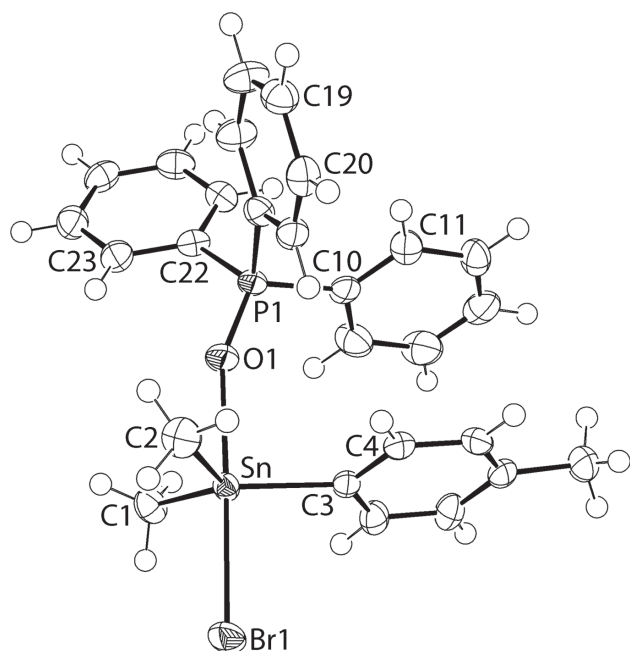




See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink\*

# Crystal structure of bromido-dimethyl-4-tolyl-(triphenylphosphine oxide)tin(IV), C<sub>27</sub>H<sub>28</sub>BrOPSn

**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.12 × 0.09 × 0.05 mm
Wavelength:	Cu K $\alpha$ radiation (1.54178 Å)
$\mu$ :	10.7 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	30870, 4495, 0.042
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4337
$N(\text{param})_{\text{refined}}$ :	283
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

## Source of material

All chemicals and solvents were used as purchased without purification. The melting point of the compound was measured on a Mel-Temp II digital melting point apparatus and was uncorrected. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer as a Nujol mull in a KBr cell from 4000 to 400 cm<sup>-1</sup>.

Dimethyldi(4-tolyl)tin (2.0 g, 6 mmol) in dry dimethylformamide (30 mL) was prepared from the reaction of dimethyltin dichloride and 4-tolylmagnesium bromide in a 1:2 molar ratio. A chilled dimethylformamide solution (5 mL) of bromine (0.97 g, 6 mmol) was added dropwise into the solution followed by stirring at room temperature for 1 h. Triphenylphosphine oxide (Sigma-Aldrich, 1.67 g, 6 mmol) in chloroform (25 mL) was added into the mixture which was then refluxed for 1 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. These were filtered, washed with a minimum amount of hexane and air-dried. Yield: 0.34 g (62%). **M.pt.**: 398–400 K. **Anal. Calc.** for C<sub>27</sub>H<sub>28</sub>BrOPSn: C 54.23; H 4.69%. Found: C 54.70; H 5.08%. **IR** (cm<sup>-1</sup>) 1600 (*m*)  $\nu$ (C–C), 1180 (*m*)  $\nu$ (P–O), 1087 (*s*)  $\nu$ (C–O), 1011 (*m*)  $\nu$ (C–O), 485 (*w*)  $\nu$ (Sn–O).

## Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2–1.5U_{\text{eq}}(\text{C})$ . Owing to poor agreement, two reflections, i.e. (–1 0 7) and (1 1 6), were omitted from the final cycles of

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## Abstract

C<sub>27</sub>H<sub>28</sub>BrOPSn, monoclinic,  $P2_1/n$  (no. 14),  $a = 10.9369(1)$  Å,  $b = 12.2170(1)$  Å,  $c = 18.8402(1)$  Å,  $\beta = 91.869(1)^\circ$ ,  $V = 2516.01(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0279$ ,  $wR_{\text{ref}}(F^2) = 0.0754$ ,  $T = 100(2)$  K.

