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Pentacoordinated Structures of Triphenyltin Esters of Anthranilic Acid, *o*-(Dimethylamino)benzoic Acid, and *p*-Aminobenzoic Acid Formed by Intramolecular Carboxylate Group Coordination[1,2]

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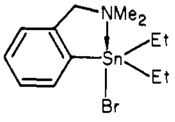
Triphenyltin esters of anthranilic acids were formed by the reaction of bis(triphenyltin) oxide with anthranilic acid, *o*-(dimethylamino)benzoic acid, and *p*-aminobenzoic acid (**4**–**6**), respectively. X-ray analysis revealed pseudo-pentacoordinated structures containing Ph_3Sn coordinated to the carboxylate group. The structural distortion in each is a displacement from the tetrahedron toward the trigonal bipyramid. Infrared and ^1H NMR spectra confirm that the structures are retained in solution in that coordination takes place via the two carboxylate oxygen atoms. Intramolecular hydrogen bonding is present in the triphenyltin anthranilate (**4**), while intermolecular hydrogen bonding is found in the para isomer, **6**. Biological implications are discussed. **4** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$) with $a = 12.476$ (4) Å, $b = 21.974$ (3) Å, $c = 7.962$ (2) Å, and $\beta = 98.64$ (2)°. Refinement gave $R = 0.033$ and $R_w = 0.039$. For **5**, the orthorhombic space group *Pccn* ($Z = 8$) was obtained with $a = 37.111$ (12) Å, $b = 17.119$ (4) Å, and $c = 7.479$ (2) Å. Refinement gave $R = 0.037$ and $R_w = 0.047$. The monoclinic space group $P2_1/c$ ($Z = 4$) was obtained for **6** with $a = 15.920$ (3) Å, $b = 9.111$ (3) Å, $c = 17.468$ (4) Å, and $\beta = 99.38$ (2)°. The structure refined to $R = 0.029$ and $R_w = 0.036$.

Introduction

Biochemically, triorganotin compounds have a highly specific action on mitochondrial oxidative phosphorylation.[5] The toxicity of R_3SnX compounds also is relatively independent of the type of attached electronegative substituent. This behavior has suggested that a substitution reaction resulting in displacement of the electronegative substituent is important in understanding observed toxicity variations.[6] For example, the very potent inhibitor action of the five-coordinated mixed triorganotin bromide **1** toward mitochondrial ATPase[7] (greater than that of the related four-coordinated triorganotin species) relative to the feeble action of the five-coordinated tributyltin derivative **2**[8] is consistent with the ease of displacement of bromide in **1**. The latter is aided by intramolecular coordination by the axially positioned Me_3N group, whereas in **2** there is no efficient leaving group. Here, tributyltin oxide $(Bu_3Sn)_2O$[9] is more toxic than **2**.



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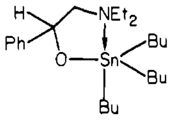

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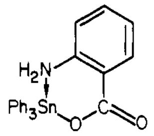
The specific nature of the interaction of triorganotin compounds at mitochondria is uncertain, although a high- and a low-affinity site has been identified in rat liver mitochondria.[10] Binding studies have implicated a histidine residue at the high-affinity ATPase site[7,11] and a thiol group at the low-affinity site.[12] Whether the tin at these sites is four- or five-coordinated is uncertain, although Mössbauer data are consistent with four- or possibly cis five-coordinated tin at the high-affinity binding site.[7] Recent studies on cat hemoglobin provided evidence for binding of triethyltin at two distinct sites[13] and implicated histidine and cysteine residues giving a pentacoordinated geometry.[13,14]

Further definition of the mechanism of toxic action of triorganotin compounds is hindered partly by the lack of knowledge of the competitive roles played by the biologically important ligands, N, O, and S, in their binding at tin and partly by the lack of knowledge regarding factors that will stabilize five-coordinated tin in various geometrical representations. To aid in this area, we undertook to examine the coordination of triphenyltin oxide with anthranilic acid and related carboxylic derivatives.

From an NMR study, Khoo and Smith[15] indicated that $(Ph_3Sn)_2O$ coordinates via a carboxylate oxygen and the amino nitrogen atom of anthranilic acid, giving the formulation **3**.



3

It is of interest to learn whether this structure exists in the solid state. Accordingly, an X-ray study was undertaken. The structural study was extended to include the related substances formed from the reaction of bis(triphenyltin) oxide with *o*-(dimethylamino)benzoic acid and *p*-aminobenzoic acid.

Whatever the coordination geometry of the anthranilic acid complex, hydrogen bonding is expected to be present. This feature will be absent in the triphenyltin ester of *o*-(dimethylamino)benzoic acid and allow an assessment of its influence. Infrared and NMR data were accumulated on the ester derivatives to establish whether there are any discernible structural changes between the solid and solution states.

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(1) Pentacoordinated Molecules. 56. Part 55: Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.

(2) Presented in part at the Fourth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead, Montreal, Quebec, Canada, Aug 8–11, 1983; see Abstract P2.

(3) Represents in part material from: Swisher, Robert G. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1982.

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Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer Model R12A NMR spectrometer at 60 MHz. Chemical shifts were measured in ppm relative to tetramethylsilane as an internal standard. The infrared spectra were recorded by using KBr windows on a Perkin-Elmer Model 180 spectrometer.

