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## Organotin esters of 3-benzoylpropionic acid. Crystal structure of triphenyltin(IV) 3-benzoylpropionate, $(C_6H_5)_3SnOC(O)(CH_2)_2C(O)C_6H_5$

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### Abstract

Tin-119m Mössbauer (80 K) and solution carbon-13 NMR spectra are reported for six organotin 3-benzoylpropionates,  $R_nSn[OC(O)(CH_2)_2C(O)C_6H_5]_{4-n}$  ( $n = 2$ ,  $R = CH_3$ ,  $n-C_3H_7$ ,  $n-C_4H_9$ ;  $n = 3$ ,  $R = CH_3$ ,  $n-C_4H_9$ ,  $C_6H_5$ ). The diorganotin bis-3-benzoylpropionates adopt *trans*- $C_2SnO_4$  octahedral geometries and the triorganotin 3-benzoylpropionates *trans*- $C_3SnO_2$  trigonal bipyramidal geometries in the solid state, but the coordination numbers are lower in solution. From the variable-temperature Mössbauer decay coefficient, a rigid polymeric structure was predicted for the triphenyltin ester, and this configuration was confirmed by an X-ray diffraction study at 296 K. Molecules of triphenyltin 3-benzoylpropionate (space group  $P2_1/n$  with  $a$  12.881(2),  $b$  11.384(2),  $c$  17.080(2) Å,  $\beta$  104.06(2)°;  $Z = 4$ ) are carboxylate-bridged into a polymeric chain; the ketonic oxygen is not involved in coordination.

### Introduction

Triorganotin(IV) carboxylates are generally five-coordinate carboxylate-bridged polymers whose repeat units are propagated in a zig-zag or helical manner in the crystal lattice [1]. A substituent in the carboxylate group carrying a donor atom makes possible an alternative bonding to carboxyl bridging, and this option is adopted in trimethyltin glycinate, whose tin–nitrogen bridging interaction is apparently strong enough for the tin-119m Mössbauer effect to be observed at room temperature [2]. Although polymeric, triorganotin carboxylates generally do not

yield room temperature Mössbauer spectra [3], except for triphenyltin pyruvate [4], which has a ketonic group linked to the carboxylate. Variable-temperature Mössbauer data on triphenyltin levulinate, which has two methylene carbon atoms separating the ketonic and carboxyl oxygen atoms in the ester unit, support the assignment of a flexible, helical chain [5] configuration in which the carboxyl oxygen, rather than the ketonic oxygen, participates in intermolecular coordination to tin. In the infrared spectra of triorganotin levulinates, bands around  $1700\text{ cm}^{-1}$  have been ascribed to the uncoordinated ketonic group [6] and a carboxylate-bridged distorted helical configuration has been proposed for these esters by analogy with the crystallographically authenticated triphenyltin acetate [7]. The triorganotin esters of 2-benzoylbenzoic acid are also reported to be carboxylate-bridged [8]. The triorganotin acetylacetates, which possess only one methylene carbon separating the carboxyl and ketonic carbons, might be expected to be more rigid than the levulinates, but their reported infrared spectra [9] are rather similar to those of the levulinates.

We report here, the preparation and spectral properties of di- and tri-organotin esters of 3-benzoylpropionic acid,  $\text{C}_6\text{H}_5\text{C(O)(CH}_2)_2\text{C(O)OH}$ . The ultimate demonstration of whether or not a ketonic group in the organotin esters of ketocarboxylic acids is involved in coordination must come from diffraction studies, and so we undertook the X-ray crystal structure determination of triphenyltin 3-benzoylpropionate.

## Experimental

3-Benzoylpropionic acid was prepared by a published method [10]. The organotin compounds were prepared by conventional methods from the organotin chloride, hydroxide, or oxide [6,8]. Large crystals of the triphenyltin 3-benzoylpropionate were grown from an alcoholic solution of the compound. The tin-119m Mössbauer and carbon-13 NMR spectra were recorded as described previously [6]. The analytical data for the six organotin 3-benzoylpropionates are given in Table 1, Mössbauer

