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Structure of Triphenyltin 2-[2-Bromo-4-(dimethylamino)phenylazo]benzoate

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Abstract. [2'-Bromo-4'-(dimethylamino)azobenzene-2-carboxylato]triphenyltin, $[\text{Sn}(\text{C}_{15}\text{H}_{13}\text{BrN}_2\text{O}_2)(\text{C}_6\text{H}_5)_3]$, $M_r = 697.2$, triclinic, $P\bar{1}$, $a = 10.044$ (4), $b = 19.707$ (6), $c = 7.899$ (3) Å, $\alpha = 96.1$ (5), $\beta = 107.7$ (7), $\gamma = 90.3$ (5)°, $V = 1480$ Å³, $Z = 2$, $D_x = 1.56$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 84$ cm⁻¹, $F(000) = 690$, $T = 288$ K, final $R = 0.049$ for 2257 observed reflections. The structure is stabilized by a network of hydrophobic and π - π interactions between C29...C24 (3.37 Å) and N1...C32 (3.38 Å), respectively. The compound forms a distorted *cis* SnC₃O₂ five-coordinated geometry at Sn owing to the formation of a four-membered chelate with the carboxylate group. The configuration at the Sn atom is a distorted trigonal bipyramid.

Introduction. Organotin carboxylates constitute an interesting class of organometallics with diverse

chemical and biological properties. Various substituted organotin carboxylates are known to exhibit significant biological activities (Maji, Ghatak, Ganguly & Ray, 1989; Blunden, Cusack & Hill, 1985; Evans & Hill, 1983; Srivastava, Srivastava & Bhatia, 1977; Evans & Smith, 1975; Polster & Halacka, 1972; Kochkin, Verenikina & Chekmareva, 1961; Kochkin & Verenikina, 1961; Kochkin & Golyshva, 1961; Koopmans, 1961).

The title compound (Maji, Ghatak, Ganguly & Ray, 1989) is an organotin ester. Characterization of this compound was made on the basis of IR and UV spectral data and elemental analysis. The IR spectral data revealed the presence of a carboxylate carbonyl (C=O) group and an Sn—O bond in the organotin ester, and the UV spectrum in non-nucleophilic solvent showed a large bathochromic shift owing to a $\pi \rightarrow \pi^*$ transition in the azo chromophore of the molecule (Majee & Banerjee, 1977) indicating N→Sn coordination.

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The literature shows that the conformation of this type of compound largely depends on the nature of the groups attached to the metal atom (Harrison, King & Molloy, 1980; Harrison, Lambert, King & Majee, 1983; Alcock & Timms, 1968; Calogero, Ganis, Peruzzo & Tagliavini, 1980). Bancroft, Davis, Payne & Sham (1975) attempted to rationalize and predict the configurational isomers (*cis* or *trans*) of this type of organotin compound from a chemical structure point of view.

The activity of the compound under study was measured by conventional Agar-cup method and found reasonably active against Gram-positive bacteria. The detailed mode of its action is still unknown and a crystallographic study has been undertaken to obtain a complete assignment of the stereochemical disposition of substituted phenyl rings and to make an attempt to draw a rational conclusion on the structure-activity relationship (SAR).

Experimental. Elemental analysis for C, H, N, Br and Sn found 57.58, 4.27, 5.86, 11.72 and 16.56%, respectively (calculated for $C_{33}H_{28}BrN_3O_2Sn$: 56.83, 4.02, 6.02, 11.48 and 17.03%, respectively). The IR spectrum shows characteristic absorptions [asym. (COO) 1620 cm^{-1}] for an organotin ester-like linkage (Graziani, Casellato & Plazzogna, 1980) and also indicates that the Sn atom is five coordinate (Hester, 1970, 1971; Graziani, Bombieri, Forsellini, Furlan, Peruzzo & Tagliavini, 1977). An absorption at 520 cm^{-1} suggests the presence of an Sn—O bond in the compound.

Orange-red good needle-shaped crystals of triphenyltin arylazobenzenecarboxylate were obtained from petroleum ether (boiling range 333–353 K) by slow evaporation; dimensions were $0.34 \times 0.25 \times 0.15\text{ mm}$. Cell parameters were obtained from least-squares refinement of the setting angles of 25 reflections ($4 \leq \theta \leq 16^\circ$).