Synthesis. Both the preparation of (*o*-aminobenzoato)triphenyltin, $Ph_3Sn[o\text{-}(H_2N)C_6H_4CO_2]$ (4), and (*p*-aminobenzoato)triphenyltin, $Ph_3Sn[p\text{-}(NH_2)C_6H_4CO_2]$ (6), followed a procedure by Khoo and Smith.[15] Reaction of bis(triphenyltin) oxide with *o*-aminobenzoic acid (anthranilic acid) in refluxing benzene solution gave 4. In a similar fashion with the use of *p*-aminobenzoic acid, 6 was obtained.

Preparation of [*o*-(Dimethylamino)benzoato]triphenyltin, $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ (5). The ester 5, which is a new compound, was synthesized analogously to (*o*-aminobenzoato)triphenyltin (4). To 50 mL of spectral grade benzene in a 100-mL round-bottom flask was added 1.00 g (1.40 mmol) of (*o*-dimethylamino)benzoic acid with stirring. The flask was fitted with a Dean–Stark moisture trap and a water-cooled condenser. The solution was refluxed at 80 °C for 2 h. The solvent and water byproduct were removed by evaporation. The yellow oil that remained was dissolved in a mixture of 5 mL of anhydrous diethyl ether and 40 mL of Skelly-F (a mixture of aliphatic hydrocarbons, bp 35–60 °C). Upon refrigeration, a white powder formed. Recrystallization from an ether–Skelly-F mixture produced long, clear needlelike crystals; mp 79–80 °C; yield 1.03 g (72%). Anal. Calcd for $C_{27}H_{25}O_2NSn$: C, 63.07; H, 4.87; N, 2.73. Found: C, 63.08; H, 4.91; N, 2.75.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[16] All crystals were mounted in thin-walled glass capillary tubes, which were sealed as a precaution against moisture sensitivity.

X-ray Crystallographic Study for $Ph_3Sn[o\text{-}(H_2N)C_6H_4CO_2]$ (4). A colorless, multifaceted crystal (approximately 0.30 × 0.25 × 0.15 mm), obtained by recrystallization from petroleum ether, was used for the X-ray study.

Crystal Data for $C_{25}H_{21}O_2NSn$ (4). Uniquely determined monoclinic space group $P2_1/c$ [C_{2h}^5–No. 14],[17] $a = 12.476$ (4) Å, $b = 21.974$ (3) Å, $c = 7.962$ (2) Å, $\beta = 98.64$ (2)°, $Z = 4$, $\mu_{Mo\,K\alpha} = 1.214$ mm^{-1}. A total of 3797 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{Mo\,K\alpha} \leq 50°$. No corrections were made for absorption.

The structure was solved by using standard Patterson and difference-Fourier techniques and was refined by full-matrix least-squares procedures.[18] The 29 independent non-hydrogen atoms were refined anisotropically, while the 21 independent hydrogen atoms were refined as isotropic scatterers. The final agreement factors[19] were $R = 0.033$ and $R_w = 0.039$ for the 2964 reflections having $I \geq \sigma_I$. A final difference-Fourier synthesis showed a maximum density of 0.31 e/Å^3.

X-ray Crystallographic Study for $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ (5). Crystals were grown from a diethyl ether–Skelly-F mixture. A crystal having the dimensions 0.40 × 0.40 × 0.15 mm, which was cut from a long,colorless needle, was used for the X-ray study.

Crystal Data for $C_{27}H_{25}O_2NSn$ (5). Uniquely determined orthorhombic space group *Pccn* [D_{2h}^{10}–No. 56],[20] $a = 37.111$ (12) Å, $b = 17.119$ (4) Å, $c = 7.479$ (2) Å, $Z = 8$, $\mu_{Mo\,K\alpha} = 1.107$ mm^{-1}. A total of 2712 independent reflections (hkl) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{Mo\,K\alpha} \leq 43°$. No corrections were made for absorption.

The structure was solved and refined by using the techniques that were applied for 4. The 31 independent non-hydrogen atoms were refined anisotropically. The 19 independent phenyl 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 six methyl hydrogen atoms were omitted from the refinement. The final agreement factors were $R = 0.037$ and $R_w = 0.047$ for the 1799 reflections having $I \geq 3\sigma_I$. A final difference-Fourier synthesis showed a maximum density of 0.41 e/Å^3.

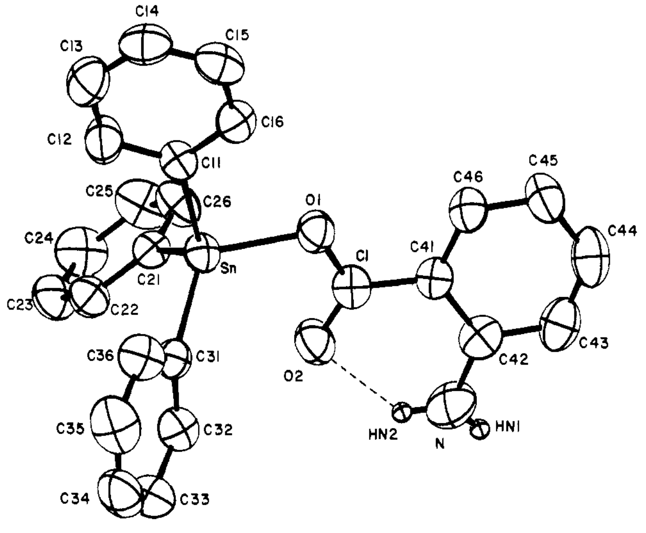

Figure 1. ORTEP plot of $Ph_3Sn[o\text{-}(H_2N)C_6H_4CO_2]$ (4) with thermal ellipsoids shown at the 50% probability level. All but the amino hydrogen atoms, which are shown as spheres of arbitrary radius, have been omitted for purposes of clarity.

