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Tri-*n*-butyltin 2,6-Difluorobenzoate, a Unique Macrocyclic Tetramer Containing a 16-Membered $Sn_4C_4O_8$ Ring, and Other Related Compounds

Marcel Gielen,[*,†] Abdelaziz El Khloufi,[†] Monique Biesemans,[†,‡]
François Kayser,[†,‡] and Rudolph Willem[†,‡]

Faculty of Applied Sciences, Laboratory for General and Organic Chemistry (AOSC), Room 8G512, and High Resolution NMR Centre, Free University of Brussels (V.U.B.), Pleinlaan 2, B-1050 Brussels, Belgium

Bernard Mahieu

Catholic University of Louvain, INAN, B-1348 Louvain-la-Neuve, Belgium

Dominique Maes, John N. Lisgarten, and Lode Wyns

Free University of Brussels (V.U.B.), Department of Ultrastructure, Institute of Molecular Biology, Paardenstraat 65, B-1640 Sint-Genesius Rode, Belgium

Alex Moreira, Tapan K. Chattopadhay, and Rex A. Palmer

Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E7HX, UK

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The X-ray crystal structure determination of tri-*n*-butyltin 2,6-difluorobenzoate, compound 4, revealed the compound to exist as a macrocyclic tetramer with $\bar{4}$ symmetry. The five-coordinated tin atoms have distorted trigonal bipyramidal geometries with the three butyl groups occupying equatorial positions and the carboxylate ligands bridging the tin atoms as bidentate ligands in apical positions. Crystals of the compound 2,6-$F_2C_6H_3CO_2SnBu_3$, M_r = 447.12, are tetragonal, space group $I\bar{4}$, with $Z = 8$ in a unit cell of dimensions a = 15.631(3) Å, c = 16.882(1) Å with R = 0.037 for 3151 unique reflections. In the cyclotetramer, each tin atom exhibits one strong and one weak Sn–O bond. The synthesis and spectral characterization of eight other related tri-*n*-butyltin carboxylates are presented. As for compound 4, its solution structure is monomeric, with a tetrahedral tin atom.

Introduction

A recent review by Tiekink[1] reveals that, basically, triorganotin carboxylates belong to three classes of structure in the crystalline state: **a**, **b**, and **c** (see Figure 1). Structure class **a** is characterized by a four-coordinate distorted tetrahedral tin atom; a typical example of class **a** is triphenyltin salicylate,[2] in which the bonding oxygen–tin distance is 2.083(2) Å and the nonbonding one, 3.071(2) Å. In trimethyltin salicylate, however, tin is five-coordinate as the trimethyltin moiety is bound to a monodentate carboxylate group as well as to the *o*-hydroxyl group of a neighboring monomer unit.[3]

Structure class **b** contains a five-coordinate tin atom with a bidentate carboxylate moiety. This geometry is based on a distorted trigonal bipyramid with the carboxylate oxygen atoms spanning one apical and one equatorial position. A typical example of class **b** is triphenyltin *o*-(dimethylamino)benzoate,[4] in which the two bonding tin–oxygen distances are 2.564(7) and 2.115(6) Å, respectively. Both structures **a** and **b** are monomeric. It is interesting to note that triphenyltin *o*-aminobenzoate[4] is characterized by a quite long coordination bond (2.823(3) Å) as compared to that of the dimethylamino analog (2.564(7) Å) due, in part, to the presence of an intramolecular hydrogen bond between the carbonyl oxygen and the *o*-NH_2 group.

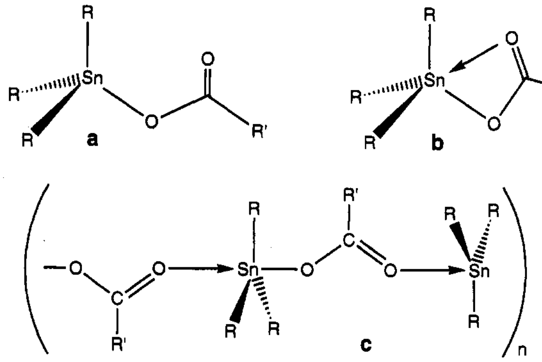

Figure 1. Three structure classes for compounds of the type R′COOSnR$_3$.[1]

Structure class **c** is polymeric, with bidentate carboxylates bridging the five-coordinate tin atoms of the polymeric chain. A typical example is triphenyltin acetate,[5] in which

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[†] Faculty of Applied Sciences, Free University of Brussels.

[‡] High Resolution NMR Centre, Free University of Brussels.

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the two bonding tin–oxygen distances are 2.185(3) and 2.349(3) Å. The O–Sn–O angle is 173.6(1)°. The crystal structure of only one tri-*n*-butyltin carboxylate of this class, tri-*n*-butyltin indole-3-acetate,[6] has so far been determined. Its coordination bond between the carbonyl oxygen and tin is 2.524(3) Å, a distance significantly longer than 2.199(3) Å for the covalent O–Sn bond, and the O–Sn–O angle is 173.5(2)°. The choice of structures in these systems is dictated[7,8] by both steric and electronic effects.

This paper presents a structure type unreported up to now for triorganotin carboxylates. It consists of a macrocyclic tetramer. The physical characteristics of some other related compounds are likewise reported.

