chemical shift obtained for **2**, $\delta = -107.9$, is in the range (−64.4 to −120.9 ppm) observed for a series of triphenyltin benzoates reported by Holecek and co-workers.[11] This range lies below the chemical shift value for ^{119}Sn in Ph_4Sn of −128.1 ppm and indicates the essential tetrahedral character of form B in $CDCl_3$ solution for **2**, hence confirming the infrared interpretation for this derivative. The ^{119}Sn chemical shift for **1** has been determined[11] to be −104.9 ppm, close to that for **2**.

Biochemical Implications. The somewhat surprising change in structure between the cis form B and the trans form A on going from **1** to **2** or **3** that involves closely related formulations points up the difficulties in assessing biochemical models for toxic action. Both cis[9-10] and trans[7b] forms have been proposed for the mode of action of trialkyltin binding histidine and/or cysteine residues. Not only must the present type of study be extended to evaluate the role of a change in donor atom but, given the apparent small energy difference between forms A and B, the more ambitious task of assessing the influence of enzyme constraints must be undertaken.

Acknowledgment. The support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. 1, 83500-87-2; **2**, 102493-31-2; **3**, 102493-33-4; bis(triphenyltin) oxide, 1262-21-1.

Supplementary Material Available: Listings for **1**–**3**, respectively, of anisotropic thermal parameters (Tables A–C), fixed hydrogen atom parameters (Tables D–F), additional bond lengths and angles (Tables G–I), and deviations from selected least-squares mean planes (Tables J–L) (14 pages). Ordering information is given on any current masthead page.

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