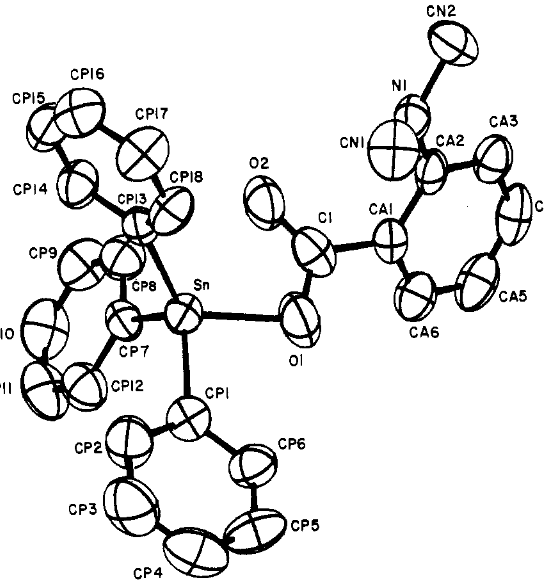

Figure 2. ORTEP plot of $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ (5) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

X-ray Crystallographic Study for $Ph_3Sn[p\text{-}(H_2N)C_6H_4CO_2]\cdot{}^1/_2C_6H_6$ (6). A colorless crystal (0.18 × 0.25 × 0.30 mm), obtained by recrystallization from a benzene–Skelly-B mixture, was used for the X-ray study.

Crystal Data for $C_{25}H_{21}O_2NSn\cdot{}^1/_2C_6H_6$ (6). Uniquely determined monoclinic space group $P2_1/c$ [C_{2h}^5–No. 14],[17] $a = 15.920$ (3) Å, $b = 9.111$ (3) Å, $c = 17.468$ (4) Å, $\beta = 99.38$ (2)°, $Z = 4$, $\mu_{Mo\,K\alpha} = 1.054$ mm^{-1}. A total of 4380 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{Mo\,K\alpha} \leq 50°$. No corrections were made for absorption.

The structure was solved and refined by using the same techniques that were applied for 4. The 32 independent non-hydrogen atoms were refined anisotropically. The 19 independent phenyl hydrogen atoms were treated as described for 5. Coordinates for the two independent amino hydrogen atoms were obtained from a difference-Fourier synthesis. HN1 was included in the refinement as a fixed isotropic scatterer, while HN2 was refined isotropically. The hydrogen atoms of the benzene of solvation were omitted from the refinement.

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(18) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_I$. Mean atomic scattering factors were taken from: Reference 17, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Sn and O were taken from the same source (pp 149–150).

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

(20) Reference 17, p 144.

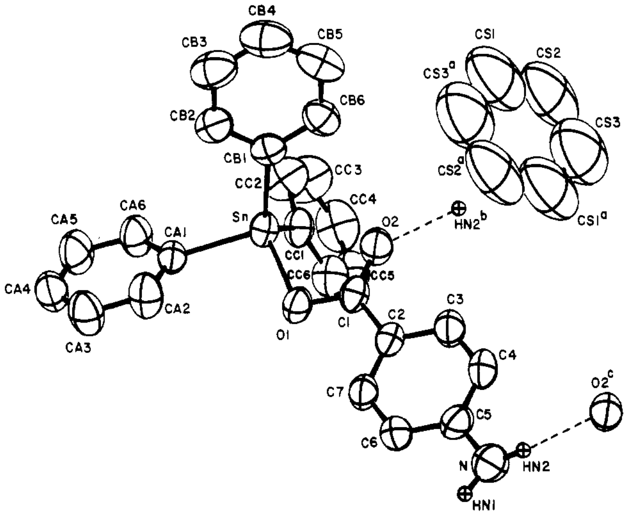

Figure 3. ORTEP plot of $Ph_3Sn[p\text{-}(H_2N)C_6H_4CO_2]\cdot{}^1/_2C_6H_6$ (**6**) with thermal ellipsoids shown at the 50% probability level. All but the amino hydrogen atoms, shown as spheres of arbitrary radius, have been omitted for purposes of clarity. A symmetry-related half-solvent molecule, HN2, and O2 are shown, where the symmetry operators are $a = 1 - x, 1 - y, 1 - z$; $b = 1 - x, y - {}^1/_2, {}^1/_2 - z$; $c = 1 - x, {}^1/_2 + y, {}^1/_2 - z$. Hydrogen-bonding interactions are represented by dashed lines.