Results and Discussion

Synthesis. The tri-*n*-butyltin compounds were synthesized by a 1:1 condensation of tri-*n*-butyltin acetate with the appropriate substituted benzoic acids.[9]

$$\mathrm{XYZC_6H_2CO_2H + CH_3CO_2SnBu_3 \rightarrow XYZC_6H_2CO_2SnBu_3 + CH_3COOH}$$

1: X,Y,Z = 2-F, H, H
2: X,Y,Z = 2,3-F_2, H
3: X,Y,Z = 2,5-F_2, H
4: X,Y,Z = 2,6-F_2, H
5: X,Y,Z = 3,5-F_2, H
6: X,Y,Z = 3-CH_3O, 2-OH, H
7: X,Y,Z = 4-CH_3O, 2-OH, H
8: X,Y,Z = 5-CH_3O, 2-OH, H
9: X,Y,Z = 6-$(CH_3)_2CH$, 3-CH_3, 2-OH

After having distilled off the acetic acid generated, together with the solvent ethanol/toluene, the compounds were purified either by recrystallization or by distillation under vacuum. Details are given in the Experimental Section.

X-ray Diffraction Data and Structure of Tri-*n*-butyltin 2,6-Difluorobenzoate. The atomic fractional coordinates of tri-*n*-butyltin 2,6-difluorobenzoate, compound 4, are given in Table 1. The atom numbering is shown in ORTEP drawing, Figure 2, and the molecular structure of the macrocyclic tetramer 4, in Figure 3. Selected interatomic parameters are listed in Table 2. Compound 4 displays an unusual macrocyclic tetrameric structure. The cyclotetramer has $\bar{4}$ symmetry. Operation of the transformations $(y + {}^1/_2, -x + {}^1/_2, -z + {}^3/_2)^b$, $(-x + 1, -y, z)^c$, and $(-y + {}^1/_2, x - {}^1/_2, -z + {}^3/_2)^d$ on the asymmetric unit (Figure 2) results in formation of the tetrameric unit (Figure 3). The contributing moieties are designated a(xyz), b, c, and d in Figure 3.

Table 1. Atomic Fractional Coordinates of Tri-*n*-butyltin 2,6-Difluorobenzoate, Compound 4

	x	*y*	*z*
Sn(1)	0.35351(2)	0.17839(2)	0.71891(2)
O(41)	0.4349(2)	0.2875(3)	0.6890(2)
O(42)	0.5454(2)	0.2318(3)	0.7535(2)
F(44)	0.5717(3)	0.3078(3)	0.5562(2)
F(48)	0.5613(3)	0.4213(3)	0.8110(3)
C(11)	0.3554(4)	0.1948(3)	0.8437(3)
C(12)	0.3677(5)	0.2892(4)	0.8684(4)
C(13)	0.3640(5)	0.3034(5)	0.9564(4)
C(14)	0.3721(5)	0.3974(5)	0.9776(5)
C(21)	0.4265(4)	0.0866(4)	0.6538(4)
C(22)	0.3940(4)	0.0713(4)	0.5711(4)
C(23)	0.4093(6)	0.1466(5)	0.5145(4)
C(24)	0.3813(8)	0.1313(7)	0.4326(5)
C(31)	0.2454(4)	0.2341(4)	0.6603(4)
C(32)	0.1864(4)	0.2855(4)	0.7127(5)
C(33)	0.1064(4)	0.3176(5)	0.6694(5)
C(34)	0.1229(8)	0.3813(9)	0.6112(9)
C(42)	0.5119(3)	0.2869(3)	0.7116(4)
C(43)	0.5640(3)	0.3622(3)	0.6848(4)
C(44)	0.5896(4)	0.3726(4)	0.6075(4)
C(45)	0.6327(5)	0.4426(5)	0.5797(5)
C(46)	0.6498(5)	0.5080(5)	0.6316(6)
C(47)	0.6274(4)	0.5015(4)	0.7096(7)
C(48)	0.5852(4)	0.4278(4)	0.7342(4)

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Compound 4[a]

Sn(1)–C(11)	2.122(5)
Sn(1)–C(21)	2.138(5)
Sn(1)–C(31)	2.143(6)
Sn(1)–O(41)	2.186(4)
Sn(1)–O(42)^1	2.514(4)
O(42)–Sn(1)^2	2.514(4)
C(11)–Sn(1)–C(21)	125.8(2)
C(11)–Sn(1)–C(31)	114.8(2)
C(21)–Sn(1)–C(31)	117.1(3)
C(11)–Sn(1)–O(41)	97.3(2)
C(21)–Sn(1)–O(41)	95.4(2)
C(31)–Sn(1)–O(41)	92.0(2)
C(11)–Sn(1)–O(42)^1	85.6(2)
C(21)–Sn(1)–O(42)^1	79.8(2)
C(31)–Sn(1)–O(42)^1	90.2(2)
O(41)–Sn(1)–O(42)^1	175.2(1)
C(42)–O(41)–Sn(1)	118.7(3)
C(42)–O(42)–Sn(1)^2	146.0(4)
C(43)–C(48)–C(47)	123.7(7)

[a] Symmetry transformations used to generate equivalent atoms: (1) $-y + {}^1/_2, x - {}^1/_2, -z + {}^3/_2$; (2) $y + {}^1/_2, -x + {}^1/_2, -z + {}^3/_2$.

