

Oxobis[triphenyltin(IV)]

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Abstract. $C_{36}H_{30}OSn_2$, monoclinic $P2_1/c$, $a = 11.773$ (3), $b = 12.964$ (4), $c = 20.653$ (7) Å, $\beta = 101.703$ (13)°; $M_r = 715.98$; $D_c = 1.541$ g cm $^{-3}$; $Z = 4$; $\mu(\text{Mo } K\alpha) = 15.07$ cm $^{-1}$. Final R for 6056 reflections = 0.0336. The SnOSn angle is 137.3 (1)°, and the Sn...Sn distance 3.641 (1) Å.

Introduction. The compound was prepared by dehydration of Ph_3SnOH (Schmitz-Dumont, 1941); crystals were grown from benzene. The space group was

uniquely assigned from the systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. A crystal, $0.25 \times 0.2 \times 0.15$ mm, cleaved from a large thick plate was used for data collection. Data were collected on a Philips PW1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions were derived by least squares from the positions of 25 reflections each measured 21 times during data collection. The intensities of 6346 reflections within the quadrant $+h + k \pm l$ with $3 \leq \theta \leq 30^\circ$ were measured by the ω - 2θ scan technique with a scan speed of 0.06° s $^{-1}$ in ω and a scan width of $(0.9 + 0.1 \tan \theta)^\circ$ in ω .

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Table 1. Atom coordinates ($\times 10^4$; for H $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Sn(1)	2438 (0)	1645 (0)	3755 (0)	C(233)	5898 (4)	449 (5)	2335 (3)
Sn(2)	2406 (0)	1806 (0)	1991 (0)	C(234)	5751 (5)	459 (5)	1990 (3)
O	2475 (2)	2272 (2)	2897 (1)	C(235)	4686 (6)	-720 (4)	1630 (3)
C(111)	2525 (3)	9 (3)	3629 (2)	C(236)	3732 (4)	-76 (3)	1620 (2)
C(112)	3404 (4)	-439 (3)	3380 (2)	H(112)	402 (3)	-8 (3)	333 (2)
C(113)	3393 (5)	-1474 (4)	3223 (3)	H(113)	392 (4)	-169 (3)	305 (2)
C(114)	2477 (5)	-2084 (3)	3313 (2)	H(114)	245 (5)	-288 (5)	313 (3)
C(115)	1599 (5)	-1660 (3)	3578 (3)	H(115)	103 (4)	-217 (3)	361 (2)
C(116)	1621 (4)	-620 (3)	3736 (2)	H(116)	109 (4)	-35 (3)	396 (2)
C(121)	3859 (3)	2321 (3)	4420 (2)	H(122)	293 (3)	348 (3)	468 (2)
C(122)	3690 (4)	3230 (3)	4751 (2)	H(123)	448 (4)	429 (3)	542 (2)
C(123)	4607 (5)	3695 (4)	5186 (2)	H(124)	635 (5)	353 (4)	555 (2)
C(124)	5683 (5)	3256 (4)	5293 (3)	H(125)	647 (4)	202 (3)	512 (2)
C(125)	5852 (4)	2363 (5)	4987 (3)	H(126)	498 (4)	147 (3)	434 (2)
C(126)	4954 (4)	1905 (4)	4550 (2)	H(132)	99 (3)	170 (3)	486 (2)
C(131)	803 (3)	2135 (3)	3955 (2)	H(133)	-59 (4)	232 (4)	509 (2)
C(132)	514 (4)	1992 (3)	4559 (2)	H(134)	-212 (4)	293 (3)	426 (2)
C(133)	-565 (5)	2313 (4)	4668 (2)	H(135)	-154 (4)	325 (3)	324 (2)
C(134)	-1331 (4)	2778 (4)	4177 (3)	H(136)	13 (3)	262 (3)	303 (2)
C(135)	-1045 (4)	2933 (4)	3572 (3)	H(212)	402 (3)	291 (3)	107 (2)
C(136)	8 (4)	2605 (3)	3460 (2)	H(213)	386 (4)	441 (3)	56 (2)
C(211)	2454 (3)	3211 (2)	1462 (2)	H(214)	248 (4)	568 (4)	52 (2)
C(212)	3306 (3)	3399 (3)	1103 (2)	H(215)	114 (4)	533 (3)	118 (2)
C(213)	3315 (4)	4331 (3)	763 (2)	H(216)	109 (3)	387 (3)	117 (2)
C(214)	2502 (4)	5066 (3)	795 (2)	H(222)	38 (4)	78 (3)	255 (2)
C(215)	1659 (3)	4891 (3)	1150 (2)	H(223)	-139 (3)	0 (3)	224 (2)
C(216)	1637 (3)	3966 (3)	1483 (2)	H(224)	-210 (3)	-24 (3)	107 (2)
C(221)	789 (3)	1041 (2)	1660 (2)	H(225)	-104 (4)	42 (3)	31 (2)
C(222)	141 (4)	683 (3)	2103 (2)	H(226)	69 (4)	108 (3)	71 (2)
C(223)	-940 (4)	228 (4)	1887 (3)	H(232)	503 (4)	171 (3)	266 (2)
C(224)	-1376 (4)	130 (3)	1226 (3)	H(233)	670 (4)	70 (4)	261 (2)
C(225)	-755 (5)	464 (4)	779 (2)	H(234)	635 (4)	-87 (4)	194 (2)
C(226)	327 (5)	918 (4)	999 (2)	H(235)	453 (5)	-123 (4)	143 (2)
C(231)	3868 (3)	845 (3)	1968 (2)	H(236)	295 (3)	-34 (3)	134 (2)
C(232)	4952 (4)	1104 (3)	2321 (2)				