2314 [2257 with $I > 3\sigma(I)$] unique reflections were collected out of a total of 4112 reflections measured on an Enraf-Nonius CAD-4 diffractometer with Ni-filtered Cu $K\alpha$ radiation and ω - 2θ -step scan mode. Ranges of h , k and l are -11 to 10 , -22 to 21 and 0 to 8 , respectively, and maximum 2θ was 102° . 3 standard reflections, measured every 100 reflections, showed 0.5% variation in intensity. Data were corrected for Lorentz-polarization factors but not for absorption. The structure was solved by Patterson and successive difference Fourier methods using *SHELXS86* (Sheldrick, 1986), and refined by full-matrix least squares on F using *SHELX76* (Sheldrick, 1976). All non-H atoms were refined anisotropically and geometrically generated H atoms isotropically. The refinement converged to $R = 0.049$ ($wR = 0.049$) for 361 refined parameters; $(\Delta/\sigma)_{\max} = 0.25$. The function minimized was $\sum w(|F_o| - |F_c|)^2$

Table 1. Final fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-H atoms

$$U_{eq} = (1/3)\sum_i \sum_j a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Sn1	0.31082 (11)	0.17445 (5)	0.13033 (13)	0.0413
Br1	0.61675 (16)	0.42773 (9)	0.01732 (21)	0.0656
C1	0.3472 (13)	0.2716 (7)	0.2916 (17)	0.0743
C2	0.3514 (14)	0.2720 (7)	0.4656 (20)	0.0867
C3	0.3887 (16)	0.3315 (8)	0.5828 (19)	0.0609
C4	0.4200 (15)	0.3908 (8)	0.5204 (20)	0.0585
C5	0.4141 (16)	0.3904 (7)	0.3511 (23)	0.0738
C6	0.3795 (15)	0.3305 (8)	0.2295 (20)	0.0632
C7	1.4746 (14)	0.1448 (6)	0.0243 (17)	0.0440
C8	1.5238 (15)	0.1848 (7)	-0.0824 (21)	0.0602
C9	1.6312 (18)	0.1634 (10)	-0.1421 (21)	0.0743
C10	1.7004 (16)	0.1059 (11)	0.0950 (25)	0.0867
C11	1.6599 (17)	0.0676 (8)	0.0118 (24)	0.0738
C12	1.5476 (16)	0.0875 (7)	0.0742 (20)	0.0585
C13	0.2595 (14)	0.0981 (6)	1.2772 (16)	0.0528
C14	0.3550 (16)	0.0834 (8)	1.4337 (21)	0.0594
C15	0.3233 (21)	0.0350 (9)	1.5290 (23)	0.0872
C16	0.1969 (22)	0.0014 (8)	1.4734 (26)	0.0978
C17	0.1046 (18)	0.0118 (9)	1.3176 (25)	0.0766
C18	0.1328 (15)	0.0630 (7)	1.2155 (17)	0.0538
C19	1.1183 (15)	0.2097 (7)	-0.1719 (18)	0.0469
C20	0.9846 (13)	0.2189 (6)	-0.3182 (16)	0.0359
C21	0.9676 (15)	0.1886 (7)	-0.4901 (18)	0.0530
C22	0.8463 (15)	0.2001 (8)	-0.6233 (19)	0.0568
C23	0.7490 (16)	0.2413 (7)	-0.5865 (19)	0.0622
C24	0.7686 (14)	0.2740 (7)	0.4174 (19)	0.0525
C25	0.8865 (14)	0.2627 (6)	-0.2796 (16)	0.0399
C26	0.8715 (14)	0.3547 (6)	0.1229 (17)	0.0440
C27	0.9901 (14)	0.3387 (7)	0.2485 (18)	0.0632
C28	1.0236 (14)	0.3642 (7)	0.4232 (18)	0.0609
C29	0.9315 (14)	0.4077 (6)	0.4833 (18)	0.0611
C30	0.8110 (14)	0.4257 (7)	0.3587 (19)	0.0602
C31	0.7820 (13)	0.3990 (6)	0.1834 (17)	0.0632
C32	1.0979 (18)	0.4185 (8)	0.7941 (20)	0.0736
C33	0.8666 (19)	0.4721 (8)	0.7295 (20)	0.0810
O1	1.1158 (9)	0.1654 (5)	-0.0645 (12)	0.0566
O2	1.2252 (10)	0.2459 (5)	-0.1478 (13)	0.0620
N2	0.8333 (12)	0.3290 (5)	-0.0618 (15)	0.0489
N1	0.9226 (11)	0.2901 (5)	-0.0999 (14)	0.0449
N3	0.9628 (13)	0.4302 (6)	0.6622 (16)	0.0607