Table 1  
Analytical data for organotin 3-benzoylpropionates

	M.p. ( $^{\circ}\text{C}$ )	Analysis (Found (calcd.) (%))	
		C	H
$(\text{CH}_3)_2\text{Sn}[\text{OC(O)(CH}_2)_2\text{C(O)C}_6\text{H}_5]_2$	74–75	52.30 (52.52)	5.05 (4.77)
$(n\text{-C}_3\text{H}_7)_2\text{Sn}[\text{OC(O)(CH}_2)_2\text{C(O)C}_6\text{H}_5]_2$	92–93	55.84 (55.84)	5.70 (5.73)
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{OC(O)(CH}_2)_2\text{C(O)C}_6\text{H}_5]_2$	65–66	56.84 (57.27)	6.34 (6.14)
$(\text{CH}_3)_3\text{SnOC(O)(CH}_2)_2\text{C(O)C}_6\text{H}_5$	139–140	46.35 (45.79)	5.18 (5.28)
$(n\text{-C}_4\text{H}_9)_3\text{SnOC(O)(CH}_2)_2\text{C(O)C}_6\text{H}_5$	56–57	54.25 (56.57)	7.96 (7.71)
$(\text{C}_6\text{H}_5)_3\text{SnOC(O)(CH}_2)_2\text{C(O)C}_6\text{H}_5$	133–134	63.74 (63.79)	4.59 (4.56)

Table 2

Mössbauer data for organotin 3-benzoylpropionates at 80 K ( $\text{mm s}^{-1}$ )

	IS	QS	$\Gamma_1$	$\Gamma_2$
$(\text{CH}_3)_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5]_2$	1.16	3.61	1.00	1.04
$(n\text{-C}_3\text{H}_7)_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5]_2$	1.39	3.67	0.97	1.04
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5]_2$	1.23	3.31	0.95	0.99
$(\text{CH}_3)_3\text{SnOC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5$	1.26	3.77	1.05	1.05
$(n\text{-C}_4\text{H}_9)_3\text{SnOC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5$	1.42	3.91	1.04	1.06
$(\text{C}_6\text{H}_5)_3\text{SnOC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5$	1.25	3.70	1.02	1.03

data in Table 2, and carbon-13 NMR data in Table 3. The slope of the variable-temperature Mössbauer plot for triphenyltin 3-benzoylpropionate (6 points between 80 and 130 K) is  $0.0126 \text{ K}^{-1}$ . The X-ray data were recorded with a crystal ( $0.28 \times 0.40 \times 0.08 \text{ mm}$ ) of triphenyltin 3-benzoylpropionate, using an Enraf–Nonius CAD4 diffractometer and graphite-filtered  $\text{Cu-K}\alpha$  ( $\lambda 1.54184 \text{ \AA}$ ) radiation at a temperature of  $23 \pm 1^\circ \text{C}$ . Lorentz polarization, reflection averaging (agreement on  $I$  2.8%) and extinction (coefficient 0.0000014) corrections were applied. The maximum  $2\theta$  angle was  $120^\circ$ . Of the 3955 total reflections, 3600 were unique and the 3325 with  $|F_o|^2 > 3.0\sigma(|F_o|^2)$  were used in the refinements. The structure was solved by direct methods and refined on the minimization function  $\Sigma w(|F_o| - |F_c|)^2$ , with the least-squares weight set at  $4|F_o|^2/\sigma^2(|F_o|^2)$ . The non-hydrogen atoms were refined anisotropically and the hydrogen atoms refined isotropically. The final unweighted and weighted agreement factors were 0.034 and 0.050, respectively. In the final difference electron density map, the highest peak was  $0.58(8) \text{ e\AA}^{-3}$  and the lowest peak  $-0.68(8) \text{ e\AA}^{-3}$ . Crystal data for triphenyltin 3-benzoylpropionate are listed in Table 4 and the final atomic coordinates for the non-hydrogen atoms in Table 5. Selected bond distances and angles are listed in Table 6. Full listings of bond dimensions, anisotropic thermal parameters, least-squares planes calculations and structure factor tables are available from the authors.