The carboxylate groups bridge two neighboring tin atoms such that the Sn–O bonds formed by the bridging ligands are asymmetric with values of 2.186(4) and 2.514(4) Å, respectively (Table 2), as are the comparable bonds in the linear polymers of class c (see Figure 1); the oxygen atoms occupy the apical positions of the trigonal bipyramidal tin atoms, with O–Sn–O angles of 175.2(1)°. The three equatorial butyl groups and the tin atom are nearly coplanar, the sum of the equatorial C–Sn–C angles being 357.7(4)°. The very large C(42)–O(42)–Sn(1) (no. 2 symmetry transformation in Table 2) angle of 146.0(4)° is noteworthy. The 2,6-difluorophenyl groups are planar (rms deviation: 0.009(4) Å), displaying a torsional angle of 74.9(8)° with respect to the plane of the carboxylate moiety. Intermolecular interactions between the tetramers appear to be exclusively van der Waals in nature.

In triphenyltin acetate, a polymeric compound of class c, the corresponding bond is significantly shorter (2.349(3) Å).[5] It should be stressed, however, that, in tri-*n*-butyltin indole-3-acetate, likewise of class c, this bond exhibits a comparable length (2.524(3) Å).[6] Only one compound was shown to have a comparable cyclotetrameric structure, trimethyltin(IV) diphenylphosphinate,[10a] which also contains a 16-membered macrocycle like

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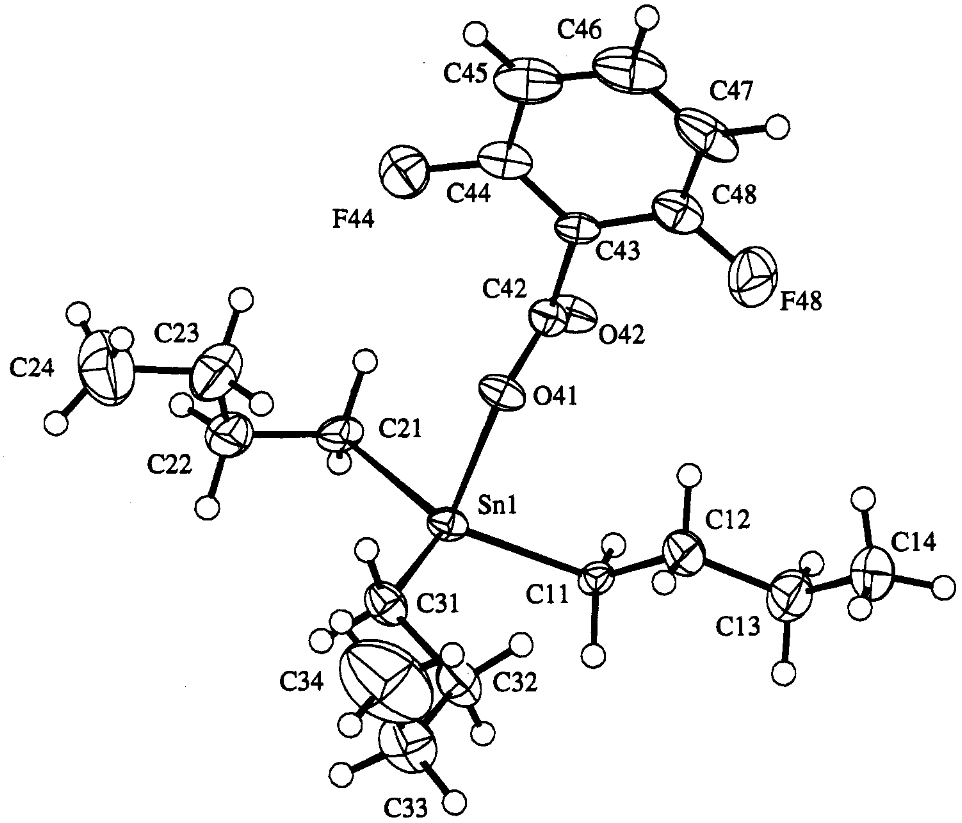

Figure 2. ORTEP drawing of a monomeric tri-*n*-butyltin 2,6-difluorobenzoate moiety in the cyclotetramer, with atom numbering.