Table I. Atomic Coordinates in Crystalline $(C_6H_5)_3Sn[o\text{-}(H_2N)C_6H_4CO_2]$ (4)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	6874.9 (2)	717.1 (1)	2030.1 (4)
O1	6985 (2)	−196 (1)	1605 (4)
O2	8414 (3)	75 (1)	457 (4)
N	9324 (4)	−781 (3)	−1314 (8)
C11	5346 (3)	691 (2)	2910 (5)
C12	4979 (4)	1195 (2)	3697 (7)
C13	3970 (5)	1186 (3)	4228 (8)
C14	3321 (4)	681 (3)	3979 (7)
C15	3684 (4)	177 (3)	3221 (7)
C16	4680 (4)	182 (2)	2687 (6)
C21	8259 (3)	996 (2)	3766 (5)
C22	8652 (4)	1581 (2)	3629 (6)
C23	9548 (4)	1786 (2)	4711 (6)
C24	10070 (4)	1410 (3)	5934 (7)
C25	9694 (4)	825 (3)	6108 (7)
C26	8794 (4)	621 (2)	5016 (7)
C31	6747 (3)	1274 (2)	−172 (5)
C32	7622 (4)	1407 (2)	−977 (6)
C33	7536 (5)	1822 (2)	−2318 (7)
C34	6552 (6)	2101 (3)	−2850 (7)
C35	5679 (5)	1974 (3)	−2062 (7)
C36	5763 (4)	1564 (2)	−730 (6)
C41	7894 (3)	−975 (2)	361 (5)
C42	8660 (3)	−1173 (2)	−665 (6)
C43	8678 (4)	−1801 (2)	−1047 (7)
C44	7994 (4)	−2200 (2)	−446 (8)
C45	7258 (4)	−2007 (2)	589 (8)
C46	7215 (4)	−1400 (2)	956 (6)
C1	7792 (3)	−331 (2)	793 (5)

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

The final agreement factors were $R = 0.029$ and $R_w = 0.036$ for the 3308 reflections having $I \geq 2\sigma_I$. A final difference-Fourier synthesis showed a maximum density of 0.295 e/Å^3.

Table II. Atomic Coordinates in Crystalline $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ (5)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn	1436.3 (1)	−125.9 (3)	2082.5 (8)
O1	1284 (2)	863 (3)	563 (9)
O2	894 (2)	−37 (4)	−35 (9)
C1	1009 (3)	621 (6)	−289 (12)
N1	239 (2)	956 (3)	−799 (9)
CA1	869 (2)	1162 (4)	−1722 (9)
CA2	496 (2)	1238 (4)	−2019 (11)
CA3	391 (2)	1616 (4)	−3607 (11)
CA4	647 (3)	1933 (4)	−4741 (11)
CA5	1002 (3)	1899 (5)	−4359 (12)
CA6	1116 (2)	1521 (4)	−2836 (11)
CN1	307 (3)	1114 (5)	1128 (12)
CN2	−147 (2)	989 (6)	−1317 (15)
CP1	1781 (2)	539 (4)	3764 (10)
CP2	1931 (3)	225 (5)	5266 (13)
CP3	2139 (3)	640 (7)	6402 (14)
CP4	2207 (2)	1424 (7)	6098 (14)
CP5	2065 (3)	1748 (5)	4630 (13)
CP6	1855 (2)	1332 (5)	3448 (11)
CP7	1708 (2)	−875 (4)	233 (10)
CP8	1514 (2)	−1288 (5)	−1074 (12)
CP9	1700 (2)	−1772 (5)	−2248 (11)
CP10	2062 (3)	−1859 (5)	−2170 (13)
CP11	2253 (2)	−1467 (6)	−903 (13)
CP12	2078 (2)	−970 (5)	318 (11)
CP13	1062 (2)	−741 (4)	3723 (10)
CP14	1031 (2)	−1536 (5)	3580 (11)
CP15	794 (2)	−1958 (5)	4654 (12)
CP16	587 (2)	−1572 (5)	5914 (11)
CP17	613 (2)	−772 (5)	6065 (11)
CP18	855 (2)	−370 (5)	4975 (12)

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

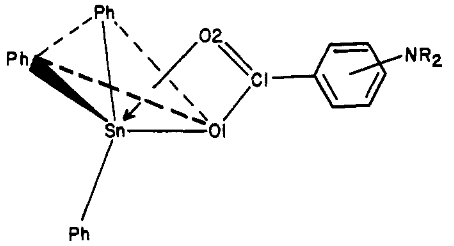

Figure 4. Schematic representation of distortion in the triphenyltin aminobenzoates **4**–**6**.

Results

The atom labeling schemes for **4**–**6** are shown in the ORTEP plots of Figures 1–3, respectively. Atomic coordinates are listed in Tables I–III. Selected bond lengths and angles for the three compounds are given in Tables IV–VI. NMR and infrared data are listed in Table VII. Anisotropic thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from some least-squares mean planes are provided as supplementary material.