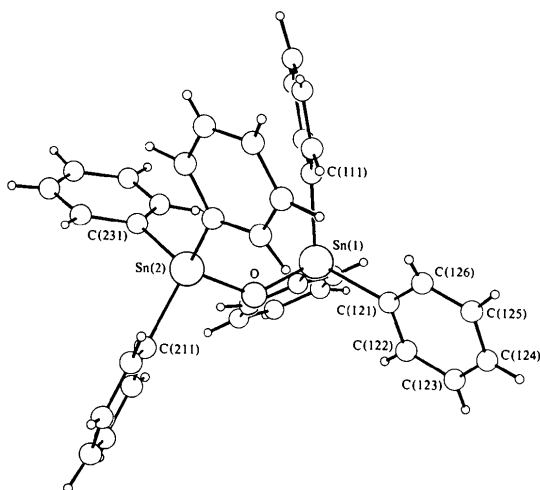
Table 2. *Geometry of SnOSn bridge*

(a) Distances (Å)

Sn(1)—O	1.957 (2)	Sn(2)—O	1.953 (2)
Sn(1)—C(111)	2.142 (3)	Sn(2)—C(211)	2.130 (3)
Sn(1)—C(121)	2.126 (3)	Sn(2)—C(221)	2.133 (3)
Sn(1)—C(131)	2.146 (4)	Sn(2)—C(231)	2.133 (4)
Sn(1)···Sn(2)	3.641 (1)		

(b) Angles (°)

O—Sn(1)—C(111)	106.9 (1)	O—Sn(2)—C(211)	103.1 (1)
O—Sn(1)—C(121)	104.8 (1)	O—Sn(2)—C(221)	108.2 (1)
O—Sn(1)—C(131)	103.7 (1)	O—Sn(2)—C(231)	109.0 (1)
C(111)—Sn(1)—C(121)	115.8 (1)	C(221)—Sn(2)—C(211)	110.4 (1)
C(121)—Sn(1)—C(131)	111.9 (1)	C(221)—Sn(2)—C(231)	113.1 (1)
C(131)—Sn(1)—C(111)	112.5 (1)	C(231)—Sn(2)—C(211)	112.5 (1)
Sn(1)—O—Sn(2)	137.3 (1)		

Fig. 1. The $O(SnPh_3)_2$ molecule, showing the numbering of the atoms.

