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Chain Structures of Trimethyltin Esters of Salicylic Acid and *o*-Anisic Acid. Tin-119m Mössbauer Study of a Series of Trimethyltin and Triphenyltin Carboxylates[1]

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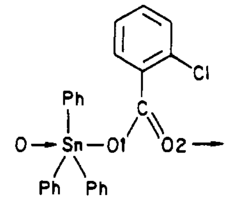
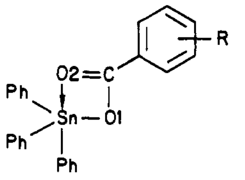
The synthesis, crystal structure, ^{119m}Sn Mössbauer parameters, and infrared and NMR data are reported for the trimethyltin esters of *o*-anisic and salicylic acids, $Me_3SnO_2CC_6H_4OMe$-2 (**1**) and $Me_3SnO_2CC_6H_4OH$-2 (**2**), respectively. Mössbauer parameters for a series of triorganotin esters are determined on substances whose X-ray structures have been established. Both **1** and **2** possess chain polymer structures showing conformational differences related to the presence of hydrogen bonding in **2** and its absence in **1**. The ^{119m}Sn Mössbauer quadrupole splitting parameter (QS) falls in the range 2.30–2.55 mm s^{-1} for triorganotin esters having a discrete geometry formed by intramolecular oxygen atom coordination, while for those having a chain formulation formed by intermolecular donor atom coordination a QS range of 3.59–3.74 mm s^{-1} is observed. Hydrogen-bonded members show a QS range of 2.97–3.47 mm s^{-1}. The correlation of crystallographic and Mössbauer data reveals the importance of hydrogen bonding in accounting for the occasional intermolecular nitrogen atom or hydroxyl oxygen atom coordination in place of carboxyl oxygen atom coordination, giving an intermediate chain form. Infrared and NMR data indicate that all forms become monomeric in solution. The anisic acid derivative **1** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$) with $a = 10.623$ (1) Å, $b = 9.993$ (2) Å, $c = 13.068$ (1) Å, and $\beta = 112.08$ (1)°. The salicylate **2** crystallizes in the orthorhombic space group $Pna2_1$ ($Z = 4$) with $a = 16.488$ (2) Å, $b = 6.806$ (1) Å, and $c = 10.756$ (1) Å. The final conventional unweighted residuals are 0.026 (**1**) and 0.036 (**2**).

Introduction

In the previous paper,[1b] the appearance of the triphenyltin ester of 2-chlorobenzoic acid in the chain polymeric form A contrasts with the discrete structural form B reported for other triphenyltin benzoates.[3,4] With reference to the tin centers these structures are referred to as trigonal-bipyramidal *trans*-R_3SnX_2 and *cis*-R_3SnX_2 geometries, respectively. Usually trimethyltin carboxylates adopt the chain form A.[5] The stabilizing effect of the more electronegative phenyl group axially oriented in form B has been cited[3a] to account for differences between the two classes of tin esters.



A (*trans*-R_3SnX_2)



B (*cis*-R_3SnX_2)

Although limited ^{119m}Sn Mössbauer data have been reported, known examples of triorganotin carboxylates show a much lower quadrupole splitting (QS) value for form B[6-8] compared to form A.[9,10] For example, *O*-(triphenylstannyl)dibenzoylmethane, $(Ph_3SnO)(Ph)C{=}CHC(Ph)O$, whose X-ray structure[7] shows it exists in the discrete form B, has a ΔE_Q values of 2.25 mm s^{-1}.[7] Typical of the polymeric chain form A, established for trimethyltin acetate by X-ray analysis,[11] is a ΔE_Q value of 3.68 mm s^{-1}.[9]

Trimethyltin glycinate, which has a QS value of 3.14 mm s^{-1} [10] and exists in the solid state in a chain structure,[12] is unusual in that the nitrogen atom acts as the intermolecular bridging ligand (and hence axial sites about tin are occupied by oxygen and nitrogen atoms). We have theorized that this interesting structural change is probably due to hydrogen bonding between the NH_2 group and the carboxyl oxygen atom, which serves to enhance the donor character of the nitrogen atom at the expense of oxygen.[3b]

In order to study the influence of hydrogen bonding on the structural form assumed by triorganotin carboxylates and to examine the usefulness of tin Mössbauer data in aiding the structural classification of these interesting substances, a crystallographic and ^{119m}Sn Mössbauer study of the trimethyltin esters of *o*-anisic acid and salicylic acid, $Me_3SnO_2CC_6H_4OMe$-2 (**1**) and $Me_3SnO_2CC_6H_4OH$-2 (**2**), respectively, is reported here. The latter ester has the potential for hydrogen bonding of the type seen in the glycinate, whereas the former ester is the related methoxy derivative. To extend the study, Mössbauer data are obtained on additional triphenyl- and trimethyltin aromatic esters.

Experimental Section

Carbon-13 NMR spectra were recorded on a Varian 200-MHz instrument operating at 50.31 MHz. ^{1}H and ^{119}Sn{^{1}H} NMR spectra were recorded on a Varian 300-MHz instrument operating at 300 MHz and 111.862 MHz, respectively. Deuteriochloroform was used for locking. Carbon and proton chemical shifts are referenced to Me_4Si, while tin chemical shifts are expressed relative to tetramethyltin. All chemical shifts are given in ppm.