## Discussion

The organotin 3-benzoylpropionates are sharp-melting white to tan-colored solids. The tin-119m Mössbauer isomer shift (IS) and quadrupole splitting (QS) values indicate higher-than-four coordination at tin, as reflected in the QS/IS ratio ( $> 2.1$ ) [11]. The QS values for the dialkyltin derivatives are in the range expected for *trans*-[ $\text{SnR}_2$ ] octahedral geometries and the carbon–tin–carbon angle predicted from point-charge model calculations [12] is  $146^\circ$  for the dimethyltin homologue. Trigonal bipyramidal geometries with planar  $\text{R}_3\text{Sn}$  groups may be inferred for the triorganotin derivatives whose QS values are similar to those for the levulinates [6] and benzoylbenzoates [8]. In the IR spectrum, all the six 3-benzoylpropionates exhibit bands around  $1700 \text{ cm}^{-1}$ . In chloroform solution, the time-averaged one-bond coupling constant,  $^1J(^{119}\text{Sn}-^{13}\text{C})$ , recorded for the triorganotin compounds are in the normal range for tetrahedral tin. Thus, the  $^1J$  values of 358.2 and 646.9 Hz found for the tri-*n*-butyltin and triphenyltin 3-benzoylpropionates, respectively, are close to those for tri-*n*-butyltin acetate (360.7 Hz [13]) and triphenyltin acetate (648.2 Hz [14]). The  $^1J$  values for the diorganotin bis-3-benzoylpropionates are

Table 3  
Carbon-13 NMR data for  $R_n\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5]_{4-n}$  compounds in  $\text{CDCl}_3$

Compound	$R^a$	$\text{CH}_2\text{CH}_2$	$\text{C}(\text{O})\text{O}$	$\text{C}(\text{O})$	$\text{C}_6\text{H}_5$
$(\text{CH}_3)_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}_6\text{H}_5]_2$	4.4(648.8)	33.8, 28.3	181.4	201.6	136.5, 133.1, 128.5, 127.9
$(n\text{-C}_3\text{H}_7)_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5]_2$	27.7(571.5) 18.2(33.7)	34.1, 28.2	182.7	197.9	136.6, 133.1, 128.5, 128.0
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5]_2$	17.8(99.6) 25.1(575.9) 26.5(35.9) 26.2(99.7)	33.9, 28.1	182.1	197.8	136.5, 133.0, 128.5, 127.9
$(\text{CH}_3)_3\text{SnOC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5$	-2.4(403.5)	34.3, 28.8	178.3	201.1	136.7, 132.9, 128.4, 127.9
$(n\text{-C}_4\text{H}_9)_3\text{SnOC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5$	16.4(358.2) 27.7(20.8) 26.9(64.7) 13.5	34.3, 28.8	177.7	201.3	136.8, 132.8, 128.3, 127.9
$(\text{C}_6\text{H}_5)_3\text{SnOC}(\text{O})(\text{CH}_2)_2\text{C}(\text{O})\text{C}_6\text{H}_5$	138.1(646.9) <i>i</i> 136.7(48.4) <i>o</i> 128.8(63.0) <i>m</i> 130.0(13.2) <i>p</i>	34.3, 28.2	179.2	198.0	137.1, 132.9, 128.4, 127.9

<sup>a</sup> Coupling constants (Hz) in parentheses for  $^nJ(^{119}\text{Sn}-^{13}\text{C})$ ; *i*, ipso; *o*, ortho; *m*, meta; *p*, para.

Table 4

## Crystal data for triphenyltin 3-benzoylpropionate

Molecular formula	C <sub>28</sub> H <sub>24</sub> O <sub>3</sub> Sn
Molecular weight	527.19
Cell constants	<i>a</i> 12.881(1), <i>b</i> 11.384(2), <i>c</i> 17.080(2) Å β 104.06(2)°; <i>V</i> 2429.4 Å <sup>3</sup> ; <i>Z</i> = 4
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Density (calcd)	1.44 g cm <sup>-3</sup>
Absorption coefficient	87.6 cm <sup>-1</sup>

larger than the value of 419.9 Hz found for the four-coordinate di-*n*-butyltin dichloride, but smaller than that of 673.8 Hz reported for the di-*n*-butyltrichlorostannate anion [15]. The <sup>1</sup>*J* values for the three diorganotin esters are tentatively