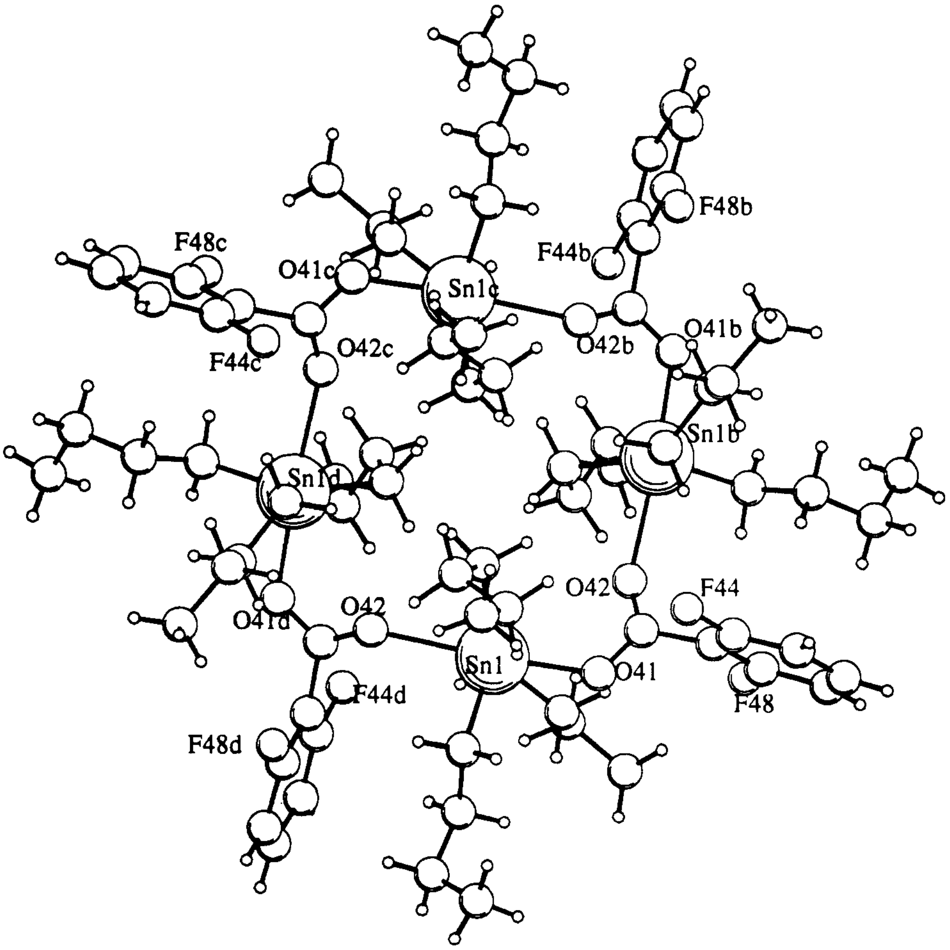

Figure 3. Drawing of the cyclotetramer.

compound 4. There are, however, two striking differences. In trimethyltin(IV) diphenylphosphinate, the two tin–oxygen distances are equal (2.243(5) and 2.245(6) Å) and actually smaller than the average of the two Sn–O bonds of compound 4. Accordingly, the diphenylphosphinate remains tetrameric in solution.[10b] In contrast the different Sn–O bond lengths (2.186(4) and 2.514(4) Å) in compound 4 are in agreement with a monomeric structure in benzene solution, as found by cryoscopy. Another striking difference is that, in the phosphinate, two methyl groups are directed toward the inner side of the macrocyclic cavity whereas, in compound 4, only a single butyl group does so. It is not clear whether this is due to the feature of the macrocycle or simply to the larger size of the butyl group with respect to the methyl group. It should be mentioned that Simons and Grahams[8] have prepared soluble forms of trimethyltin formate and acetate that are monomeric in the nucleophilic solvent methanol whereas, in CCl_4 and CH_2Br_2, the degree of association lies between three and four.

Spectroscopic Characterization of Compounds 1–9. Mössbauer Spectroscopy. The quadrupole splittings range from 3.75 to 3.94 mm/s for compounds 1–5, including 4, and from 3.35 to 3.59 mm/s for compounds 6–9, as expected for trigonal bipyramidal geometries,[11] in agreement with the X-ray diffraction data for compound 4. The isomer shifts range from 1.48 to 1.53 mm/s, and the line widths are normal (0.90–1.03 mm/s). It must be noticed that compounds 2, 3, and 5 exhibit a very large recoil-free fraction (relative absorbance up to 20% at 80 K) whereas all the others behave customarily (typically 8% of relative absorbance at 80 K). These observations are in favor of a polymeric structure for compounds 2, 3, and 5.

^{1}H NMR. The assignment of the aromatic proton resonances was achieved on the basis of multiplicities, integrations, $^nJ(^1H,^1H)$ coupling constants and by comparison with their dibutyltin homologs.[12] All salicylates display a broad signal between 11.0 and 12.1 ppm, assigned to the phenolic hydroxylic proton. This confirms that the phenol function does not react with di-*n*-butyltin oxide.[13,14] The butyl groups displayed the usual complex pattern.[15]

^{19}F NMR. Most ^{19}F resonances obtained at 235.4 MHz are broad and do not display resolved $^{19}F–^1H$ coupling patterns. The chemical shifts are reviewed in Table 3. The ^{19}F chemical shift of fluorobenzene (−113.3; tt: 9; 6) enables the evaluation of the increment of the aromatic fluorine induced by the CO_2SnBu_3 group which was found to be +2.9 ppm. The upfield shift induced by the ortho-difluoro substitution in compound 2 is noteworthy. The assignment of the ^{19}F resonances of compound 2 was achieved by comparison with the chemical shifts of the di-*n*-butyltin dibenzoate analog (2-F: −135.3; 3-F: −137.3) where the ortho $^3J(^{19}F–^1H)$ coupling of 10 Hz, associated with fluorine-3, is well characteristic. A similar approach was used for compound 3 on the basis, however, of the ^{19}F spectrum of the free ligand.

^{13}C NMR. The assignment of the ^{13}C resonances of the butyl groups of the tri-*n*-butyltin fluorobenzoates and salicylates is based on the $^nJ(^{13}C,^{119/117}Sn)$ coupling constants. The aromatic ^{13}C resonances were assigned using chemical shift increments of aromatic systems,[16,17] on the basis of ^{13}C DEPT spectra and, in the fluorobenzoates, from the $^nJ(^{13}C,^{19}F)$ coupling patterns and constants. All the chemical shifts have the values normally expected and can be found in the experimental section.