^{119m}Sn Mössbauer spectra were obtained by using a constant-acceleration microprocessor spectrometer (Cryophysics Ltd., Oxford, England), with a 512-channel data store. A 10-mCi Ba^{119m}SnO$_3$ source was used at room temperature, and the samples were packed in Perspex disks and cooled to 80 K.

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer using KBr cells. Solid spectra were recorded in Nujol and solution spectra in chloroform. Infrared and NMR concentrations were in the range of 20–50 g/1000 g of solvent. This concentration range is the same as was used for the molecular weight determinations.

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(1) (a) Pentacoordinated Molecules. 66. (b) Previous paper in the series: Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Vollano, J. F.; Holmes, J. M. *Inorg. Chem.*, preceding article in this issue.

(2) Affiliations: P.J.S., International Tin Research Institute, where the Mössbauer measurements were performed; all other authors, University of Massachusetts, where the synthesis and crystallographic studies were carried out.

(3) (a) Swisher, R. G.; Vollano, J. F.; Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1984**, *23*, 3147. (b) Vollano, J. F.; Day, R. O.; Rau, D. N.; Chandrasekhar, V.; Holmes, R. R. *Inorg. Chem.* **1984**, *23*, 3153.

(4) References for X-ray structures of $Ph_3SnONPhCOPh$, (p-$MeC_6H_4)_3SnSC_5H_4N$-2, (triphenylstannyl)-8-mercaptoquinoline, respectively: (a) King, T. J.; Harrison, P. G. *J. Chem. Soc., Dalton Trans.* **1974**, 2298. (b) Furmanova, N. G.; Kravtsov, D. N.; Rokhlina, E. M. *J. Struct. Chem. (Engl. Transl.)* **1981**, *22*, 569. (c) Furmanova, N. G.; Struchkov, Yu. T.; Rokhlina, E. M.; Kravtsov, D. N. *J. Struct. Chem. (Engl. Transl.)* **1980**, *21*, 766. X-ray studies of triphenyltin *o*-((2-hydroxy-5-methylphenyl)azo)benzoate (**19**)[6] and *o*-(triphenylstannyl)dibenzoylmethane (**24**),[7] which display similar ΔE_Q values (Table IV), also have been performed. All five of these derivatives exist in the discrete form B.

(5) See references cited in Table IX of ref 3b.

(6) Harrison, P. G.; Lambert, K.; King, T. J.; Majee, B. *J. Chem. Soc., Dalton Trans.* **1983**, 363.

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(10) Ho, B. Y. K.; Zuckerman, J. J. *Inorg. Chem.* **1973**, *12*, 1552.

(11) Chih, H.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1973**, *3*, 285.

(12) Ho, B. Y. K.; Molloy, K. C.; Zuckerman, J. J.; Reidinger, F.; Zubieta, J. A. *J. Organomet. Chem.* **1980**, *187*, 213.

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Molecular weights were measured by using a Knaver vapor pressure osmometer in chloroform at 37 °C. The concentrations were in the range of 30 g/1000 g of solvent to 5 g/1000 g of solvent. Molecular weights were determined by using benzil for calibration. All the molecular weights corresponded to monomeric species and were within ±5% of expected valves.

Preparation of Trimethyltin 2-Methoxybenzoate, $Me_3SnO_2CC_6H_4OMe$-2 (1). To a suspension of trimethyltin hydroxide (0.70 g, 3.87 mmol) in 200 mL of benzene was added *o*-anisic acid (0.59 g, 3.87 mmol). The reaction mixtuure was heated under reflux for 4 h with a Dean–Stark separator. After the reflux period the solvent was removed from the reaction mixture, affording a white solid. It was recrystallized from a CH_2Cl_2/Skelly mixture (1:1): mp 188–190 °C; yield 1.10 g (90.2%). ^{1}H NMR ($CDCl_3/Me_4Si$): δ 8.07–8.10 (m), 7.47–7.50 (m), 6.94–6.97 (m), 3.90 (s, 3 H, *o*-CH_3), 0.52 (s, 9 H, CH_3); $^2J(^{119}Sn\text{–}C\text{–}^1H)$ = 57.4 Hz. ^{13}C NMR ($CDCl_3/Me_4Si$): δ 2.42 (CH_3), 54.67 (o-CH_3), 110.67 (C1), 158.02 (C2), 169.9 (COO), 119.3, 120.5, 131.9, 132.0 (not assigned unambiguously). ^{119}Sn NMR ($CDCl_3/Me_4Sn$): δ 126.86; $^2J(^{119}Sn\text{–}^{13}C)$ = 394.0 Hz. IR: solid, 1550, 1400 (ν_{COO}), 545 cm^{-1} (ν_{SnC_3}); solution, 1630, 1350 (ν_{COO}), 540, 510 cm^{-1} (ν_{SnC_3}). Anal. Calcd for $C_{11}H_{16}O_3Sn$: C, 41.95; H, 5.12. Found: C, 41.83; H, 5.11. M_r: calcd, 314.9; found, 305.1.