Table 5

## Positional coordinates and isotropic thermal parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> ) <sup>a</sup>
Sn	0.76624(2)	0.19903(2)	0.21759(1)	2.837(6)
O(1)	0.7794(2)	0.5177(2)	0.2474(1)	3.48(5)
O(2)	0.8117(2)	0.3716(2)	0.1716(1)	3.92(5)
O(3)	0.8604(5)	0.7053(3)	0.0051(2)	9.5(1)
C(1)	0.9009(3)	0.2042(3)	0.3198(2)	3.23(8)
C(2)	0.9391(4)	0.3095(3)	0.3543(3)	4.15(9)
C(3)	1.0267(4)	0.3133(4)	0.4198(3)	5.4(1)
C(4)	1.0770(4)	0.2103(4)	0.4508(3)	6.3(1)
C(5)	1.0387(4)	0.1046(5)	0.4187(3)	7.0(1)
C(6)	0.9513(4)	0.1015(4)	0.3526(3)	5.6(1)
C(7)	0.6144(3)	0.2679(3)	0.2213(2)	3.30(7)
C(8)	0.6018(3)	0.3330(3)	0.2872(2)	3.78(8)
C(9)	0.5024(3)	0.3815(4)	0.2878(3)	5.2(1)
C(10)	0.4168(4)	0.3661(5)	0.2252(3)	6.1(1)
C(11)	0.4268(4)	0.3025(4)	0.1601(4)	6.2(1)
C(12)	0.5253(3)	0.2513(4)	0.1566(2)	4.55(9)
C(13)	0.7916(3)	0.1246(3)	0.1097(2)	3.20(7)
C(14)	0.8729(3)	0.1695(4)	0.0762(3)	4.76(9)
C(15)	0.8925(4)	0.1208(5)	0.0072(3)	6.1(1)
C(16)	0.8337(4)	0.0267(5)	-0.0286(3)	6.5(1)
C(17)	0.7545(4)	-0.0179(4)	0.0012(2)	5.6(1)
C(18)	0.7317(3)	0.0314(4)	0.0704(2)	4.10(8)
C(19)	0.8611(3)	0.5666(4)	-0.0949(2)	4.51(9)
C(20)	0.8752(3)	0.6536(5)	-0.1494(3)	5.6(1)
C(21)	0.8839(4)	0.6527(6)	-0.2242(3)	7.5(1)
C(22)	0.8775(5)	0.5113(7)	-0.2479(3)	9.3(2)
C(23)	0.8619(6)	0.4255(6)	-0.1977(3)	9.2(2)
C(24)	0.8535(4)	0.4512(5)	-0.1200(3)	6.3(1)
C(25)	0.8015(3)	0.4797(3)	0.1848(2)	3.33(7)
C(26)	0.8226(3)	0.5655(3)	0.1233(2)	4.40(9)
C(27)	0.8341(3)	0.5103(3)	0.0448(2)	3.92(8)
C(28)	0.8510(3)	0.6030(4)	-0.0136(2)	4.66(9)

<sup>a</sup> The *B* isotropic equivalent displacement parameter is defined as  $B = 4/3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab \cos \gamma B_{1,2} + ac \cos \beta B_{1,3} + bc \cos \alpha B_{2,3}]$ .

Table 6

Selected bond distances (Å) and bond angles (°)

Sn–O(1)′	2.2658(6)	Sn–O(2)	2.2460(6)	Sn–C(1)	2.1422(8)
Sn–C(7)	2.1223(8)	Sn–C(13)	2.1242(8)	O(1)–C(25)	1.250(1)
O(2)–C(25)	1.263(1)	O(3)–C(28)	1.206(1)		
O(1)′–Sn–O(2)	174.63(2)	O(1)′–Sn–C(1)	91.19(3)		
O(1)′–Sn–C(7)	91.63(3)	O(1)′–Sn–C(13)	88.27(3)		
O(2)–Sn–C(1)	91.89(3)	O(2)–Sn–C(7)	90.44(3)		
O(2)–Sn–C(13)	86.41(3)	C(1)–Sn–C(7)	122.35(3)		
C(1)–Sn–C(13)	116.95(3)	C(7)–Sn–C(13)	120.69(3)		
Sn–O(1)′–C(25)′	132.00(5)	Sn–O(2)–C(25)	137.94(5)		
Sn–C(1)–C(2)	120.54(7)	Sn–C(1)–C(6)	120.83(7)		
Sn–C(7)–C(8)	120.68(6)	Sn–C(7)–C(12)	120.80(7)		
Sn–C(13)–C(14)	119.65(7)	Sn–C(13)–C(18)	122.75(6)		
O(1)–C(25)–O(2)	123.05(8)	O(1)–C(25)–C(26)	119.30(8)		
O(2)–C(25)–C(26)	117.58(8)	O(3)–C(28)–C(19)	119.5(1)		
O(3)–C(28)–C(27)	121.43(9)				

interpreted in terms of an equilibrium mixture of four- and six-coordinate tin in solution. The  $^{13}\text{C}$  resonances of the 3-benzoylpropionate group appear at roughly the same positions for all the six organotin derivatives.