Table 3. ^{19}F NMR Chemical Shifts and $^nJ(^{13}C,^{19}F)$ Coupling Constants, Obtained from ^{13}C Spectra, for $CDCl_3$ Solutions of Tri-*n*-butyltin Mono- and Difluorobenzoates, $XYC_6H_3CO_2SnBu_3$, Compounds 1–5[a]

compd	X and/or Y	δ(^{19}F)	$^1J(^{13}C,^{19}F)$	$^2J(^{13}C,^{19}F)$	$^3J(^{13}C,^{19}F)$
1	2-F	−110.4	259	23 (C3)	7 (C6) 3 (C5)[b]
2	2,3-F_2	−136.8 (2-F)	248	13 (C3)	
		−138.1 (3-F)	260	13 (C2) 16 (C4)	
3	2,5-F_2	−116.8 (2-F)	255	26 (C3)	
		−119.5 (5-F)	243	25 (C6) 26 (C4)	
4	2,6-F_2	−111.8	254	26 (C3 or C5)	7 (C6 or C2) 10 (C4)
5	3,5-F_2	−110.0	249	25 (C2 or C6) 25 (C4)	12 (C3 or C5)

[a] Chemical shifts are in ppm (reference: $CFCl_3$); $^nJ(^{13}C,^{19}F)$ in hertz. All ^{19}F resonances are broad singlets except the 2-F resonance of compound 2 that exhibits a $^3J(^{19}F,^{19}F)$ of 20 Hz. [b] $^4J(^{13}C,^{19}F)$. The ^{13}C atoms to which the fluorine atoms are coupled are given between parentheses in the case of the ^2J and ^3J couplings.

Holecek et al.[18-20] noticed the $^1J(^{13}C,^{119}Sn)$ coupling constant to be a function of the coordination number of triorganotin compounds, ranging between 327 and 387 Hz for tetracoordinated compounds, and between 442 and 509 Hz for pentacoordinated ones. The triorganotin fluorobenzoates $F_nC_6H_{5-n}CO_2SnR_3$ as well as the salicylates exhibit $^1J(^{13}C,^{119}Sn)$ coupling constants ranging from 350 to 360 Hz indicating tetracoordination in chloroform solution, in agreement with our cryoscopy measurements demonstrating compound 4 to be a monomer in benzene.

The $^nJ(^{13}C,^{19}F)$ coupling constants are presented in Table 3. The values of the $^1J(^{13}C,^{19}F)$ coupling constants are comparable to those of the diorganotin analogs and vary from 245 to 261 Hz.[21] They are lying in the normal range of 230 to 265 Hz found for all fluorobenzenes.[22] In none of the compounds is the $^2J[^{13}C(1),^{19}F(2)]$ coupling observed (carbon C(1) bearing the tributylstannyl carboxylate group). This is in agreement with $^2J(^{13}C,^{19}F)$ couplings in 2-substituted fluoro aromatics being much smaller than the usual values between 15 and 25 Hz,[22] all the ^{13}C resonances being, in addition, broad. For the remaining aromatic carbon atoms the $^2J(^{13}C,^{19}F)$ couplings are observed in two ranges, 23–26 Hz and 13–16 Hz. The $^2J(^{13}C,^{19}F)$ couplings in the former range (Table 3) arise from H–C*–C–F moieties and those in the latter range, from F–C*–C–F ones. Though significantly smaller, these couplings seem to have higher values than those mentioned

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Table 4. ^{119}Sn NMR Data for $CDCl_3$ Solutions of the Substituted Tri-*n*-butyltin Benzoates 1–9, and Some Other Reference n-Bu_3SnX Compounds[23]

compound	X	$\delta(^{119}Sn)$ in ppm[a]
1	2-F-C_6H_4-COO	118.2
2	2,3-F_2-C_6H_3-COO	125.1
3	2,5-F_2-C_6H_3-COO	125.2
4	2,6-F_2-C_6H_3-COO	132.6
5	3,5-F_2-C_6H_3-COO	125.6
6	3-OCH_3-2-OH-C_6H_3-COO	130.4
7	4-OCH_3-2-OH-C_6H_3-COO	124.1
8	5-OCH_3-2-OH-C_6H_3-COO	130.7
9	6-$(CH_3)_2CH$-3-CH_3-2-OH-C_6H_2-COO	122.7
	Cl	152.8
	Br	141.6
	CH_3COO	104.8
	C_6H_5COO	112.7

[a] Chemical shifts with respect to tetramethyltin.

in the literature for 2-substituted fluoro aromatics,[22] as well as the unobserved $^2J[^{13}C(1),^{19}F(2)]$ ones of the present compounds.

The $^3J(^{13}C,^{19}F)$ values range from 7 to 12 Hz, in fair agreement with the literature[22] mentioning them to lie between 1 and 11 Hz. Only one single long-range $^4J(^{13}C,^{19}F)$ coupling of 3 Hz could be observed, namely for the carbon C(5) of compound **1**.

^{119}Sn NMR Data. The ^{119}Sn chemical shift data obtained from $CDCl_3$ solutions of compounds **1**–**9**, are described in Table 4. A single resonance in the range of 118 to 133 ppm, compatible with the tetrahedral geometry proposed for the solution structure, is observed for each compound; for comparison, the ^{119}Sn chemical shifts of a few tri-*n*-butyltin compounds R_3SnX[23] are also presented in Table 4. Substitution of a halide for a carboxylate induces only a slight upfield shift of the ^{119}Sn resonance that is unlikely to arise from a significant additional coordination by the oxygen atom of the carbonyl group. Note the low-field shift of 5.5 ppm upon single fluorine substitution and of 10–20 ppm upon multiple aromatic substitution in the aromatic carboxylates. There is no apparent correlation between the ^{119}Sn chemical shift and the electron-releasing or -withdrawing character of the substituents on the benzene ring (compare the methoxy salicylates and the fluorobenzoates).