Preparation of Trimethyltin Salicylate, $Me_3SnO_2CC_6H_4OH$-2 (2). Trimethyltin hydroxide (0.80 g, 4.43 mmol) was dissolved in 200 mL of benzene, and salicylic acid (0.61 g, 4.43 mmol) was added. After the reaction was refluxed for 2 h, during which time the water formed in the reaction was removed azeotropically by using a Dean–Stark apparatus, benzene was distilled off by vacuum, affording an oil. The oil was dissolved in a small amount of hot benzene (5 mL), hexane was added to it until a slight turbidity appeared, and this was kept for crystallization at 0 °C. Platelike crystals of **2** were formed: mp 98–100 °C; yield 1.10 g (82.7%). ^{1}H NMR ($CDCl_3/Me_4Si$): δ 7.35–7.39 (m), 7.85–7.90 (m), 0.67 (s, CH_3, 9 H); $^2J(^{119}Sn\text{–}C\text{–}^1H)$ = 57.10 Hz. ^{13}C NMR ($CDCl_3/Me_4Si$): δ −2.13 (CH_3), 115.11 (C1), 161.91 (C2), 175.1 (COO), 117.5, 119.0, 131.1, 135.5 (not assigned unambiguously); $^1J(^{119}Sn\text{–}^{13}CH_3)$ = 396.4 Hz. ^{119}Sn NMR ($CDCl_3/Me_4Sn$): δ 148.23 (s). IR: solid, 1630, 1350 (ν_{COO}), 542, 510 cm^{-1} (ν_{SnC_3}); solution, 1630, 1350 (ν_{COO}), 540, 510 cm^{-1} (ν_{SnC_3}). Anal. Calcd for $C_{10}H_{14}O_3Sn$: C, 39.92; H, 4.69. Found: C, 39.84; H, 4.60. M_r: calcd, 300.9; found, 287.2.

Crystallography. All X-ray crystallographic studies were performed by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[13]

Crystals were mounted in thin-walled glass capillaries, which were sealed as a precaution against moisture sensitivity.

X-ray Studies for $Me_3SnO_2CC_6H_4OMe$-2 (1). The crystal used for the X-ray studies was cut from a colorless fused group of multifaceted chunks and had dimensions of 0.25 × 0.33 × 0.36 mm.

Crystal Data: $C_{11}H_{16}O_3Sn$ (**1**), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^5–No. 14][14]), a = 10.623 (1) Å, b = 9.993 (2) Å, c = 13.068 (1) Å, β = 112.08 (1)°, Z = 4, $\mu_{MoK\alpha}$ = 1.986 mm^{-1}. A total of 2251 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{MoK\alpha} \leq 50°$. No corrections were made for absorption.

The structure was solved by using standard Patterson and difference Fourier techniques and was refined by using full-matrix least squares.[15] The 15 independent non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the refinement as fixed isotropic scatterers. Coordinates for the 12 independent methyl hydrogen atoms were obtained from a difference Fourier synthesis. Coordinates for the four independent phenyl hydrogen atoms were calculated and updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement factors[16] were R = 0.026 and R_w = 0.038 for the 1979 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $Me_3SnO_2CC_6H_4OH$-2 (2). The crystal used for the X-ray studies, cut from a colorless polycrystalline mass, was an approximate triangular prism with edge lengths of 0.23, 0.30, and 0.30 mm and a height of 0.30 mm. Data collection and reduction, solution, and refinement were the same as described for **1** unless otherwise noted.

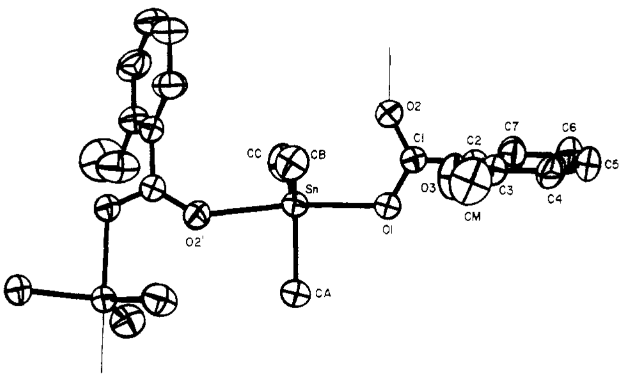

Figure 1. ORTEP plot of $Me_3SnO_2CC_6H_4OMe$-2 (**1**) with thermal ellipsoids at the 50% probability level. A symmetry related ($^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$) molecule is included to complete the coordination sphere of the tin atom. The extention of the polymeric chain is indicated by solid lines. Hydrogen atoms are omitted for purposes of clarity.

