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# Structural chemistry of organotin carboxylates

## XI *. X-Ray crystal structure of dimethyltin dibenzoate

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### Abstract

The crystal and molecular structure of the title compound, $[Me_2Sn(O_2CPh)_2]$, shows the Sn atom to exist in a skew-trapezoidal planar geometry. The carboxylate ligands chelate the Sn centre with asymmetric Sn–O bond distances of 2.156(9), 2.51(1) and 2.128(9), 2.510(9) Å; the C–Sn–C angle of 147.2(7)° is larger than those in related structures. There is a close intermolecular Sn $\cdots$ O contact of 2.96(1) Å in the crystal lattice between centrosymmetrically-related molecules.

### Introduction

Of the numerous structural types known for organotin carboxylates, the simplest is that found for the compounds of the general formula $[R_2Sn(O_2CR')_2]$. X-Ray crystallographic studies on six derivatives have shown these compounds to be monomeric, with six-coordinate Sn centres and skew-trapezoidal planar geometries [2–6]. The only exception to this rule is found for the $[Me_2Sn(O_2CC_5H_4N\text{-}o)_2]$ compound [7] which is polymeric owing to the participation of the N-hetero atom in coordination to the Sn atom; in this example the Sn atom is seven-coordinate. Recently, the molecular structure [6] of $[^nBu_2Sn(O_2CC_6H_4Br\text{-}o)_2]$ was shown to be similar to the other monomeric compounds of this type in the literature [2–5]. An additional feature was also noted in this structure, however, that being the presence of a close intermolecular Sn $\cdots$ O interaction of 3.451(5) Å; the structure was thus described as a weakly-bridged dimer [6]. This interaction is very weak so that the deviation from the common structural type is minimal.

The relatively uncomplicated structural motif for the $[R_2Sn(O_2CR')_2]$ compounds offers the opportunity to monitor the effect on the structure as the electronic nature and steric profile of the R and R′ substituents are varied.

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* For Part X, see ref. 1.

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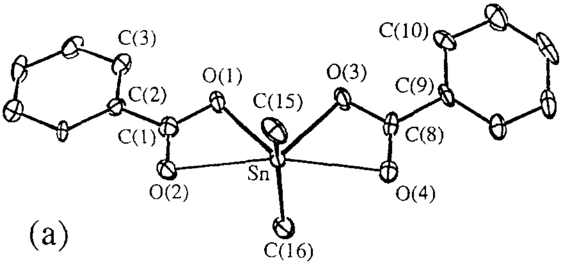
Information thus gained may aid the interpretation, and enable rationalization, of the large number of structures found for organotin carboxylates and, by extension, of other metal carboxylate structures. This strategy is not realized for the [$Me_2Sn(O_2CPh)_2$] compound, the subject of this paper, for which a close Sn · · · O intermolecular contact of 2.96(1) Å is noted.

## Results and discussion

The molecular structure of [$Me_2Sn(O_2CPh)_2$] is shown in Fig. 1a and selected interatomic parameters are listed in Table 1. The Sn atom is coordinated by two asymmetrically coordinating carboxylate ligands (average $\Delta$(Sn–O) 0.37 Å) and two methyl groups at 2 × 2.10(1) Å. The geometry about the Sn atom is best described as skew-trapezoidal planar with the basal plane being defined by the four O atoms. The methyl groups are disposed over the longer Sn–O bonds such that the C–Sn–C angle is 147.2(7)°.

The C–Sn–C angle in [$Me_2Sn(O_2CPh)_2$] is approximately 12° greater than the C–Sn–C angles of about 135° in [$Me_2Sn(O_2CMe)_2$] [2] and [$Me_2Sn(O_2CC_6H_4$-$NH_2$-$p$$)_2$] [3]. The reason for this expansion is unclear although the steric influence



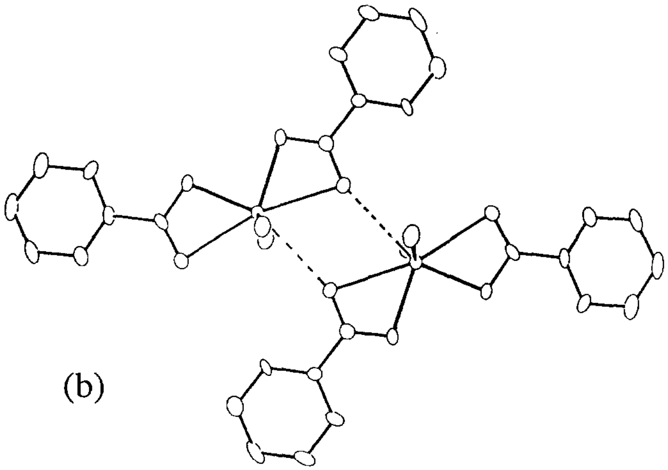


Fig. 1. (a) Molecular structure and crystallographic numbering scheme employed for [$Me_2Sn(O_2CPh)_2$]; (b) Mode of association between centrosymmetrically related molecules in the crystal lattice.