These data combined with the $^1J(^{13}C,^{119/117}Sn)$ coupling constants previously discussed tend to confirm that the tri-*n*-butyltin carboxylates exhibit a tetracoordinated geometry[18–20] in solution. The pentacoordination of the tri-*n*-butyltin carboxylates in the solid state no longer holds in solution. Actually tetracoordination is present in both solid and solution states for the triphenyltin carboxylates.[4]

Experimental Section

X-ray Diffraction Analysis of Compound 4. White, opaque, irregular crystals were obtained from a recrystallization of compound **4** from petroleum ether. The details of data collection and structure analysis are summarized in Table 5. Data were initially obtained using an ENRAF-NONIUS CAD-4 diffractometer and Cu Kα radiation at room temperature. This data set enabled the structure to be determined using the heavy atom technique. A sharpened Patterson map calculated with SHELXS-86[22] revealed the Sn–Sn vectors at the correct positions and weights consistent with space group $I\bar{4}$. Subsequent completion of the structure analysis in this space group confirms it to be the correct choice. The structure was completed using successive Fourier syntheses and refined by full-matrix least-square methods using SHELXL-92.[23]

Table 5. Crystal Data, Experimental Data and Structure Refinement of Tri-*n*-butyltin 2,6-Difluorobenzoate, Compound 4

Crystal Data	
$2,6\text{-}F_2C_6H_3CO_2SnBu_3$	Mo Kα radiation; $\lambda = 0.71069$ Å
$M_r = 447.12$	cell parameters from 25 reflections with
tetragonal	$\theta = 11.5\text{–}14$ deg
$I\bar{4}$	$\mu = 1.264\ mm^{-1}$
$a = 15.631(3)$ Å	$T = 150(2)$ K
$c = 16.882(1)$ Å	$0.30 \times 0.30 \times 0.20$ mm
$Z = 8$	
$V = 4124.7(11)$ Å^3	
$D_x = 1.440\ mg/m^3$	$F(000) = 1824$
Data Collection	
Enraf–Nonius FAST diffractometer	θ-range: 2.61–25.20°
no absorption correction	$-11 \le h \le 18$
5462 measured reflections	$-18 \le k \le 17$
3151 independent reflections	$-19 \le l \le 19$
$R_{int} = 0.067$	
Refinement	
full-matrix least-squares on F^2	absolute structure parameter = –0.04(3)
R[all data]: $R = 0.037$; $R_w = 0.089$	$\Delta\rho_{max} = 1.11\ e\ A^{-3}$
$R[I > 2\sigma(I)]$: $R = 0.035$; $R_w = 0.086$	$\Delta\rho_{min} = -0.50\ e\ A^{-3}$
$S = 0.64$	data/restraints/parameters = 3151/0/241

This structure displayed a considerable degree of static disorder in the butyl side chains and consequently it was decided to measure a fresh set of data at low temperature in an attempt to overcome this problem. This second data set was measured at 150 K on a Nonius FAST diffractometer employing Mo Kα radiation. The structure was solved by the heavy atom method using SHELXS-86.[24] The refinement was performed by full-matrix least-squares methods using SHELXL-92[25] with anisotropic temperature factors for all the non-H atoms and isotropic temperature factors for the H atoms. The H atoms were placed in calculated positions on the corresponding C atoms and not refined, with the C–H distances of 0.99 Å in CH_2, 0.98 Å in CH_3, and 0.95 Å in aromatic CH groups. During the course of refinement the absolute structure parameter[26] converged to a value of –0.04(3), indicating that the correct hand had been selected for the structure. All tables and drawings refer to this absolute configuration. No geometrical constraints were applied. Calculations were carried out on a LOFGREN 486 PC. Geometrical calculations were performed with SHELXL-92.[25] Molecular illustrations were drawn with SNPI.[27] No absorption correction was considered necessary as the absorption coefficient for Mo Kα was quite small (Table 5) and the added advantage of carrying out the diffraction measurements at low temperature resulted in a highly satisfactory structure. Refinement on F^2 inevitably results in relatively high values for R_w and values of the conventional R factors based on F are therefore given for comparison (Table 5).

Syntheses. Equimolar amounts of tri-*n*-butyltin acetate and substituted benzoic acid are poured into a three-necked 250-mL flask equipped with a Dean–Stark funnel containing 200 mL of

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(23) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; p 98.

(24) Sheldrick, G. M. *SHELXS-86. Program for Crystal Structure Determination*; University of Göttingen, Göttingen, Federal Republic of Germany, 1990.

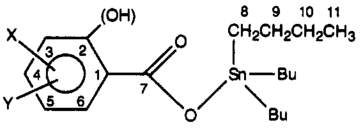
(25) Sheldrick, G. M. *SHELXL-92. Program for Crystal Structure Determination*; University of Göttingen, Göttingen, Federal Republic of Germany, 1993.

(26) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(27) Karaulov, S. *SNPI. Molecular plotting program*; University of Wales, Cardiff, U.K., 1993.

a toluene/ethanol 3/1 mixture. The mixture is refluxed for 4 h. The ternary azeotrope acetic acid/ethanol/toluene followed by the binary azeotrope toluene/ethanol are distilled off to 50% of the initial volume. The remaining solution is evaporated under reduced pressure. Except for the 2,6-difluorobenzoate, that is recrystallized from petroleum ether, the tri-*n*-butyltin compounds are viscous oils, some of which crystallized in the refrigerator while the others were distilled under reduced pressure.