Discussion

Solid-State Structural Aspects. All three triphenyltin ester structures **4**–**6** can be referred to an idealized geometry in which the Sn is involved in four covalent bonds having a distorted tetrahedral geometry about the tin center, while the carboxyl oxygen atom is involved in a fifth weaker bonding interaction with tin in which it approaches a tetrahedral face. The Sn–aminobenzoate system and the Sn–C_{Ph} bond opposite the aforementioned tetrahedral face tend toward coplanarity (Figure 4). Tin-119m Mössbauer data give quadrupolar splittings that are consistent with the presence of five-coordinated tin in this structural representation.[21]

The average deviation of the atoms from the axial plane, Sn, O1, O2, C_{ax}, ranges between ±0.016 and ±0.14 Å, with the *p*-aminobenzoate derivative **6** showing the least atom deviation (Table VIII). The dihedral angle between the axial

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(21) Smith, P. J., personal communication.

Table III. Atomic Coordinates in Crystalline $Ph_3Sn[p\text{-}(H_2N)C_6H_4CO_2]\cdot{}^1/_2C_6H_6$ (6)[a]

atom type[b]	coordinates 10^4x	10^4y	10^4z
Sn	1606.1 (1)	1447.2 (3)	1209.1 (1)
O1	2240 (1)	2527 (3)	2178 (1)
O2	3212 (1)	2259 (3)	1435 (1)
N	5284 (2)	6011 (5)	4210 (2)
C1	3014 (2)	2738 (4)	2043 (2)
C2	3603 (2)	3555 (4)	2624 (2)
C3	4420 (2)	3875 (4)	2487 (2)
C4	4973 (2)	4686 (5)	3009 (2)
C5	4726 (2)	5222 (5)	3686 (2)
C6	3903 (2)	4896 (5)	3826 (2)
C7	3359 (2)	4080 (4)	3300 (2)
CA1	382 (2)	1362 (4)	1561 (2)
CA2	106 (3)	2376 (5)	2048 (3)
CA3	−687 (3)	2249 (6)	2271 (3)
CA4	−1216 (3)	1126 (5)	1992 (3)
CA5	−961 (3)	125 (5)	1492 (3)
CA6	−164 (2)	246 (5)	1288 (2)
CB1	1493 (2)	2717 (4)	179 (2)
CB2	684 (3)	3244 (4)	−134 (2)
CB3	560 (3)	3999 (6)	−833 (3)
CB4	1224 (4)	4245 (6)	−1218 (3)
CB5	2031 (4)	3737 (5)	−919 (3)
CB6	2166 (3)	2970 (5)	−222 (2)
CC1	2088 (2)	−721 (4)	1188 (2)
CC2	1803 (3)	−1616 (5)	562 (3)
CC3	2076 (4)	−3084 (6)	568 (3)
CC4	2626 (3)	−3621 (5)	1169 (4)
CC5	2911 (3)	−2755 (5)	1791 (3)
CC6	2636 (3)	−1300 (4)	1808 (2)
CS1	5301 (8)	4001 (10)	−494 (6)
CS2	5830 (6)	4378 (14)	231 (7)
CS3	5491 (7)	5408 (14)	701 (6)

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

Table IV. Selected Distances (Å) and Angles (deg) for $Ph_3Sn[o\text{-}(H_2N)C_6H_4CO_2]$ (4)[a]

Distances			
Sn-O1	2.043 (3)	C1-O1	1.310 (5)
Sn-O2	2.823 (3)	C1-O2	1.237 (5)
Sn-C11	2.129 (4)	N-C42	1.352 (7)
Sn-C21	2.134 (4)	N-HN1	0.73 (5)
Sn-C31	2.124 (4)	N-HN2	0.88 (5)
C1-C41	1.467 (6)	O2- - -HN2	2.04 (6)
Angles			
O1-Sn-C11	96.5 (1)	O1-C1-C41	115.8 (4)
O1-Sn-C21	108.8 (1)	O2-C1-C41	124.4 (4)
O1-Sn-C31	115.3 (1)	O1-C1-O2	119.8 (4)
C11-Sn-C21	118.2 (2)	C1-C41-C46	119.3 (4)
C11-Sn-C31	109.1 (2)	C1-C41-C42	121.5 (4)
C21-Sn-C31	108.8 (2)	N-C42-C41	122.0 (4)
O2-Sn-O1	50.8 (1)	N-C42-C43	120.6 (5)
O2-Sn-C11	146.6 (1)	C42-N-HN1	112 (4)
O2-Sn-C21	83.3 (1)	C42-N-HN2	120 (4)
O2-Sn-C31	83.9 (1)	HN1-N-HN2	127 (5)
Sn-O1-C1	112.3 (3)	N-HN2- - -O2	131 (4)
Sn-O2-C1	77.0 (2)	C1-O2- - -HN2	101 (4)

[a] See footnotes *a* and *b* of Table I.