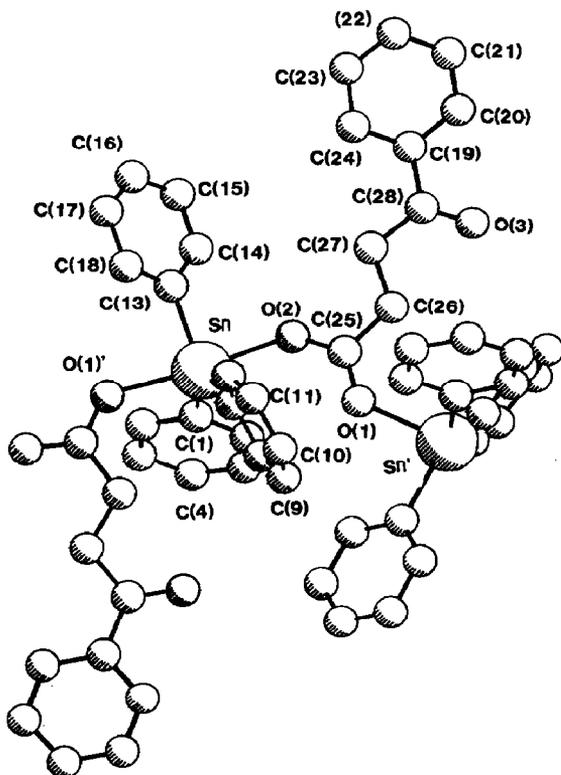


Fig. 1. Structure of triphenyltin 3-benzoylpropionate. Two  $2_1$  screw-related molecules are drawn (symmetry transformation:  $1.5 - x, 0.5 + y, 0.5 - z$ ) to illustrate the coordination of the Sn atom. Hydrogen atoms are omitted.

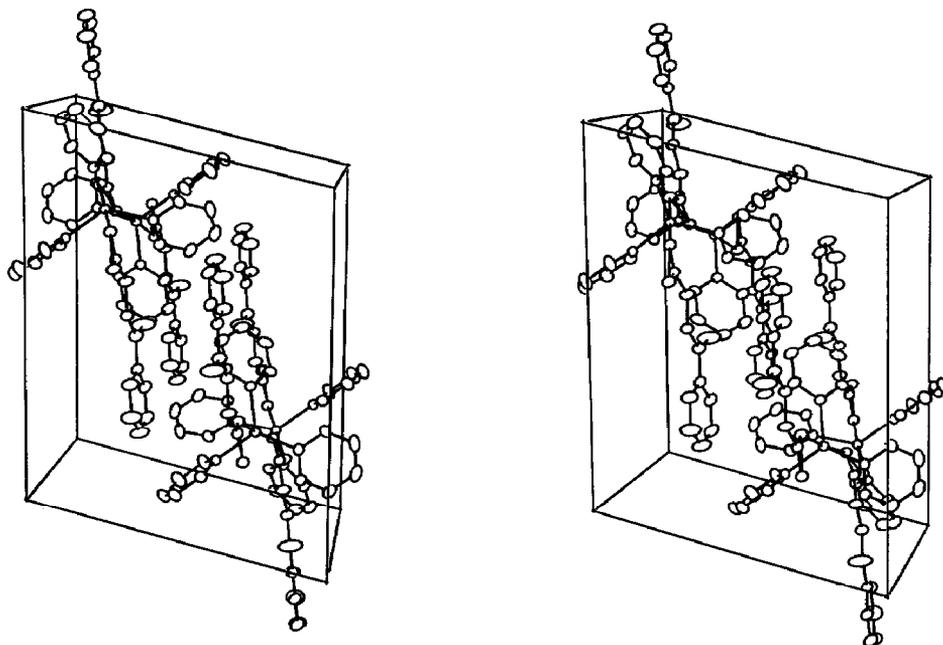


Fig. 2. Stereoview of the unit cell contents of triphenyltin 3-benzoylpropionate.

The crystal structure of triphenyltin 3-benzoylpropionate is shown in Fig. 1 and 2. The tin is five-coordinate, with the axial positions of the trigonal bipyramid being occupied by oxygen atoms, one being the ester oxygen, and the other the carbonyl oxygen from the adjacent symmetry-related molecule. The sum of the carbon-tin-carbon angles in the trigonal plane ( $116.95(3)$ ,  $120.69(3)$ ,  $122.35(3)^\circ$ ) is  $359.99(9)^\circ$ . The three tin-bonded phenyl groups are tilted at  $9.0(5)$ ,  $60.2(2)$  and  $123.2(1)^\circ$  with respect to this plane. The apical angle subtended at tin is  $174.64(2)^\circ$ . The tin-oxygen distances are almost identical ( $2.2460(6)$ ,  $2.2658(6)$  Å).

