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Di-n-butyltin(IV) di-*o*-bromobenzoate, a weakly-bridged dimer

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Abstract

The six-coordinated tin in di-n-butyltin di-*o*-bromobenzoate has a skew-trapezoidal bipyramidal geometry with a C–Sn–C angle of 140.5(3)°. The molecules are packed in the unit cell as weakly-bridged dimers (Sn · · · O 3.451(5) Å).

Introduction

Diorganotin dicarboxylates $[R_2Sn(O_2CR')_2]$ have been generally assigned carboxylate-bridged structures on the basis of their spectroscopic characteristics, but there has yet been no crystallographic confirmation of this, and the few esters studied in fact adopt chelated skew-trapezoidal bipyramidal structures [1]. Among the related R_3SnO_2CR' esters, the R = alkyl compounds are polymeric chains [2] whereas the R = R' = aryl derivatives are typically tetrahedral monomers [3], although an exception to this is provided by triphenyltin *o*-chlorobenzoate [4]. *Ortho*-halo substituted triphenyltin benzoates are also polymeric species, as deduced from tin-119*m* Mössbauer quadrupole splittings [5]. We thought it likely that *ortho*-halo-substituted di-n-butyltin dibenzoates would also have a polymeric structure, and a study on di-n-butyltin di-*o*-bromobenzoate was undertaken to examine this possibility.

Experimental

Di-n-butyltin oxide (2.5 g, 10 mmol) and *o*-bromobenzoic acid (4.0 g, 20 mmol) were melted together in a few drops of toluene to give the crude ester. Colorless crystals of di-n-butyltin di-*o*-bromobenzoate, m.p. 78°C, were obtained by the slow evaporation of a solution in hexane. Anal. Found: C, 41.73; H 3.94. $C_{22}H_{26}Br_2O_4Sn$

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Table 1

Atomic coordinates ($\times 10^5$ for Sn and Br; $\times 10^4$ for other atoms) and equivalent isotropic temperature factors [a] ($Å^2 \times 10^4$)

Atom	x	y	z	U_{eq}
Sn(1)	61608(4)	41241(6)	10109(2)	546(2)
Br(1)	16692(6)	44391(10)	−1187(4)	794(3)
Br(2)	75158(8)	14219(12)	29885(5)	1036(4)
O(1)	4795(3)	3397(5)	1360(2)	660(8)
O(2)	4094(3)	4262(5)	437(2)	668(8)
O(3)	7010(3)	3448(6)	1894(2)	719(8)
O(4)	8304(4)	4183(6)	1423(2)	780(8)
C(1)	3961(5)	3672(7)	924(3)	526(8)
C(2)	2863(5)	3211(6)	1045(3)	495(8)
C(3)	1843(5)	3480(7)	664(3)	560(8)
C(4)	873(5)	3040(8)	835(3)	704(8)
C(5)	898(6)	2288(8)	1379(4)	791(8)
C(6)	1885(6)	2005(8)	1766(3)	756(8)
C(7)	2854(6)	2483(7)	1593(3)	651(8)
C(8)	8037(5)	3705(7)	1893(3)	579(8)
C(9)	8883(5)	3482(7)	2473(3)	555(8)
C(10)	8753(5)	2604(7)	2973(3)	651(8)
C(11)	9622(6)	2500(8)	3497(4)	846(8)
C(12)	10570(6)	3253(8)	3517(4)	909(8)
C(13)	10700(6)	4140(8)	3022(4)	900(8)
C(14)	9859(5)	4255(8)	2506(3)	707(8)
C(15)	6188(5)	6432(7)	1107(3)	687(8)
C(16)	5467(7)	7049(7)	1508(4)	836(8)
C(17)	5627(8)	8714(8)	1613(4)	1096(9)
C(18)	4931(8)	9398(9)	1955(5)	1243(9)
C(19)	6343(6)	2476(8)	360(3)	764(8)
C(20)	7238(8)	1384(9)	543(5)	1238(9)
C(21)	7290(8)	217(9)	25(5)	1274(9)
C(22)	7890(9)	818(10)	−383(6)	1801(9)

[a] U_{eq} defined as one third of the trace of the orthogonalized U tensor.

calcd.: C 41.74, H 4.11%. Carbon-13 NMR in $CDCl_3$ [δ in ppm (^nJ in Hz)] for $(H_3C^4\text{–}H_2C^3\text{–}H_2C^2\text{–}H_2C^1)_2Sn(O_2C\text{–}C_6H_4\text{-}o\text{-}Br)_2$: C^1 25.6 (570.6), C^2 26.6 (38.2), C^3 26.2 (94.0), C^4 13.4 ppm (−Hz); CO_2 175.6 ppm; C_6H_4 121.9, 127.0, 132.0, 132.2, 132.5, 134.2 ppm. A crystal measuring 0.34 × 0.36 × 0.44 mm was used for the diffraction analysis, and data were collected on a Nicolet *R*3*m*/*V* diffractometer up to 2θ 55°. Direct phase determination using 2981 $|F_o| \geq 6\sigma|F_o|$ out of 5417 unique Mo-K_α reflections yielded most of the non-H atoms and the others were derived from successive difference Fourier syntheses. The non-H atoms were subjected to anisotropic refinement, and H atoms were placed in calculated positions (C–H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms. Refinement converged at $R_F = 0.047$, $R_G = 0.059$ ($w = [\sigma^2(F_o) + 0.0010|F_o|^2]^{-1}$); the max/min transmission factors are 0.167 and 0.103. Computations were performed by using the SHELXTL-PLUS program package [6] on a DEC MicroVAX-II computer. The atomic coordinates are listed in Table 1.