CCDC no.: 1949171

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Sn	0.02929(2)	0.84769(2)	0.61965(2)	0.01561(8)
Br1	−0.09685(3)	1.02526(3)	0.65607(2)	0.02819(10)
P1	0.24204(7)	0.62021(6)	0.56279(4)	0.01706(16)
O1	0.1374(2)	0.68686(19)	0.58834(12)	0.0225(5)
C1	−0.0219(3)	0.7513(3)	0.70769(17)	0.0233(7)
H1A	0.0508	0.7159	0.7290	0.035*
H1B	−0.0807	0.6953	0.6916	0.035*
H1C	−0.0595	0.7983	0.7431	0.035*
C2	−0.0636(3)	0.8264(3)	0.51999(18)	0.0266(7)
H2A	−0.0190	0.8647	0.4832	0.040*
H2B	−0.1464	0.8564	0.5222	0.040*
H2C	−0.0681	0.7482	0.5086	0.040*
C3	0.2009(3)	0.9286(2)	0.62478(16)	0.0171(6)
C4	0.2567(3)	0.9601(3)	0.56236(17)	0.0202(6)
H4	0.2160	0.9476	0.5178	0.024*
C5	0.3707(3)	1.0092(3)	0.56474(17)	0.0221(7)
H5	0.4065	1.0310	0.5217	0.026*
C6	0.4342(3)	1.0275(2)	0.62886(18)	0.0215(7)
C7	0.3771(3)	0.9979(3)	0.69132(18)	0.0238(7)
H7	0.4177	1.0109	0.7359	0.029*
C8	0.2621(3)	0.9500(3)	0.68939(17)	0.0220(7)
H8	0.2246	0.9316	0.7326	0.026*
C9	0.5622(3)	1.0747(3)	0.6307(2)	0.0290(7)
H9A	0.6219	1.0151	0.6280	0.044*
H9B	0.5763	1.1154	0.6750	0.044*
H9C	0.5712	1.1241	0.5902	0.044*
C10	0.3890(3)	0.6785(3)	0.58721(17)	0.0199(6)
C11	0.4762(3)	0.7036(3)	0.53737(17)	0.0227(7)
H11	0.4603	0.6875	0.4886	0.027*
C12	0.5867(3)	0.7521(3)	0.55885(19)	0.0268(7)
H12	0.6456	0.7697	0.5247	0.032*
C13	0.6106(3)	0.7746(3)	0.6293(2)	0.0307(8)
H13	0.6860	0.8075	0.6438	0.037*
C14	0.5249(3)	0.7495(3)	0.6792(2)	0.0347(9)
H14	0.5420	0.7652	0.7280	0.042*
C15	0.4140(3)	0.7013(3)	0.65867(18)	0.0294(8)
H15	0.3556	0.6841	0.6932	0.035*
C16	0.2389(3)	0.6062(3)	0.46734(16)	0.0189(6)
C17	0.2626(3)	0.5076(3)	0.43386(17)	0.0253(7)
H17	0.2770	0.4435	0.4615	0.030*
C18	0.2655(4)	0.5019(3)	0.36059(19)	0.0296(8)
H18	0.2828	0.4342	0.3382	0.035*
C19	0.2431(3)	0.5948(3)	0.31973(17)	0.0248(7)
H19	0.2445	0.5909	0.2694	0.030*
C20	0.2188(3)	0.6930(3)	0.35292(17)	0.0233(7)
H20	0.2037	0.7567	0.3251	0.028*
C21	0.2163(3)	0.6994(3)	0.42593(17)	0.0214(6)
H21	0.1992	0.7673	0.4481	0.026*
C22	0.2394(3)	0.4838(3)	0.59848(16)	0.0197(6)
C23	0.1263(3)	0.4352(3)	0.61167(16)	0.0230(7)
H23	0.0530	0.4763	0.6055	0.028*
C24	0.1214(3)	0.3270(3)	0.63378(17)	0.0253(7)
H24	0.0447	0.2946	0.6431	0.030*
C25	0.2272(3)	0.2661(3)	0.64233(17)	0.0247(7)

**Table 2** (continued)

Atom	x	y	z	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
H25	0.2230	0.1916	0.6565	0.030*
C26	0.3399(3)	0.3140(3)	0.63007(17)	0.0257(7)
H26	0.4128	0.2723	0.6363	0.031*
C27	0.3464(3)	0.4223(3)	0.60876(16)	0.0228(7)
H27	0.4237	0.4549	0.6011	0.027*

refinement. The maximum and minimum residual electron density peaks of 1.03 and 0.79 eÅ<sup>−3</sup>, respectively, were located 0.99 and 0.89 Å from the Sn atom, respectively.