Table 2. Bond lengths (\AA) and angles ($^\circ$) of the organotin ester

Sn1—C1	2.151 (1)	Sn1—C13	2.148 (2)
Sn1—O1	2.089 (7)	Sn1—C7	2.120 (2)
Br1—C31	1.906 (1)	Sn1—O2	2.660 (9)
C28—C27	1.354 (2)	C29—C30	1.378 (2)
C29—N3	1.371 (2)	C27—C26	1.378 (2)
C31—C26	1.399 (2)	C31—C30	1.368 (2)
C26—N2	1.428 (2)	C1—C2	1.364 (2)
C1—C6	1.379 (1)	C2—C3	1.387 (2)
C5—C4	1.323 (3)	C5—C6	1.400 (2)
C4—C3	1.372 (3)	C18—C13	1.400 (1)
C18—C17	1.382 (3)	C13—C14	1.410 (2)
C14—C15	1.350 (3)	C17—C16	1.353 (3)
C15—C16	1.390 (3)	O1—C19	1.281 (2)
O2—C19	1.245 (2)	C19—C20	1.502 (2)
C7—C12	1.378 (2)	C7—C8	1.401 (2)
C12—C11	1.372 (3)	C11—C10	1.383 (3)
N2—N1	1.271 (2)	N1—C25	1.395 (2)
C20—C21	1.386 (2)	C20—C25	1.406 (2)
C21—C22	1.380 (1)	C25—C24	1.380 (2)
C24—C23	1.356 (1)	C8—C9	1.354 (3)
C9—C10	1.356 (1)	N3—C33	1.448 (3)
N3—C32	1.465 (1)	C22—C23	1.366 (2)
C28—C29	1.423 (2)		
C13—Sn1—C7	111.0 (0.5)	C13—Sn1—O1	93.8 (0.5)
C1—Sn1—C7	114.3 (0.5)	C1—Sn1—O1	112.8 (0.4)
Sn1—O1—C19	106.1 (0.8)	O2—Sn1—C1	85.8 (0.4)
N2—N1—C25	114.1 (1.0)	O2—Sn1—O1	53.4 (0.3)
C33—N3—C32	115.7 (1.3)	C19—C20—C25	118.8 (1.1)
C26—N2—N1	112.7 (1.0)	C29—N3—C33	120.9 (1.2)
C19—O2—Sn1	80.2 (0.8)		

with $w = 1/(\sigma^2|F_o|)$. A final difference Fourier synthesis showed peaks lying between 0.3 and 0.2 e Å⁻³. The geometrical parameters of the molecule were computed with the program *PARST* (Nardelli, 1983). Atomic scattering factors were taken from *SHELXS86* and all computations were carried out using *PC/AT(386)* and *MicroVAX II* systems.

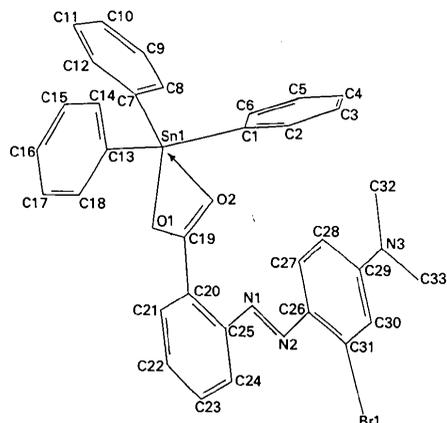


Fig. 1. Chemical diagram of the molecule with atom numbering.

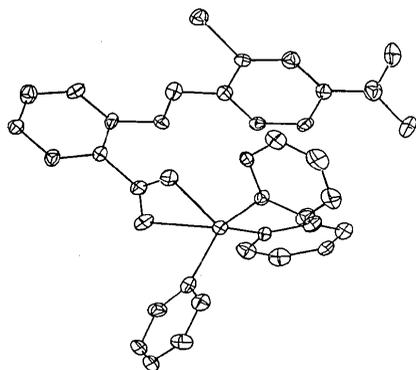


Fig. 2. An *ORTEP* (Johnson, 1965) view of the molecule (minimum overlap) with 50% probability ellipsoids.

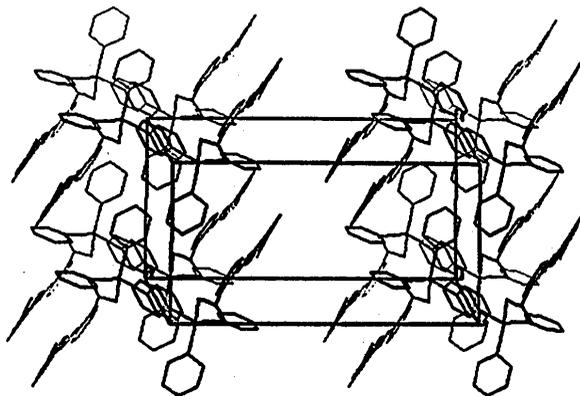


Fig. 3. Packing diagram of the molecules.