Structural data [5,16-27] for seventeen other carboxylate-bridged triorganotin esters are shown for comparison in Table 7. As noted previously [1], the repeat distance of a carboxylate-bridged triorganotin polymer is the axial length parallel to the direction of propagation of the polymer divided by 2 (or 4). The repeat distance for the title compound is 5.692 Å, which is at the higher limit associated with the average of 5.19 Å [1]. A particularly large repeat distance of 5.704 Å has been observed in triphenyltin 2-chlorobenzoate [27], which, unlike triphenyltin benzoate [28] and most other triphenyltin arylcarboxylates [29] is polymeric. The difference in tin-oxygen bond distances is largest, at 0.51 Å, for tribenzyltin acetate [25], and for this compound the deviation of the tin atom from the equatorial plane is also the largest, at 0.206 Å. In the structures listed in Table 7, the O-Sn-O' angle is not sensitive to the nature of substituents on the tin or the carboxylate group as is the Sn-O-C angle. The latter angle has the  $sp^2$  value of  $120^\circ$  for most of the compounds, except for the 2-chlorobenzoate and the title compound. The angle most sensitive to substituent changes is the Sn-O'-C' angle, which has values ranging from 123 to  $157^\circ$ . Thus, there is considerable  $sp$  character on this ether-type oxygen, the hybridization of which, has not as far as we are aware, ever been rigorously explained in the literature. The Sn-O'-C' angle is believed to open

Table 7  
Structural data <sup>a</sup> for carboxylate-bridged <sup>b</sup> triorganotin carboxylates

Triorganotin carboxylate	Sn-O (Å)	Sn-O' (Å)	Sn-O-C (°)	Sn-O'-C' (°)	O-Sn-O' (°)	Δ <sup>c</sup> (Å)	Ref.
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CCH <sub>3</sub>	2.205	2.391	122.5	136.6	171.6	0.090	16
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CCF <sub>3</sub>	2.177	2.458	121.0	147.0	174.8	0.101	16
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -4-NH <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>	2.169	2.477			173.5		17
	2.168	2.416			174.1		
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -2-N(CH <sub>3</sub> ) <sub>2</sub>	2.201	2.426			170.0		17
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -2-Cl	2.200	2.414			174.2		17
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -2-OCH <sub>3</sub>	2.208	2.381	118.0	141.7	170.8	0.119	18
(CH <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> )SnO <sub>2</sub> CCH <sub>3</sub>	2.201	2.370	121.3	136.9	174.0	0.104	19
(CH <sub>2</sub> =CH)SnO <sub>2</sub> CCH <sub>3</sub>	2.199	2.331	118.6	138.0	172.7	0.081	20
(CH <sub>2</sub> =CH) <sub>2</sub> SnO <sub>2</sub> CCH <sub>2</sub> Cl	2.210	2.338	118.8	136.8	174.2	0.077	20
(CH <sub>2</sub> =CH) <sub>3</sub> SnO <sub>2</sub> CCl <sub>3</sub>	2.170	2.485	122.8	157.4	173.4	0.134	21
(CH <sub>2</sub> =CH) <sub>3</sub> SnO <sub>2</sub> C(C <sub>2</sub> H <sub>4</sub> FeC <sub>3</sub> H <sub>4</sub> )	2.119	2.423	123.3	156.5	172.5	<sup>d</sup>	22
(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> SnO <sub>2</sub> CCH <sub>2</sub> SC(S)(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )	2.190	2.393	121.5	142.6	173.9	0.092	23
(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> SnO <sub>2</sub> CCH <sub>2</sub> (3-C <sub>3</sub> H <sub>6</sub> N)	2.199	2.524	118.2	139.8	173.5	0.194 <sup>e</sup>	24
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> SnO <sub>2</sub> CCH <sub>3</sub>	2.139	2.649	123.9	131.6	168.6	0.206 <sup>f</sup>	25
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CH	2.219	2.317	125.9	123.1	173.6	0.098	26
	2.185	2.318	127.3	125.5	173.1	0.084	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCH <sub>3</sub>	2.185	2.349	121.0	142.7	173.6	0.094	7
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -2-Cl	2.201	2.384	135.9	146.4	173.8	0.027	27
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> C(O)C <sub>6</sub> H <sub>5</sub>	2.2658(6)	2.2460(6)	137.94(5)	132.00(5)	174.63(2)	-0.015(1)	this work