Table V. Selected Distances (Å) and Angles (deg) for $Ph_3Sn[o\text{-}(Me_2N)C_6H_4CO_2]$ (5)[a]

Distances			
Sn-O1	2.115 (6)	C1-O1	1.272 (9)
Sn-O2	2.564 (7)	C1-O2	1.22 (1)
Sn-CP1	2.126 (8)	N-CA2	1.404 (9)
Sn-CP7	2.138 (7)	N-CN1	1.49 (1)
Sn-CP13	2.131 (7)	N-CN2	1.49 (1)
C1-CA1	1.51 (1)	CN1,O2	3.06 (1)
Angles			
O1-Sn-CP1	92.9 (3)	O1-C1-CA1	115.6 (9)
O1-Sn-CP7	104.9 (3)	O2-C1-CA1	123.9 (9)
O1-Sn-CP13	122.1 (3)	O1-C1-O2	120.2 (9)
CP1-Sn-CP7	114.8 (3)	C1-CA1-CA6	118.3 (7)
CP1-Sn-CP13	108.4 (3)	C1-CA1-CA2	120.5 (7)
CP7-Sn-CP13	112.6 (3)	N-CA2-CA1	122.2 (7)
O2-Sn-O1	54.0 (2)	N-CA2-CA6	121.2 (7)
O2-Sn-CP1	143.7 (3)	CA2-N-CN1	116.9 (7)
O2-Sn-CP7	90.3 (2)	CA2-N-CN2	118.2 (7)
O2-Sn-CP13	82.7 (2)	CN1-N-CN2	114.2 (7)
Sn-O1-C1	102.2 (9)		
Sn-O2-C1	82.9 (6)		

[a] See footnotes *a* and *b* of Table II.

Table VI. Selected Distances (Å) and Angles (deg) for $Ph_3Sn[p\text{-}(H_2N)C_6H_4CO_2]\cdot{}^1/_2C_6H_6$ (**6**)[a]

Distances			
Sn-O1	2.072 (2)	C1-O1	1.306 (4)
Sn-O2	2.629 (2)	C1-O2	1.236 (4)
Sn-CA1	2.138 (3)	N-C5	1.371 (5)
Sn-CC1	2.122 (4)	N-HN2	0.87 (4)
Sn-CB1	2.122 (4)	O2- - -HN2	2.16 (4)
C1-C2	1.468 (5)		
Angles			
O1-Sn-CA1	97.4 (1)	O1-C1-C2	117.8 (3)
O1-Sn-CC1	109.1 (1)	O2-C1-C2	123.3 (3)
O1-Sn-CB1	113.3 (1)	O1-C1-O2	118.9 (3)
CA1-Sn-CC1	108.7 (1)	C1-C2-C7	121.8 (3)
CA1-Sn-CB1	107.9 (1)	C1-C2-C3	119.8 (3)
CC1-Sn-CB	118.3 (1)	N-C5-C4	120.6 (3)
O2-Sn-O1	54.0 (1)	N-C5-C6	121.1 (4)
O2-Sn-CA1	151.3 (1)	C5-N-HN2	118 (3)
O2-Sn-CC1	85.4 (1)	N-HN2- - -O2[b]	175 (4)
O2-Sn-CB1	85.4 (1)	C1-O2- - -HN2[c]	142 (1)
Sn-O1-C1	105.7 (2)		
Sn-O2-C1	81.4 (2)		

[a] See footnotes *a* and *b* of Table III. [b] Coordinates are related to those in the coordinate list by $1 - x$, ${}^1/_2 + y$, ${}^1/_2 - z$.
[c] Coordinates are related to those in the coordinate list by $1 - x$, $y - {}^1/_2$, ${}^1/_2 - z$.

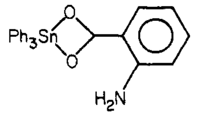
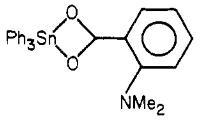
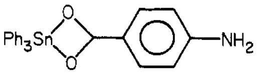
plane and the equatorial plane defined by O1 and the carbon atoms of the other two phenyl groups is close to 90°, that expected for the formation of a trigonal bipyramid. Comparison of the axial $Sn-C_{Ph}$ bond with the equatorial $Sn-C_{Ph}$ bond lengths shows an axial–equatorial bond length difference Δ, which is greatest again for **6** (0.016 (3) Å), again in accord with **6** expressing the greatest distortion toward the trigonal bipyramid (Table VIII).

However, the degree of distortion still is considerably removed from the ideal trigonal bipyramid. The displacement of the tin atom out of the equatorial plane toward the axial C_{Ph} atom varies from 0.543 Å for **6** to 0.645 Å for **4**. Consistent with the smallest displacement for the tin atom in **6** is the presence of the largest $O2-Sn-C_{Ph}$ axial angle, 151.3 (1)°. This angle ranges down to 143.7 (3)° for **5** (Table VIII).

On the basis of the above, the Sn–O2 distance for **6** (2.629 (2) Å) should be the shortest, i.e., for the most trigonal-bipyramidal derivative. However, this distance is shortest for **5** (2.564 (9) Å). The van der Waals sum for an oxygen and a tin atom is 3.7 Å,[21] over 1 Å longer than the Sn–O2 lengths observed here. The shorter Sn–O2 length for **5** is in agreement with the greater electron-donating properties of the Me_2N substituent over that for the NH_2 group, which is present in **4** and **6**. Two additional effects are operating here. First, the presence of hydrogen bonding in **4** and **6** tends to increase the Sn–O2 distances. Second, steric hindrance caused by the NMe_2 group in **5** tends to tilt O2 out of the axial plane. The steric hindrance apparently is effective in increasing the distortion of **5**, from the trigonal bipyramid relative to that for **6** (see Table VIII).