Spectroscopic Characterization. Mössbauer parameters are given in mm/s: QS = quadrupole splitting, IS = isomer shift. ^{1}H and ^{13}C NMR chemical shifts are given in ppm (reference TMS). Calculated ^{13}C chemical shifts using aromatic chemical shift increments[16] are given between brackets. ^{19}F chemical shifts are referenced to $CFCl_3$. The coupling constants are given in hertz between parentheses with the spectral pattern. Abbreviations for spectral patterns: d = doublet, t = triplet, s = singlet, b = broad, up = unresolved pattern, m = complex pattern. $^3J(^1H,^{19}F)$ and $^nJ(^{13}C,^{119/117}Sn)$ couplings are given in italics. $^2J(^{13}C,^{119/117}Sn)$ and $^3J(^{13}C,^{119,117}Sn)$ coupling satellites are not resolved. ^{13}C resonances without pattern indication are singlets.



Compound 1, tri-*n*-butyltin 2-fluorobenzoate: bp 51–53 °C/0.05 Torr; mp 42–43 °C, yield 92%; Mössbauer parameters, QS 3.88, IS 1.50, band widths 0.89 and 0.91; ^{1}H NMR 7.09, dd (*10*, 8) H(3); 7.43–7.50, m, H(4); 7.16, dd (8, 8) H(5); 7.95, ddd (*8*, 8, 2), H(6); 1.61–1.73, m, H(8); 1.30–1.43, m, H(9) and H(10); 0.92, t (7), H(11); ^{13}C NMR 120.2 [117.2], C(1); 162.1 [165.2], d (259), C(2); 116.6 [115.2], d (23), C(3); 133.6 [134.6], bs, C(4); 123.5 [123.8], d (3), C(5); 132.6 [132.0], C(6); 169.2, C(7); 16.6 (^1J = *356/340*), C(8); 27.7 ($^2J \approx$ *20*), C(9); 26.9 ($^3J \approx$ *64*), C(10); 13.5 C(11).

Compound 2, tri-*n*-butyltin 2,3-difluorobenzoate: mp 36–37 °C, yield 94%; Mössbauer parameters, QS 3.94, IS 1.53, band widths 1.02 and 1.03; ^{1}H NMR 7.29, up, H(4); 7.10, up, H(5); 7.68, up, H(6); 1.62–1.74, m, H(8); 1.30–1.49, m, H(9) and H(10); 0.92, t (7), H(11); ^{13}C NMR 121.5 [118.8], C(1); 151.0 [152.2], dd (248, 13), C(2); 150.3 [150.2], dd (260, 13), C(3); 120.0 [121.6], d (16), C(4); 123.2 [125.4], C(5); 127.1 [127.6], C(6); 167.9, C(7); 16.6 (^1J = *353/338*), C(8); 27.6 ($^2J \approx$ *20*), C(9); 26.8 ($^3J \approx$ *64*), C(10); 13.4, C(11).

Compound 3, tri-*n*-butyltin 2,5-difluorobenzoate: bp 51–52 °C/0.05 Torr; mp 30–31 °C, yield 92%; Mössbauer parameters, QS 3.87, IS 1.51, band widths 1.03 and 1.04; ^{1}H NMR 7.09–7.16, m, H(3); 7.06, ddd (*9*, 9, *5*), H(4); 7.64, ddd (*9*, *5*, 3), H(6); 1.63–1.75, m, H(8); 1.29–1.50, m, H(9) and H(10); 0.93, t (7), H(11); ^{13}C NMR 122.2 [118.8], C(1); 158.1 [160.8], d (255), C(2); 117.8 [116.8], dd (26, 8), C(3); 119.9 [121.6], d (26), C(4); 157.8 [158.6], d (243), C(5); 118.6 [117.1], d (25), C(6); 167.6, C(7); 16.6 (^1J = *353/338*), C(8); 27.6 ($^2J \approx$ *20*), C(9); 26.8 ($^3J \approx$ *64*), C(10); 13.4, C(11).

Compound 4, tri-*n*-butyltin 2,6-difluorobenzoate: mp 84–85 °C (recrystallization from petroleum ether), yield 81%; Mössbauer parameters, QS 3.86, IS 1.52, band widths 1.03 and 1.01; ^{1}H NMR 6.90, dd (*8*, 8), H(3) = H(5); 7.31, tt (8, *6*), H(4); 1.62–1.71, m, H(8); 1.29–1.44, m, H(9) and H(10); 0.92, t (7), H(11); ^{13}C NMR 113.5 [104.4], C(1); 160.2 [166.6], dd (254, 7), C(2) = C(6); 111.5 [110.8], d (26), C(3) = C(5); 130.9 [135.8], t (10), C(4); 165.9, C(7); 16.8 (^1J = *350/335*), C(8); 27.6 ($^2J \approx$ *21*), C(9); 26.9 ($^3J \approx$ *63*), C(10); 13.5, C(11).