Table I. Atomic Coordinates in Crystalline $Me_3SnO_2CC_6H_4OMe$-2 (**1**)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	1729.5 (2)	806.1 (2)	2212.5 (2)
O1	242 (2)	−774 (2)	2132 (2)
O2	1867 (2)	−2274 (3)	2574 (3)
O3	291 (3)	−2024 (3)	4315 (2)
CA	127 (4)	2216 (4)	1747 (4)
CB	2850 (4)	469 (4)	3911 (3)
CC	2330 (4)	80 (4)	943 (3)
CM	64 (6)	−2052 (6)	5348 (4)
C1	682 (3)	−1945 (3)	2416 (3)
C2	−290 (3)	−2936 (3)	2584 (3)
C3	−506 (3)	−2962 (3)	2568 (3)
C4	−1397 (4)	−3904 (5)	3699 (4)
C5	−2038 (4)	−4813 (4)	2880 (4)
C6	−1808 (4)	−4804 (5)	1938 (4)
C7	−927 (4)	−3859 (4)	1752 (3)

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

Table II. Atomic Coordinates in Crystalline $Me_3SnO_2CC_6H_4OH$-2 (**2**)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	7371.0 (3)	8665.7 (7)	7500[c]
O1	8386 (5)	8820 (8)	6302 (8)
O2	8319 (5)	5584 (10)	6079 (8)
O3	9080 (7)	3956 (11)	4290 (11)
CA	7319 (8)	11848 (18)	7733 (23)
CB	7819 (8)	7066 (19)	9026 (12)
CC	6478 (7)	7404 (17)	6327 (13)
C1	8630 (6)	7220 (14)	5793 (9)
C2	9260 (5)	7364 (12)	4850 (9)
C3	9468 (7)	5695 (14)	4131 (10)
C4	10034 (8)	5909 (20)	3176 (14)
C5	10380 (7)	7641 (18)	2927 (13)
C6	10166 (8)	9288 (18)	3611 (13)
C7	9622 (8)	9153 (14)	4543 (10)

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

Crystal Data: $C_{10}H_{14}O_3Sn$ (**2**), orthorhombic space group, $Pna2_1$ [C_{2v}^9-No. 33],[17] a = 16.488 (2) Å, b = 6.806 (1) Å, c = 10.756 (1) Å, Z = 4, $\mu_{MoK\alpha}$ = 2.111 mm^{-1}. A total of 1117 independent reflections ($+h,+k,+l$) were measured.

The 14 independent non-hydrogen atoms were refined anisotropically, while the four independent aromatic hydrogen atoms were treated as

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

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

(15) 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. Real and imaginary dispersion corrections for Sn and O were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 149–150.

(16) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. For **2**, these values are for the configuration having the lowest R_w.

(17) Reference 14; p 119.

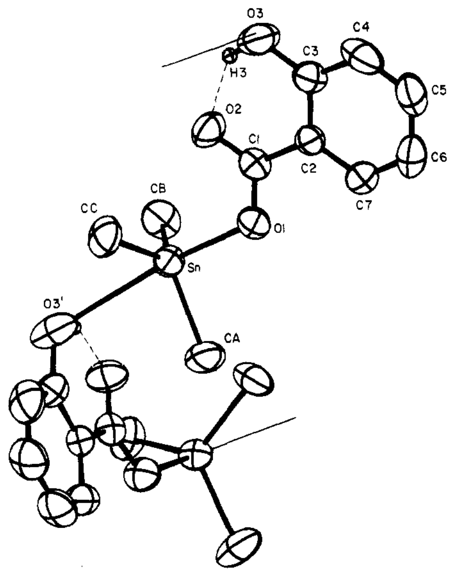


Figure 2. ORTEP plot of $Me_3SnO_2CC_6H_4OH$-2 (**2**) with thermal ellipsoids at the 50% probability level. A symmetry related ($1^1/_2 - x$, $^1/_2 + y$, $^1/_2 + z$) molecule is included to complete the coordination sphere of the tin atom. The extension of the polymeric chain is indicated by solid lines while the hydrogen-bonding interactions are shown as dashed lines. Hydrogen atoms, except for H3, which is represented by a sphere of arbitrary radius, have been omitted for purposes of clarity.

Table III. Distances (Å) and Angles (deg) for $Me_3SnO_2CC_6H_4OMe$-2 (**1**) and $Me_3SnO_2CC_6H_4OH$-2 (**2**)[a]

type[b]	1	2
Sn-O1	2.208 (2)	2.114 (7)
Sn-O2	3.110 (3)	3.029 (8)
$Sn-O_{inter}$[c]	2.381 (2)	3.08 (1)
Sn-CA	2.115 (4)	2.18 (1)
Sn-CB	2.115 (4)	2.10 (1)
Sn-CC	2.117 (4)	2.12 (1)
C1-O1	1.262 (4)	1.28 (1)
C1-O2	1.241 (4)	1.26 (1)
$O1-Sn-O_{inter}$	170.8 (1)	173.4 (2)
O1-Sn-CA	88.8 (1)	93.0 (4)
O1-Sn-CB	92.7 (1)	102.9 (4)
O1-Sn-CC	98.0 (1)	101.9 (4)
CA-Sn-CB	118.9 (2)	116.0 (8)
CA-Sn-CC	116.7 (2)	116.3 (6)
CB-Sn-CC	123.5 (2)	119.9 (5)
$CA-Sn-O_{inter}$	84.1 (1)	80.5 (4)
$CB-Sn-O_{inter}$	90.4 (1)	79.5 (4)
$CC-Sn-O_{inter}$	85.7 (1)	81.9 (4)
O2-Sn-O1	44.9 (1)	47.1 (2)
$O2-Sn-O_{inter}$	142.0 (1)	139.6 (2)
O2-Sn-CA	133.6 (1)	139.9 (4)
O2-Sn-CB	73.0 (1)	81.6 (4)
O2-Sn-CC	76.7 (1)	77.1 (4)
Sn-O1-C1	118.0 (2)	117.8 (6)
$C_{inter}-O_{inter}-Sn$	141.7 (1)	110.1 (8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 1 and 2. [c] O_{inter} is O2′ for **1** and O3′ for **2**. C_{inter} is C1′ for **1** and C3′ for **2**.