The amino groups in **4** and **6** are both involved in hydrogen-bonding interactions with the carboxyl oxygen atom. In **4**, there is an intramolecular hydrogen bond between the amino

Table VII. Proton NMR and Infrared Data on Ph_3Sn Esters

no.	compd	^1H NMR[a] (δ ±0.05): aromatic	^1H NMR[a] (δ ±0.05): N-H or N-CH_3	infrared, cm^{-1}: Nujol	infrared, cm^{-1}: CCl_4	infrared, cm^{-1}: assgnt
4		7.75[b] (m, 6 H) 7.38 (m, 9 H) 6.55 (m, 4 H)	5.60[c] (2 H)	3480 3360 1625	3500 3360 1620	N-H (st) N-H (st) C=O (st)
5		7.80 (m, 6 H) 7.50 (m, 13 H)	2.70 (s, 6 H)[d]	1615	1615	C=O (st)
6		7.78 (m, 6 H) 7.32 (m, 9 H) 6.52 (m, 4 H)	3.80[c] (2 H)	3480 3370 1625	3490 3400 1620	N-H (st) N-H (st) C=O (st)

[a] NMR spectra were all recorded in CCl_4 solution with Me_4Si as the internal reference. [b] Center of a multiplet. [c] Center of a broad absorption. [d] ^1H NMR chemical shift of *o*-(dimethylamino)benzoic acid: N-CH_3 2.80 (s).

Table VIII. Bond Parameters for the Triphenyltin Aminobenzoates Showing Distortion toward the Trigonal Bipyramid

	4	5	6
ax. C_{Ph}	C11	CP1	CA1
av atom displcmnt from ax plane, Sn,O1,O2,C_{Ph}/Å	±0.070	±0.14	±0.016
dihedral angle between ax and eq planes/deg	88.1	87.6	89.8
Δ(ax-eq) Sn-C bond distances/Å	0.000 (4)	−0.009 (7)	0.016 (3)
Sn atom displcmnt from plane of eq C atoms/Å	0.645	0.562	0.543
O2-Sn-C_{ax}/deg	146.6 (1)	143.7 (3)	151.3 (1)
sum of eq angles at Sn/deg	332.9 (4)	339.6 (9)	340.7 (3)

hydrogen atom, HN2, and the carboxyl oxygen atom, O2 [O2---HN2 = 2.04 (6) Å], forming a six-membered ring in which the six atoms are coplanar to within ±0.05 Å. In **6**, the amino hydrogen atom HN2 is hydrogen bonded to a 2_1 screw-related carboxyl oxygen atom, O2 [O2---HN2 = 2.16 (4) Å], forming a helical hydrogen-bonded chain. Both of these hydrogen bonds are much less than the sum of the oxygen and hydrogen van der Waals radii, 2.7 Å.[22] The intramolecular hydrogen bond in **4** is more effective in lengthening the affected Sn–O bond length compared to the intermolecular hydrogen bond in **6**. The respective Sn–O2 lengths, 2.823 (3) and 2.629 (2) Å, are longer than that for **5** (2.564 (7) Å), which lacks hydrogen bonding.

In **5**, deviations from the idealized planar geometry of the benzoate moiety are caused by crowding involving the dimethylamino group. Even with the distortions, CN1 is 3.06 (1) Å away from O2 as compared to the van der Waals sum for an oxygen atom and a methyl group of 3.4 Å.[22] Torsion angles about the C1–CA1, CA1–CA2, and CA2–N1 bonds are 43.8, 13.6, and 43.9°, respectively. Concomitant with these torsion angles, O2 and CN1 are displaced −1.156 and 1.088 Å, respectively, from the plane of the phenyl group (CA1 through CA6).

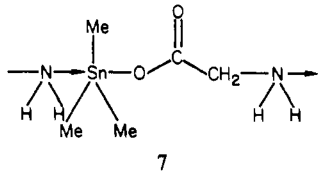
Solution Structure. As mentioned in the introduction, Khoo and Smith[15] postulated the structural form **3** for the coordination of anthranilic acid with triorganotin compounds. The conclusion that coordination occurs via the amine nitrogen atom was based on the deshielding experienced by ortho amino protons of the anthranilates relative to the amino protons of the *p*-aminobenzoates.

In view of our solid-state X-ray results showing coordination exclusively via the carboxylate oxygen atoms for **4**–**6**, we examined the infrared and ^1H NMR spectra in both the solid and solution states. The infrared results in Table VII show no significant spectral changes between the solid and solution state for any of the triphenyltin anthranilates, **4**–**6**. The lowering of the C═O stretching frequency from ~1665 cm^{-1} in the parent anthranilic acids[23] to 1615–1625 cm^{-1} in these compounds is indicative of C═O group coordination. If coordination via the nitrogen atom of anthranilic acid occurred in solution to give **3**, the N—H and C═O stretching frequencies for the *p*-aminobenzoate isomer **6** should differ from those for **4** since coordination of the para isomer to give **3** is not possible. Since these frequencies are remarkably constant between these isomeric derivatives as well as between the solid and solution state, it is concluded that the infrared data indicate that the solution state structures of **4**–**6** are the same as the X-ray structures reported herein. Molecular weight data (vapor pressure osmometry) in CCl_4 at the concentration used to record the IR spectrum showed a value near the monomeric formulation for **6**.