Compound 5, tri-*n*-butyltin 3,5-difluorobenzoate: bp 110–112 °C/0.4 torr, yield 92%; Mössbauer parameters, QS 3.75, IS 1.51, band widths 1.01 and 1.02; ^{1}H NMR 7.54, dd (*8*, 2), H(2) = H(6); 6.94, tt (*9*, 2), H(4); 1.61–1.70, m, H(8); 1.24–1.44, m, H(9) and H(10); 0.93, t (7), H(11); ^{13}C NMR 135.7 [133.3], C(1); 113.0 [113.0], d (25), C(2) = C(6); 162.6 [164.4], dd (249, 12), C(3) = C(5); 107.3 [107.2], t (25), C(4); 169.2, C(7); 16.7 (^1J = *354/338*), C(8); 27.8 ($^2J \approx$ *20*), C(9); 27.0 ($^3J \approx$ *64*): C(10); 13.6, C(11).

Compound 6, tri-*n*-butyltin 3-methoxysalicylate: bp 130–131 °C/0.4 torr, yield 97%; Mössbauer parameters, QS 3.59, IS 1.49, band widths 0.97 and 0.97; ^{1}H NMR 7.00, dd (8, 1), H(4); 6.78, dd (8, 8), H(5); 7.51, dd (8, 1), H(6); 1.61–1.73, m, H(8); 1.29–1.43, m, H(9) and H(10); 0.92, t (7), H(11); 11.73, bs, OH; 3.88, s, CH_3O; ^{13}C NMR 114.3 [118.4], C(1); 148.2 [142.9], C(2); 151.8 [146.8], C(3); 116.0 and 117.7 [120.0 and 121.8], C(4) and C(5); 122.4 [124.1], C(6); 174.5, C(7); 16.7 (^1J = *353/337*), C(8); 27.5 ($^2J \approx$ *21*), C(9); 26.7 ($^3J \approx$ *64*), C(10); 13.3, C(11); 55.9, CH_3O.

Compound 7, tri-*n*-butyltin 4-methoxysalicylate: bp 120–122 °C/0.4 torr, yield 95%; Mössbauer parameters, QS 3.35, IS 1.48, band widths 0.98 and 0.98; ^{1}H NMR 6.42, bs, H(3); 6.41, dd (8, 2), H(5); 7.80, d (8), H(6); 1.61–1.73, m, H(8); 1.29–1.48, m, H(9) and H(10); 0.92, t (7), H(11); 11.73, bs, OH; 3.79, s, CH_3O; ^{13}C NMR 107.3 [109.7], C(1); 163.5 [158.3], C(2); 100.3 [101.0], C(3); 165.0 [165.8], C(4); 106.5 [106.4], C(5); 132.4 [132.8], C(6); 174.2, C(7); 16.8 (^1J = *355/339*), C(8); 27.7 ($^2J \approx$ *21*), C(9); 26.9 ($^3J \approx$ *64*), C(10); 13.5, C(11); 55.2, CH_3O.

Compound 8, tri-*n*-butyltin 5-methoxysalicylate: bp 150–151 °C/0.5 torr, yield 91%; Mössbauer parameters, QS 3.54, IS 1.48, band widths 0.99 and 0.97; ^{1}H NMR 6.88, d (9), H(3); 7.03, dd (9, 3), H(4); 7.39, d (3), H(6); 1.62–1.74, m, H(8); 1.26–1.44, m, H(9) and H(10); 0.93, t (7), H(11); 11.05, bs, OH; 3.77, s, CH_3O; ^{13}C NMR 113.9 [118.4], C(1); 151.7 [149.6], C(2); 113.5 [116.4], C(3); 122.7 [120.0], C(4); 155.8 [152.2], C(5); 117.8 [117.4], C(6); 174.0, C(7); 16.9 (^1J = *353/337*), C(8); 27.5 ($^2J \approx$ *21*), C(9); 26.9 ($^3J \approx$ *64*), C(10); 13.4, C(11); 55.7, CH_3O.

Compound 9, tri-*n*-butyltin 6-isopropyl-3-methylsalicylate: bp 81–82 °C/0.05 Torr, yield 94%; Mössbauer parameters, QS 3.30, IS 1.47, band widths 1.02 and 0.97; ^{1}H NMR 7.18, d (8), H(4); 6.78, d (8), H(5); 1.61–1.73, m, H(8); 1.26–1.47, m, H(9) and H(10); 0.92, t (7), H(11); 12.06, bs, OH; 2.22, s, CH_3; 1.21, d (7), isopropyl CH_3; 4.05, septet (7), CH; ^{13}C NMR 112.6 [114.5], C(1); 160.1 [157.7], C(2); 123.3 [122.3], C(3); 134.1 [135.8], C(4); 115.9 [118.9], C(5); 150.0 [148.5], C(6); 175.9, C(7); 17.0 (^1J = *354/338*), C(8); 27.8 ($^2J \approx$ *21*), C(9); 26.9 ($^3J \approx$ *63*), C(10); 13.5, C(11); 15.8, CH_3; 29.2 and 24.3, $CH(CH_3)_2$.

Instruments. Mössbauer spectra were recorded as described previously.[28] All NMR spectra were recorded on a Bruker AC250 spectrometer equipped with a QNP Quattro probe (^{1}H, ^{13}C, ^{119}Sn, ^{19}F). The resonance frequencies were 250.13 MHz for ^{1}H, 62.93 MHz for ^{13}C, 93.28 MHz for ^{119}Sn, and 235.36 MHz for ^{19}F.

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Supplementary Material Available: Tables of complete bond distances, angles, anisotropic thermal parameters. Figures with crystal packing along b and c (7 pages). Ordering information is given on any current masthead page.

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