described for **1**. The hydroxyl hydrogen atom, which was located with a difference Fourier synthesis, was refined as an isotropic scatterer with B fixed at 5 Å^2. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[16] were $R = 0.036$ and $R_w = 0.046$ for the 1007 reflections having $I \geq 2\sigma_I$.

Results

The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 1, while atomic coordinates are given in Table I. The corresponding information for **2** is given in Table II and in Figure 2. Selected bond lengths and angles for both compounds are given in Table III. ^{119m}Sn Mössbauer data for the trimethyl- and triphenyltin aromatic esters, and related compounds, are listed in Table IV and selected bond distances and angles are given in Tables V and VI. Tables of thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from least-squares mean planes for both compounds are provided as supplementary material.

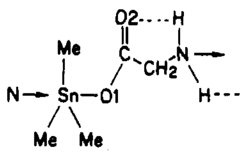
Table IV. ^{119m}Sn Mössbauer Parameters for Triphenyl- and Trimethyltin Aromatic Esters and Related Compounds

no.	compd	δ,[a,b] mm s^{-1}	ΔE_Q,[b] mm s^{-1}
	$Me_3SnOCOR$		
1	R = C_6H_4OMe-2	1.36	3.71
2	R = C_6H_4OH-2	1.40	3.47
3	R = C_6H_4Cl-2	1.33	3.63
4	R = $C_6H_4NH_2$-4[c]	1.36	3.59
5	R = $C_6H_4NH_2$-2	1.36	3.43
6	R = C_6H_4NHMe-2	1.38	3.40
7	R = $C_6H_4NMe_2$-2	1.37	3.74
8	R = Me	1.30[d]	3.68[d]
9	R = CH_2NH_2	1.26[e]	3.14[e]
10	$Me_3SnONPhCOPh$	1.34[f]	2.36[f]
	$Ph_3SnOCOR$		
11	R = $C_{10}H_7$-1	1.23	2.33
12	R = C_6H_5	1.24	2.55
13	R = C_6H_4Cl-4	1.24	2.36
14	R = C_6H_4SMe-4	1.27	2.42
15	R = $C_6H_4NH_2$-4[g]	1.24	2.39
16	R = $C_6H_4NH_2$-2	1.21	2.44
17	R = $C_6H_4NMe_2$-2	1.25	2.37
18	R = C_6H_4OMe-2	1.25	2.30
19	R = $C_6H_4(N{=}NC_6H_3OH$-2-Me-5)-2	1.28[h]	2.36[h]
20	R = $C_6H_4(N{=}NC_{10}H_6$-1-OH-4)-2	1.35[h]	3.06[h]
21	R = C_6H_4OH-2	1.34	2.97
22	R = C_6H_4Cl-2	1.34	3.71
23	R = Me	1.28[i]	3.36[i]
24	$(Ph_3SnO)(Ph)C{=}CHC(Ph)O$	1.13[j]	2.25[j]

[a] Relative to $BaSnO_3$. [b] Error ±0.05 mm s^{-1}. [c] Benzene solvate. [d] Reference 9. [e] Reference 10. [f] Reference 8. [g] 0.5 benzene solvate. [h] Reference 6. [i] Reference 20. [j] Reference 7.

Discussion

As with other trimethyltin esters of carboxylic acids,[5] both the anisic acid derivative **1** and the salicylate **2** reside in a chain polymeric form in the solid state (Figures 1 and 2). However, unlike **1** which has form A with the carboxyl oxygen atom responsible for intermolecular bridging, the salicylate **2** shows the carboxyl oxygen involved in hydrogen bonding with the *o*-hydroxyl group. Here, the oxygen atom of the ortho substituent serves as the intermolecular bridging ligand. This coordination difference is reminiscent of that which occurs in the trimethyltin glycinate[12] **9**; i.e., intermolecular coordination takes place via the amine nitrogen atom rather than the acyl oxygen atom of the carboxyl group. Again hydrogen bonding is present. We will refer to this as form C.