Crystal data $C_{22}H_{26}Br_2O_4Sn$, monoclinic, $P2_1/c$, a 12.343(2), b 9.098(2), c 21.495(2) Å, β 101.7(1)°; V 2407.6(7) $Å^3$; D_{calcd} 1.746 g cm^{-3}; μ 43.74 cm^{-1} for $Z = 4$.

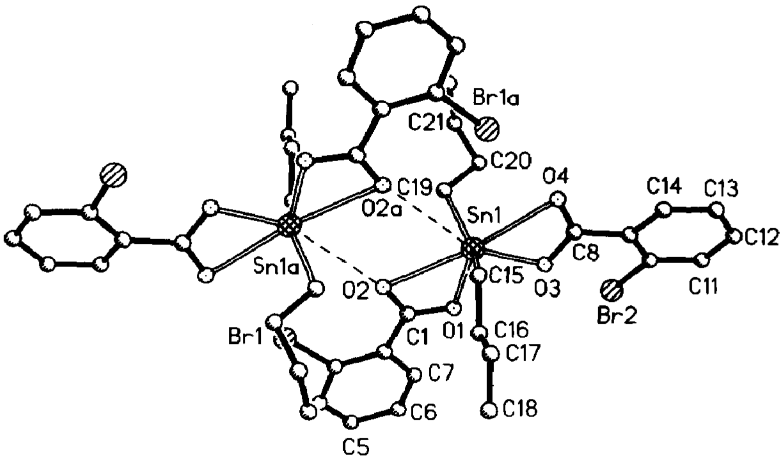

Fig. 1. Structure of di-n-butyltin di-*o*-bromobenzoate. Selected bond distances and angles: Sn(1)–O(1) 2.095(5), Sn(1)–O(2) 2.608(5), Sn(1)–O(3) 2.097(4), Sn(1)–O(4) 2.617(5), Sn(1) ··· O(2a) 3.451(5), Sn(1)–C(15) 2.110(7), Sn(1)–O(19) 2.112(7) Å; O(1)–Sn(1)–O(2) 53.8(2), O(2)–Sn(1) ··· O(2a) 68.9(2), O(2a) ··· Sn–O(4) 108.2(2), O(4)–Sn(1)–O(3) 53.6(2), O(3)–Sn(1)–O(1) 81.9(2), C(15)–Sn–C(19) 140.5(3)°.

Results and discussion

The molecular structure of di-n-butyltin di-*o*-bromobenzoate is depicted in Fig. 1, which also shows the symmetry-related molecule. The tin atom is six-coordinate [$Sn-O_{short}$ 2.095(5), 2.097(4) Å; $Sn-O_{long}$ 2.608(5), 2.617(5) Å], with a skew-trapezoidal bipyramidal polyhedron. Two tin atoms are so close that the distance between Sn(1) and the O(2) atom of the other (centrosymmetrically-related) molecule is only 3.451(5) Å, which suggests that there is a very weak interaction between them. The dimeric structure contrasts with the monomeric structure of di-n-butyltin di-*p*-bromobenzoate [1], for which no intermolecular contacts of < 4 Å were found.

The literature contains two unambiguous examples of formally seven-coordinate tin in diorganotin dicarboxylate adducts, namely di-n-butyltin bisphenylacetate hydrate (C–Sn–C 196.9(5)° and $Sn-O_{water}$ 2.342(8) Å) [7] and the ionic dimethyltin diacetate-acetate (C–Sn–C 165.8(6)° and $Sn-O_{acetate}$ 2.113(9) Å) [8]. For the title compound, the interpretation of the 3.451(5) Å contact distance as a bond would imply a distorted pentagonal bipyramid geometry: the apical C(15)–Sn–C(19) angle is 140.5(3)°, and the sum of angles in the pentagonal plane is 360.0(10)°.

The 132° C–Sn–C angle predicted [9] from the solution one-bond $^{119}Sn-^{13}C$ coupling constant of 570.6 Hz is much smaller than the experimental solid-state angle of 140.5(3)° in contrast with the much better agreement between the solution (133°) and solid-state (130.6(2)°) values for the monomeric di-*p*-bromobenzoate [1]. This result indicates that dissociation of the "dimer" in solution is accompanied by some folding of the C–Sn–C skeleton.

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