### Comment

There are over 30 crystal structure determinations of phosphineoxide adducts of organotin species in the crystallographic literature [5]. Of these, there are only two examples of triorganotinbromido adducts with monofunctional phosphineoxides, namely Ph<sub>3</sub>SnBr·O=PPh<sub>3</sub> [6] and (3-thienyl)<sub>3</sub>SnBr·O=PPh<sub>3</sub> [7]. The crystal and molecular structures of the title compound, Me<sub>2</sub>(Ph)SnBr·O=PPh<sub>3</sub> (I), a non-symmetric triorganotin compound, were determined as part of a wider, on-going study of related phosphineoxide [8] arsineoxide [9] and sulphoxide [10, 11] adducts of organotin derivatives.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom is penta-coordinated by a bromide atom [2.6725(4) Å], two methyl-carbons [Sn–C1 = 2.124(3) Å and Sn–C2 = 2.121(3) Å], the *ipso*-carbon atom of the 4-tolyl substituent [Sn–C3 = 2.120(3) Å] and the phosphineoxide-O1 atom [2.378(2) Å]. The tin-bound organo substituents occupy equatorial positions in a distorted trigonal-bipyramidal geometry, with the Sn atom lying 0.1854(19) Å out of the equatorial plane in the direction of the Br1 atom. The Br1–Sn–O1 axial angle is 178.54(6)°, and the Sn–O1–P1 angle is 157.10(15)°. Despite the difference between the tin-bound organo substituents, the angles subtended at the tin atom are close to the ideal value of 120°, *i.e.* 118.58(12)° for C1–Sn–C3 to 119.66(13)° for C2–Sn–C3. An intramolecular π···π interaction is noted as the C3-tolyl and phosphine-C10 ring are aligned and close to parallel. The inter-centroid separation is 3.699(2) Å and the angle of inclination is 9.79(16)°.

In the crystal, tolyl-C–H···π(phenyl) and phenyl-C–H···π(tolyl) [C8–H8···Cg(C22–C27)<sup>i</sup>: H8···Cg(C22–C27)<sup>i</sup> = 2.87 Å, C8···Cg(C22–C27)<sup>i</sup> = 3.690(3) Å with angle at H8 = 145° and C25–H25···Cg(C3–C8)<sup>ii</sup>: H25···Cg(C3–C8)<sup>ii</sup> = 2.86 Å, C25···Cg(C3–C8)<sup>ii</sup> = 3.658(4) Å with angle at H25 = 143° for symmetry operations (i) 1/2 – x, 1/2 + y, 3/2 – z and (ii) x, –1 + y, z] interactions lead to a helical supramolecular chain along the *b* axis direction.

Weak phenyl-C—H···Br interactions [C20—H20···Br1<sup>iii</sup>: H20···Br1<sup>iii</sup> = 2.94 Å, C20···Br1<sup>iii</sup> = 3.693(4) Å with angle at H20 = 138° for (iii)  $-x, 2-y, 1-z$ ] are noted. These connect the chains into a supramolecular layer parallel to  $(-1\ 0\ 1)$ . Layers stack without directional interactions between them.

The Hirshfeld surfaces and the overall and delineated two-dimensional fingerprint plots for (I) was calculated using Crystal Explorer 17 [12] and literature procedures [13]. There are only three contributing contacts to the overall Hirshfeld surface of (I). In descending order these are H···H [65.2%], C···H/H···C [23.1%] and Br···H/H···Br [11.6%].

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