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Recently, we have prepared and structurally characterized two other examples of trimethyltin esters,[18] $Me_3SnO_2CC_6H_4NH_2$-2

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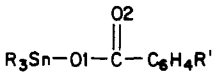
(18) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M., unpublished work. Compound **3**: space group $P2_1/n$, a = 10.461 (3) Å, b = 10.055 (4) Å, c = 12.718 (4) Å, β = 110.86 (2)°, Z = 4, R = 0.028, R_w = 0.046. Compound **4**: space group $P2_1/n$, a = 15.345 (2) Å, b = 10.029 (2) Å, c = 20.403 (3) Å, β = 94.22 (1)°, Z = 8, R = 0.044, R_w = 0.060. Compound **5**: space group $P2_1/c$, a = 11.955 (2) Å, b = 8.500 (1) Å, c = 12.513 (3) Å, β = 107.75 (5)°, Z = 4, R = 0.023, R_w = 0.033. Compound **6**: space group $C2/c$, a = 25.213 (5) Å, b = 8.345 (1) Å, c = 12.384 (2) Å, β = 99.87 (1)°, Z = 8, R = 0.029, R_w = 0.046. Compound **7**: space group $P2_1/n$, a = 10.230 (4) Å, b = 9.882 (5) Å, c = 14.365 (3) Å, β = 106.74 (2)°, Z = 4, R = 0.037, R_w = 0.049.

Table V. Selected Distances (Å) and Angles (deg) for Polymers of



$R_3Sn{-}O1{-}C({=}O2){-}C_6H_4R'$

no.	R	R′	Sn—O1	Sn—O2′(inter)	Sn—O2-(intra)	C—O1	C=O2	O1-Sn-O2′	∑C-Sn-C	ref
4	Me[a]	NH_2-4	2.169 (5)	2.477 (5)	3.157 (6)	1.28 (1)	1.25 (1)	173.5 (2)	357.8	18
			2.168 (5)	2.416 (6)	3.357 (6)	1.28 (1)	1.25 (1)	174.1 (2)	358.8	18
3	Me	Cl-2	2.200 (3)	2.414 (3)	3.143 (4)	1.277 (5)	1.219 (5)	174.2 (1)	359.2	18
7	Me	NMe_2-2	2.201 (5)	2.426 (5)	3.224 (5)	1.271 (8)	1.243 (8)	170.0 (2)	358.8	18
1	Me	OMe-2	2.208 (2)	2.381 (2)	3.110 (3)	1.262 (4)	1.241 (4)	170.8 (1)	359.1	this work
5	Me[b]	NH_2-2	2.146 (3)	2.781 (5)[b]	3.017 (3)	1.296 (5)	1.233 (5)	178.3 (1)[b]	356.6	18
22	Ph	Cl-2	2.201 (3)	2.384 (3)	3.649 (3)	1.261 (4)	1.250 (4)	173.8 (1)	359.8	1b
6	Me[b]	NHMe-2	2.128 (3)	3.162 (6)[b]	2.977 (3)	1.305 (5)	1.246 (5)	176.5 (1)[b]	353.8	18
21	Ph[c]	OH-2	2.083 (2)	3.035 (2)[c]	3.071 (2)	1.301 (3)	1.232 (3)	168.2 (1)[c]	350.4	3b
2	Me[c]	OH-2	2.114 (7)	3.08 (1)[c]	3.029 (8)	1.28 (1)	1.26 (1)	173.4 (2)[c]	352.2	this work

[a] Benzene solvate. Two independent molecules in the polymeric chain. [b] Intermolecular bond is through nitrogen. Replace Sn–O2′(inter) by Sn–N′, and replace O1–Sn–O2′ by O1–Sn–N′. [c] Intermolecular bond is through OH oxygen. Replace Sn–O2′(inter) by Sn–$O_{hydroxyl}$(inter), and replace O1–Sn–O2′ by O1–Sn–$O_{hydroxyl}$.

Table VI. Selected Distances (Å) and Angles (deg) for $Ph_3Sn(O1)C(=O2)R$ Monomers

no.	R	Sn—O1	Sn—O2	C—O1	C=O2	O2-Sn-C_{axial}	∑ of equatorial angles	∑C-Sn-C	ref
13	C_6H_4Cl-4	2.048 (4)	2.861 (4)	1.304 (7)	1.216 (7)	145.6 (2)	337.2	337.6	1b
12	C_6H_5	2.074 (4)	2.695 (5)	1.313 (8)	1.222 (8)	148.2 (2)	340.6	337.4	19
11	$C_{10}H_7$-1	2.068 (2)	2.711 (2)	1.314 (4)	1.224 (4)	150.1 (1)	338.3	340.6	19
18	C_6H_4OMe-2	2.054 (3)	2.781 (3)	1.321 (5)	1.214 (5)	145.9 (1)	340.7	338.6	3b
14	C_6H_4SMe-4	2.060 (2)	2.783 (3)	1.310 (4)	1.232 (4)	149.2 (1)	340.5	338.5	3b
17	$C_6H_4NMe_2$-2	2.115 (6)	2.564 (7)	1.272 (9)	1.219 (10)	143.7 (3)	339.6	335.8	3a
16	$C_6H_4NH_2$-2	2.043 (3)	2.823 (3)	1.310 (5)	1.237 (5)	146.6 (1)	332.9	336.1	3a
15	$C_6H_4NH_2$-4[a]	2.072 (2)	2.629 (2)	1.306 (4)	1.236 (4)	151.3 (1)	340.7	334.9	3a

[a] 0.5 benzene solvate.