Discussion. Final atomic parameters of the non-H atoms are presented in Table 1.* The bond lengths and bond angles of the molecule are given in Table 2. Fig. 1 shows a chemical diagram of the molecule with numbering scheme and an *ORTEP* (Johnson, 1965) view of the molecule with 50% probability ellipsoids is shown in Fig. 2. Fig. 3 shows a packing diagram of the molecule.

The structure reveals the presence of coordination through the carboxylate carbonyl O atom to the Sn atom [Sn1—O1 2.088 (7) and Sn1...O2 2.663 (9) Å]. The Sn coordination is a distorted trigonal bipyramid (C13—Sn1—O2 148°). It is interesting to note that the atoms O2, C19, O1 and Sn1 are coplanar and the phenyl rings, the three N atoms, Br and two C atoms of the methyl group are in another plane at 90° to the former. The structure is stabilized by a network of hydrophobic and π - π interactions between C29...C24 (3.37 Å) and N1...C32 (3.38 Å), respectively. The arylazobenzenecarboxylate unit shows a *trans* geometry at its N=N linkage. N2 forms an intramolecular hydrogen bond with C24 for self-stabilization while N1 forms a bifurcated hydrogen bond to C27 in the same molecule (2.696 Å) and C32 of another molecule (3.376 Å). The N...C bonds (1.465 Å) are comparable with those found in similar structures (Harrison & King, 1974; Harrison, Lambert, King & Majee, 1983; 1.43 Å).

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* Lists of structure factors, anisotropic thermal parameters, bond angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55451 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Monoclinic Zinc *n*-Butanoate

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Abstract. $\text{Zn}^{2+} \cdot 2\text{C}_4\text{H}_7\text{O}_2^-$, $M_r = 239.57$, monoclinic, $P2_1/c$, $a = 23.48$ (3), $b = 4.795$ (4), $c = 9.380$ (9) Å, $\beta = 90.08$ (9)°, $V = 1056$ (2) Å³, $Z = 4$, $D_x = 1.506$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.36$ mm⁻¹, $F(000) = 496$, room temperature, $R = 0.091$ for 1397 observed reflections with $I > 4\sigma(I)$. The structure consists of polymeric sheets parallel to (100) in which tetrahedrally coordinated Zn ions are connected by butanoate bridges in a *syn-anti* arrangement. There is some disorder in the stacking of the sheets.

Introduction. This structure analysis was undertaken to provide information pertinent to an investigation of the nature of the coordination of Zn in carboxylate glasses.

Experimental. The compound was prepared by reaction of ZnO with freshly distilled *n*-butanoic acid and recrystallized from methanol/water (2/1). X-ray diffraction data were obtained from a suitable crystal (*ca* 0.43 × 0.7 × 0.14 mm) on a Nicolet P3 four-circle diffractometer with Mo $K\alpha$ radiation and graphite monochromator. Cell dimensions were determined using 14 reflections at 17–21° in 2θ . Data were

collected corresponding to a primitive monoclinic supercell with $a = 46.96$ Å, *i.e.* twice the value given above to take account of reflections observed in an oscillation photograph. The intensities of 4257 reflections with $2\theta \leq 50^\circ$ and h 0–55, k 0–5 and l –11–11 were measured from ω scans with a fixed width of 0.6°, scan rates in the range 1.0–29.3° min⁻¹ related to pre-scan intensity, and stationary crystal–stationary counter background counts taken at $\pm 1.0^\circ$ in ω from the calculated position of the Bragg peak. An empirical absorption correction based on ψ -scan data was applied. The minimum and maximum transmission factors were 0.26 and 0.47. Two reference reflections, monitored periodically, showed no significant variation in intensity. The data were reduced to structure amplitudes in the usual way. No solution could be found for the structure on the basis of the supercell. Thus a was halved to give the value quoted above and the reflection data re-indexed by eliminating the uniformly weak reflections with h odd, including 795 F_o which would have been classed as observed according to the criterion given above, and then halving h for the remainder to yield a total of 1867 unique reflections ($R_{\text{int}} = 0.033$). The coordinates of Zn(1) were obtained by Patterson (vector) map analysis with *SHELXS86* (Sheldrick, 1985). All remaining non-H atoms were located in successive

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