Table 1

Selected interatomic parameters (Å; deg) for [$Me_2Sn(O_2CPh)_2$]

| | | | |
|---|---|---|---|
| Sn–O(1) | 2.156(9) | Sn–O(2) | 2.51(1) |
| Sn–O(3) | 2.128(8) | Sn–O(4) | 2.510(9) |
| Sn–C(15) | 2.10(2) | Sn–C(16) | 2.10(2) |
| C(1)–O(1) | 1.29(2) | C(1)–O(2) | 1.26(2) |
| C(8)–O(3) | 1.29(2) | C(8)–O(4) | 1.24(2) |
| O(1)–Sn–O(2) | 55.5(3) | O(1)–Sn–O(3) | 84.4(4) |
| O(1)–Sn–O(4) | 139.1(3) | O(1)–Sn–C(15) | 106.5(6) |
| O(1)–Sn–C(16) | 100.1(6) | O(2)–Sn–O(3) | 139.8(4) |
| O(2)–Sn–O(4) | 165.3(3) | O(2)–Sn–C(15) | 89.2(5) |
| O(2)–Sn–C(16) | 90.4(5) | O(3)–Sn–O(4) | 54.9(4) |
| O(3)–Sn–C(15) | 100.1(5) | O(3)–Sn–C(16) | 101.3(5) |
| O(4)–Sn–C(15) | 86.9(5) | O(4)–Sn–C(16) | 85.4(5) |
| C(15)–Sn–C(16) | 147.2(7) | | |

of a neighbouring O(2′) atom (from a centrosymmetrically related molecule), Sn ··· O(2′) is 2.96(1) Å, gives rise to one possible explanation; see Fig. 1b. If considered a significant interaction, this would result in a seven coordinate geometry for the Sn atom based on a pentagonal bipyramid. There is evidence to suggest, however, that the Sn ··· O(2′) interaction is not significant and that the expansion in the C–Sn–C angle arises owing to other factors rather than the presence of the O(2′) atom. This evidence is provided by examining the interatomic parameters about the Sn atom in each of the [$Me_2Sn(O_2CPh)_2$] and the closely related [$Me_2Sn(O_2CMe)_2$] [2] structures for which the O–Sn–O chelate angles are constant at approximately 55°. The additional interaction of the O(2) atom with a neighbouring Sn atom causes no additional lengthening of the already weak Sn–O(2) bond in [$Me_2Sn(O_2CPh)_2$] compared to the Sn–O(4) bond distance. Further, the changes in O–Sn–O angles between the [$Me_2Sn(O_2CMe)_2$] and [$Me_2Sn(O_2CPh)_2$] structures may be related to the degree of asymmetry in the Sn–O bonds formed by the carboxylate ligands rather than the close approach of the O(2′) atom in [$Me_2Sn(O_2CPh)_2$]. In [$Me_2Sn(O_2CMe)_2$], the O atoms forming the shorter Sn–O bonds subtend an angle of 79.5(1)° at the Sn atom and the angle subtended by the weakly coordinating O atoms is 170.3(1)°. These may be compared to the angles of 84.4(4) and 165.3(3)°, respectively, found in the [$Me_2Sn(O_2CPh)_2$] compound. These differences may arise as a result of the greater contribution of the resonance structure I for the carboxylate ligands to the overall structure in [$Me_2Sn(O_2CPh)_2$] compared to [$Me_2Sn(O_2CMe)_2$]. Additional support for this conclusion is found in the greater asymmetry in the Sn–O bond distances ($\Delta$(Sn–O) 0.433 Å) formed by the $^-O_2CMe$ ligand in [$Me_2Sn(O_2CMe)_2$]. The narrowing of the O(2)–Sn–O(2) angle in [$Me_2Sn(O_2CPh)_2$] in effect pushes the two methyl substituents apart, to relieve steric repulsions, and hence accounts for the increased C–Sn–C angle.