Table VII. Comparison of Parameters for Triorganotin Esters in Chain Forms A and C[a]

Chain Form C (Hydrogen Bonded)

no.	Sn–X(inter), Å	δ,[d] deg	ΔE_Q, mm s^{-1}
2	3.08 (1)[b]	11.4	3.47
5	2.781 (5)[c]	14.3	3.43
6	3.162 (6)[c]	9.2	3.40
9	2.46 (2)[c]		3.14
21	3.035 (2)[b]	9.5	2.97

Chain Form A

no.	Sn–O(inter), Å	δ,[d] deg	δE_Q, mm s^{-1}
1	2.381 (2)	79.4	3.71
3	2.414 (3)	81.1	3.63
7	2.426 (5)	62.3	3.74
22	2.384 (3)	60.4	3.71

[a] See Tables V and VI for references to the X-ray structural data. [b] Intermolecular bond is through OH oxygen. [c] Intermolecular bond is through nitrogen. [d] Dihedral angle between the mean plane containing the SnO_2C carboxylate group and the mean plane of the phenyl portiona of the benzoate.

(**5**) and $Me_3SnO_2CC_6H_4NHMe$-2 (**6**), that contain carboxyl group hydrogen bonding and intermolecular nitrogen atom coordination to give chain structures C, like **2** or **9** (Table V). This compares to the *o*-(dimethylamino) derivative $Me_3SnO_2CC_6H_4NMe_2$-2 (**7**), which, like **1**, lacks hydrogen-bonding possibilities and has the *trans*-R_3SnX_2 chain form A.[18]

Examination of the ^{119m}Sn Mössbauer quadrupole splitting parameters for these two classes of esters shows that compounds **1**, **3**, **4**, **7**, **8**, and **22** in Table IV (all of which have a chain form A structure as referenced in Table V and ref 11) have ΔE_Q values in the range 3.59–3.74 mm s^{-1}. Those compounds adopting the chain structure formed by intermolecular coordination from the hydrogen bond donor atom, **2**, **5**, **6**, **9**, and **21**, have ΔE_Q values in a somewhat lower range, 2.97–3.47 mm s^{-1}. Both of these ranges are well above the quadrupole splitting values for compounds residing in the *cis*-R_3SnX_2 discrete form B; i.e., a range of 2.30–2.55 mm s^{-1} is obtained for compounds **10**–**19** and **24**.

As expressed in Table VII, the triorganotin benzoates containing hydrogen-bonded carboxylates in chain form C show considerably longer tin–ligand intermolecular bond distances, Sn–X, compared to this distance in chain form A. The longer distances are consistent with the presence of hydrogen bonding, as commented on in the Introduction, in allowing a normally secondary donor atom to replace the acyl oxygen atom O2 in intermolecular coordination. Another consequence of hydrogen bond formation in form C is the near planarity in the benzoate portion of the ester structure. In the chain form A, the phenyl portion tends toward orthogonality with the SnO_2C group, in line with reduced steric interaction between the ortho group and acyl oxygen atom O2.

Another possible member of the chain form C class, or at least one intermediate between chain form C and discrete form B, is triphenyltin *o*-((4-hydroxynaphthyl)azo)benzoate (**20**) (Table IV). An X-ray study is lacking for this derivative. The same effect involving the hydroxyl group may be operational in the solid state. **20** has a ΔE_Q value of 3.06 mm s^{-1},[6] in the range listed in Table VII for form C compounds.

Triphenyltin acetate (**23**) is crystallographically[20] represented by Form A but contains an additional weak intramolecular O2 → Sn coordination (3.206 Å) arising from the acyl bridging oxygen. This may account for its ΔE_Q value of 3.36 mm s^{-1}, lower than those listed in Table VII for this form.

Although the trimethyltin benzoate esters studied here exist exclusively as chain structures, the trimethyltin derivative **10** has been found[21] to adopt the monomeric *cis*-R_3SnX_2 form B and

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(19) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Vollano, J. F.; Holmes, J. M., unpublished work.

(20) Molloy, K. C.; Purcell, T. G.; Quill, K.; Nowell, I. W. *J. Organomet. Chem.* **1984**, *267*, 237.

(21) Harrison, P. G.; King, T. J.; Molloy, K. C. *J. Organomet. Chem.* **1980**, *185*, 199.

shows[8] a low ΔE_Q value, which falls in the same range as the quadrupole splittings observed for the triphenyltin derivatives **11**–**19** (Table IV) that are present in form B.

In view of the distinct ranges of quadrupole splitting values found for structural forms A–C, it apears that future ^{119m}Sn Mössbauer data will provide discriminating information indicating proper structural classification of triorganotin carboxylates in the solid state.