<sup>a</sup> Calculated from the atomic coordinates whenever bond distances and angles are not reported. <sup>b</sup> Primed atom O' refers to the bridging oxygen atom. <sup>c</sup> Displacement out of the equatorial plane, in the direction of the covalently-bonded oxygen atom. <sup>d</sup> Error in the atomic coordinates of C(14). <sup>e</sup> Error in the atomic coordinates of C(5):  $z = 0.1403$ . <sup>f</sup> Conflicting  $\gamma$  angle of the unit cell in the paper, angle of 105.37° assumed.

up in response to steric bulk on the carboxylate. Angles of 123.1 and 125.5° are found in triphenyltin formate, which has two crystallographically independent asymmetric molecules in the unit cell [26]. The angles probably represent the smallest possible for a carboxylate, since the steric requirement of the hydrogen in the formate is minimal.

Triphenyltin pyridine-3-carboxylate, on the other hand, is bridged through the pyridyl nitrogen rather than the carboxyl oxygen. A characteristic feature of this structure is the near coplanarity of the pyridyl rings of adjacent molecules [30]. In contrast, triphenyltin 2-chlorobenzoate is carboxylate-bridged, but the carboxylate group has to twist by some 60° out of the plane of the benzene ring to facilitate this bridging mode [27].

Returning to the title compound, we note that in the unit cell, the  $x$  atomic coordinates (0.77 to 0.81) of the principal atoms of the repeat unit, Sn, O(1), O(2) and C(25), are close to the  $x = 0.75$  plane (which contains one of the screw axes). The  $1.5 - x$  symmetry translation brings little change in the  $x$  coordinates of these four atoms in the adjacent asymmetric unit, and the polymer backbone is therefore almost flat. The entire 3-benzoylpropionate unit is also relatively flat. In contrast, in tri-*n*-butyltin 3-indolylacetate, the  $x$  coordinates of the four principal atoms of the repeat unit range from 0.78 to 0.84 in the  $P2_1/n$  unit cell, which has an  $a$ -axis 13.388 Å long [24]; the 3-indolylacetate group is bent at the methyl carbon and the polymer backbone is more helical. The effect of steric bulk of the 3-indolylmethyl substituent is also seen in the different tin–oxygen bond distances (2.199, 2.524 Å [24]) and the deviation (0.194 Å) of the tin atom from the equatorial plane (Table 7). In the title compound, the tin atom is displaced by 0.015(1) Å in the direction opposite to the covalently-bonded oxygen, so that the configuration at tin can be considered as being “slightly past the half-way point in the  $S_N2$  displacement profile” [19,31]. This position along the pathway is also reflected in the symmetrical arrangement of the three phenyl rings of the trigonal girdle: instead of an ideal propeller-like configuration for the rings, one ring is approximately coplanar, the second is tilted at 60°, and the third at about 120° with respect to the trigonal plane.

The temperature coefficient of the Mössbauer recoil-free fraction,  $a$ , as derived from variable-temperature studies [32], provides a measure of the tightness with which the tin atom is bound into the lattice, and hence, the degree of molecular association. The  $a$  values for triphenyltin acetate (0.0191 K<sup>-1</sup> [7]) and trimethyltin acetate (0.0162 K<sup>-1</sup> [26]) are consistent with stretched helical and flat conformations, respectively, for the polymer backbone. (In the crystal lattice of trimethyltin acetate, the tin and the carboxylate atoms are located at the  $y = 0.25$  plane in the  $Pnma$  unit cell [16].) The  $a$  value for the title compound, triphenyltin 3-benzoylpropionate, is 0.0126 K<sup>-1</sup>. This value is small compared to the  $a$  value for triphenyltin levulinate (0.0217 K<sup>-1</sup> [5]), which is probably a helical polymer. Replacement of the methyl group of the levulinate by a phenyl ring seems to pose steric problems for a helical arrangement of the molecules of triphenyltin 3-benzoylpropionate in the crystal lattice, and the molecules stack instead in a chain configuration, with the 3-benzoylpropionate groups in an approximately coplanar array.

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