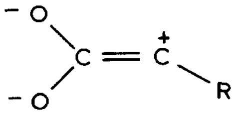


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Table 2

Crystal data and refinement details for $[Me_2Sn(O_2CPh)_2]$

| | |
|---|---|
| Formula | $C_{16}H_{16}O_4Sn$ |
| Mol. wt. | 391.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| $a$, Å | 9.458(2) |
| $b$, Å | 15.245(3) |
| $c$, Å | 11.357(3) |
| $\beta$, deg. | 96.37(2) |
| Vol., (Å$^3$) | 1627.4 |
| $Z$ | 4 |
| $D_c$, (g cm$^{-3}$) | 1.596 |
| $F(000)$ | 776 |
| $\mu$, cm$^{-1}$ | 14.47 |
| Transmission factors (max/min) | 0.870, 0.721 |
| $\theta$ limits (°) | 1.5–22.5 |
| No. of data collected | 2351 |
| No. of unique data | 2125 |
| No. of unique reflections used with $I \geqslant 2.5\sigma(I)$ | 1526 |
| $R$ (unit weights) | 0.065 |
| Residual $\rho_{max}$, (e Å$^{-3}$) | 0.58 |

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for remaining atoms) for $[Me_2Sn(O_2CPh)_2]$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn | 19423(10) | 53098(7) | 13684(9) |
| O(1) | 860(9) | 4742(7) | 2759(8) |
| O(2) | −440(10) | 4577(8) | 1051(9) |
| O(3) | 3617(10) | 5540(7) | 2746(8) |
| O(4) | 4197(10) | 6128(7) | 1132(10) |
| C(1) | −306(16) | 4499(11) | 2160(15) |
| C(2) | −1471(15) | 4111(9) | 2776(12) |
| C(3) | −1306(17) | 4095(11) | 4009(15) |
| C(4) | −2407(20) | 3762(11) | 4580(17) |
| C(5) | −3616(18) | 3416(11) | 3883(23) |
| C(6) | −3700(20) | 3376(12) | 2629(19) |
| C(7) | −2658(14) | 3778(11) | 2118(15) |
| C(8) | 4517(15) | 5969(11) | 2196(15) |
| C(9) | 5846(13) | 6271(10) | 2872(14) |
| C(10) | 6191(16) | 5984(11) | 4038(14) |
| C(11) | 7431(21) | 6298(14) | 4639(20) |
| C(12) | 8297(18) | 6855(16) | 4107(22) |
| C(13) | 7915(17) | 7142(12) | 2920(21) |
| C(14) | 6700(15) | 6827(10) | 2320(15) |
| C(15) | 2812(17) | 4261(11) | 492(16) |
| C(16) | 961(17) | 6546(10) | 1224(17) |

The interpretation of spectroscopic measurements on compounds of the $[R_2Sn(O_2CR')_2]$ formulation has led to the proposal of three different structural types. These structures are based on monomeric, dimeric or polymeric structures with the latter two involving bridging carboxylate ligands (see ref. 2 for full discussion). The overwhelming crystallographic evidence [2–6], however, favours the simple, monomeric structure as exemplified by the structure of $[Me_2Sn(O_2CPh)_2]$ reported herein.

## Experimental

The compound, $[Me_2Sn(O_2CPh)_2]$, was prepared by the metathical reaction between $Me_2SnCl_2$ (Aldrich) and caesium benzoate (Strem) in aqueous ethanol solution and crystals suitable for X-ray studies were obtained from the slow evaporation of a $CHCl_3$ solution of the compound. Intensity data were measured at 292 K on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-$K_\alpha$ radiation, $\lambda = 0.7107$ Å. The $\omega$–$2\theta$ scan technique was employed to measure 2351 reflections up to a maximum Bragg angle of 22.5°. The data were corrected for Lorentz and polarization effects and for absorption with the use of an analytical procedure [8]. Relevant crystal data are collected in Table 2.

The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure based on $F$ [8]. All atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. The analysis of variance showed no special features and hence a weighting scheme was not used. The refinement was continued until convergence; final refinement details are listed in Table 2. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed is shown in Fig. 1 drawn with ORTEP [9] at 15% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program and refinement was performed on a SUN 4/280 computer. Other crystallographic details (available from the author) comprise thermal parameters, hydrogen atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

## Acknowledgements

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