Solid- and Solution-State Structures. The infrared data are most instructive in comparing solid- and solution-state structures. For the anisic acid derivative **1**, changes in the carboxyl group stretch, ν_{COO}, and an increase in the number of tin–methyl group carbon stretches, ν_{SnC_3}, on going from the solid to a chloroform solution imply a greater structural change compared to that occuring with the salicylate derivative **2**, which shows relative invariance in these quantities. The asymmetric stretch ν_{COO} appearing at 1630 cm^{-1} is in the range associated with the discrete form B structure[3] and represents a lowering from that found in the free acids.[22] The implication is that the polymer form A found for the solid state of **1** is disrupted in solution. In the case of **2**, which we discussed in terms of a solid-state hydrogen-bonded chain form C, solution apparently causes little structural change. Molecular weight data for both **1** and **2** imply the presence of a monomer while ν_{OH} for **2** is insensitive to dilution and is extremely broad, suggesting retention of the intramolecular hydrogen bonding found for the solid. The principal occurrence on solution of **2** is the rupture of the weak intermolecular Sn–O "bond" (3.08 (1) Å compared to 2.381 (2) Å for **1**). The sum of the C–Sn–C angles of the Me$_3$Sn group for **2** is 352.2° (Table V), which implies an intermediacy of this structure between forms B and C and which helps one to understand the lack of change in infrared stretching frequencies on solution.

The single absorption for **1** in the solid corresponding to the ν_{Sn-C} stretch at 545 cm^{-1} and the two absorptions in solution, at 540 and 510 cm^{-1}, are consistent with a planar Me$_3$Sn arrangement, as found for the solid, which becomes nonplanar, i.e. more tetrahedral in a monomeric form in solution.

The solution NMR data for **1** and **2**, particularly the coupling constants $^2J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{119}\text{Sn}-^{13}\text{C})$ near 57 MHz and 395 MHz, respectively, are consistent with monomeric formulations as suggested by similar values found in comparable studies on tributyltin carboxylates.[23] Also, the fact that little change in chemical shifts over a 20-fold change in concentration is seen supports the predominance of monomeric forms for **1** and **2**. Both tin and carbon chemical shifts are very similar to those reported for analogous monomeric tributyltin carboxylates.[23]

Structural Details. The trimethyltin esters **1** and **2** both exist in the solid state in polymeric forms due to an intermolecular O → Sn linkage in which the geometry about tin is essentially trigonal bipyramidal with axial O atoms and equatorial Me groups. In **1**, where the intermolecular bond to the tin atom is through the acyl oxygen atom, translationally related molecules are connected by 2_1-screw-related molecules. In **2** where the intermolecular bond to the tin atom is through the hydroxyl oxygen atom, translationally related molecules are connected by *n*-glide-related molecules. In both compounds, the acyl oxygen atom, O2, may be involved in a secondary intramolecular bonding interaction to the tin atom, similar to that which has been reported for related triphenyltin monomeric species.[3]

In **1**, the near equivalence of the inter- and intramolecular axial Sn–O bonds [2.381 (2) and 2.208 (2) Å] is reflected in the near coplanarity of the equatorial methyl carbon atoms and the tin atom (coplanar to within ±0.08 Å) and in the sum of the equatorial angles about the tin atom (359.1°). The angle O1–Sn–O2′ is 170.8 (1)°, which approaches the ideal value of 180°. However, the tin atom is displaced 0.119 Å out of the plane of the three methyl carbon atoms in a direction toward the more strongly coordinated O1. In **2**, the intermolecular bond Sn–O3′ is weaker than the intramolecular bond Sn–O1, as evidenced by bond lengths of 3.08 (1) and 2.114 (7) Å, respectively. The difference in these bonding interactions is in evidence in the geometry about the tin atom. In this case, the tin atom is displaced 0.350 Å in a direction toward O1, and the sum of the equatorial angles about the tin atom is reduced to 352.2°. The axial angle, O1–SnO3′ [173.4 (2)°], is similar to that found for **1**.

In **2**, there is an intramolecular hydrogen bond between the hydroxyl hydrogen atom, H3, and the acyl oxygen atom, O2, forming a six-membered ring. The six atoms of this ring are coplanar to within ±0.09 Å. This hydrogen-bonding interaction precludes an intermolecular bond involving O2 and is probably responsible for the fact that the intermolecular bond is through the hydroxyl oxygen atom, O3. The structure of **2** is very similar to the analogous triphenyltin salicylate, **21**,[3b] in which the intermolecular bonding also occurs via the hydroxyl oxgyen atom. For **21** the intermolecular Sn–O3′ bond distance is 3.035 (2) Å. This distance for the trimethyltin salicylate **2** is 3.077 (13) Å. This compares with the intramolecular Sn–O2 bond distances of 3.071 (2) Å for **21** and 3.029 (8) Å for **2**. Although the structures of **2** and **21** are similar, their ΔE_Q values are at opposite ends of the range for chain form C members (Table VII). The reason for this difference (0.50 mm s^{-1}) is not known, but it is noted that **21** is the only member of this class containing the Ph$_3$Sn grouping.

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Supplementary Material Available: Listings for Me$_3$SnO$_2$CC$_6$H$_4$OMe-2 (**1**) and Me$_3$SnO$_2$CC$_6$H$_4$OH-2 (**2**), respectively, of anisotropic thermal parameters (Tables S1 and S3), hydrogen atom parameters (Tables S2 and S4), additional distances and angles (Table S5), and deviations from selected least-squares mean planes (Tables S6 and S7) (8 pages). Ordering information is given on any current masthead page.

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