The same conclusion is consistent with the NMR observations. The larger downfield proton shift for the triphenyltin anthranilate (**4**) compared to the para amino derivative **6** is in agreement with the presence in the solid state of the intramolecular hydrogen bond between the carbonyl group and the ortho amino protons of **4**. Further, if nitrogen to tin coordination is an explanation of the downfield shift for the amino protons of **4**, a downfield shift for the NCH_3 protons of **5** relative to its parent carboxylic acid should be observed. However, this chemical shift for **5** did not significantly vary from that of the parent acid (Table VII).

The larger shifts on dilution for the amino protons of *p*-aminobenzoates relative to *o*-aminobenzoates of triorganotins[15] are consistent with a decrease in intermolecular hydrogen bonding as shown to be present in the X-ray structure of **6**.

Related Substances and Biochemical Implications. It is instructive to compare the structures of trimethyltin glycinate (**7**)[24] and (ethyl L-cysteinato-*S*,*N*)chlorodimethyltin (**8**)[25] with



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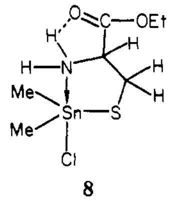

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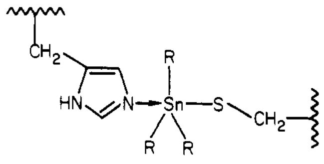
those for the triphenyltin anthranilates, **4**–**6**. In contrast to the structures of the anthranilates **4**–**6**, both **7** and **8** exhibit coordination via the nitrogen atoms. Amine coordination to tin in **8** is in keeping with pentacoordinate principles in that a relatively strain-free five-membered ring forms.[26] Intramolecular coordination at oxygen would give a strained six-membered ring (similar to what would occur if the triphenyltin anthranilates assumed the structural form **3**), while formation of the chain structure of the type **7**, either through coordination by way of oxygen or nitrogen, places the more electronegative chlorine atom at an equatorial site. Normally, the chain structure, similar to **7**, is the one preferred by the Me$_3$Sn group linked by donor groups to give a pentacoordinated geometry.[27] However, when carboxylate groups are attached to Me$_3$Sn, the preferred coordination for the chain arrangement places the more electronegative carboxylate oxygen atoms axially. The structure of **7** appears to be an isolated example that has both an amine and a carboxylate group present. The discrete, pentacoordinated structural form observed for **4**–**6**, instead of the chain rearrangement, is understandable in that the more electronegative phenyl group occupies an axial position more readily than a methyl group. Other examples involving pentacoordination of Ph$_3$Sn usually exist in the structural form analogous to **4**–**6**.[27–30]

One might consider that the larger size of the phenyl group may contribute in stabilizing the discrete structural forms for **4**–**6** relative to the chain form of the type **7**. However, an examination of ligand positioning in the trigonal bipyramid reveals an additional factor that may be more important. The donor bond in the axial position of the discrete form usually is longer than the donor bond, leading to the chain arrangement,[31] assuming of course that the same R$_3$Sn moiety is involved. On this basis, the stronger donating ligand, oxygen, may take part in preferentially stabilizing the discrete form while nitrogen coordination is made more likely in the chain form where the donor interaction appears more intimate. The donor orientation at an axial site of the discrete form, trans to an R group, accounts for the longer axial–Sn bond compared to the length of the donor bond at the axial site of the chain form, trans to another electronegative group.

Based on the above, a plausible biochemical model of toxic action of Et$_3$Sn binding implicating histidine and cysteine residues in a pentacoordinated conformation[7,13,14] would give preference to a trans arrangement, **9**, placing nitrogen and sulfur atoms at axial sites, if size effects are neglected. This does not take into account the nature of the enzyme active site, which may be effective in favoring the cis arrangement, **10**, by appropriately positioning the amino acid residues. In one such study of the binding of triethyltin to cat hemoglobin, the ^{119}Sn Mössbauer spectrum showed a quadrupole splitting of 1.74 mm s^{-1}, consistent with a cis orientation of sulfur and nitrogen for donor ligands around pentacoordinate tin.[13] An example of an X-ray structure that contains these ligands in the trans arrangement is found in the triphenyltin derivative of *p*-thiopyridone (**11**).[32]



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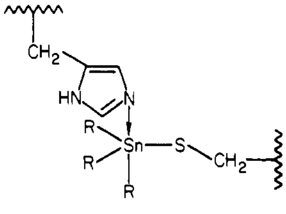

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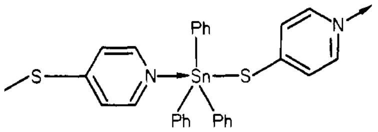

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Thus, while factors important in forming pentacoordinated tin geometries have been elucidated, the appropriate model to apply to a biochemical system as yet remains uncertain.

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Registry No. **4**, 77928-14-4; **5**, 91239-80-4; **6**, 61057-42-9; **6**·$^1/_2$C$_6$H$_6$, 91239-81-5; *o*-(dimethylamino)benzoic acid, 610-16-2; bis(triphenyltin) oxide, 1262-21-1.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Tables A–C), hydrogen atom parameters (Tables D–F), additional bond lengths and angles (Tables G–I), and deviations from least-squares mean planes (Tables J–L) for **4**–**6** (47 pages). Ordering information is given on any current masthead page.

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