Backgrounds were measured at both ends of each scan. Three reference reflections were measured every 5 h and showed only random deviations from their mean intensities. Lorentz and polarization but no absorption corrections were applied.

The structure was solved by Patterson methods with *SHELX* (Sheldrick, 1976) and refined by blocked full-matrix least squares with complex neutral-atom scattering factors (Cromer & Mann, 1968) and weights $w = 1/\sigma^2(F)$ for 6056 unique reflections having $F_o \geq 6\sigma(F_o)$. Anisotropic temperature factors were employed for the C, O and Sn atoms: H atom coordinates were refined, with three isotropic temperature factors, one for H(*ij*2) and H(*ij*6), a second for H(*ij*3) and H(*ij*5), and a third for H(*ij*4). The refinement converged to $R = \sum \Delta / \sum F_o = 0.0336$ and $R_G = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0.0409$ for 445 refined parameters. At each stage of the refinement the reduction in R_G was significant at the 0.5% level (Hamilton, 1965). The final coordinates are listed in Table 1, the geometry of the central $C_3SnOSnC_3$ fragment in Table 2, and the parameters of the phenyl rings in Table 3. Fig. 1 shows the molecule, and the numbering of the atoms.*

Discussion. The structure comprises isolated molecules, unlike Ph_3SnOH (Glidewell & Liles, 1978) whose structure consists of continuous chains. The Sn—O distance is 1.955 (2) Å, close to that determined by electron diffraction for gaseous $(Me_3Sn)_2O$, 1.940 Å (Vilkov & Tarasenko, 1969): similarly the Sn···Sn

* Lists of structure factors, anisotropic thermal parameters and geometrical parameters involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33320 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Geometry within phenyl rings*

Ring, <i>ij</i>	11	12	13	21	22	23	Mean
(a) Distances (Å) C(<i>ijk</i>)—C(<i>ijl</i>)							
<i>k</i> — <i>l</i>							
1—2	1.375 (6)	1.397 (5)	1.372 (6)	1.384 (6)	1.384 (6)	1.377 (5)	1.382 (4)
2—3	1.380 (6)	1.394 (7)	1.398 (7)	1.397 (6)	1.391 (6)	1.397 (7)	1.393 (3)
3—4	1.380 (8)	1.367 (8)	1.355 (7)	1.361 (7)	1.363 (7)	1.368 (9)	1.366 (2)
4—5	1.378 (8)	1.352 (8)	1.373 (8)	1.368 (7)	1.359 (8)	1.364 (9)	1.366 (4)
5—6	1.386 (6)	1.378 (7)	1.375 (7)	1.385 (6)	1.393 (7)	1.396 (8)	1.386 (3)
6—1	1.393 (6)	1.372 (6)	1.379 (5)	1.380 (5)	1.373 (6)	1.385 (5)	1.380 (3)
(b) Angles (°) C(<i>ijk</i>)—C(<i>ijl</i>)—C(<i>ijm</i>) or C(<i>ijk</i>)—C(<i>ijl</i>)—Sn(<i>i</i>)							
<i>k</i> — <i>l</i> — <i>m</i> (<i>i</i>)							
6—1—2	118.0 (3)	117.2 (4)	118.6 (4)	118.5 (3)	117.2 (4)	118.8 (4)	118.1 (3)
1—2—3	121.8 (4)	120.8 (4)	120.5 (4)	120.1 (4)	121.5 (4)	120.9 (4)	120.9 (2)
2—3—4	119.7 (5)	119.6 (4)	120.0 (5)	120.3 (5)	119.6 (5)	119.7 (5)	119.8 (1)
3—4—5	119.7 (4)	120.1 (5)	119.9 (5)	120.2 (4)	120.4 (5)	120.2 (6)	120.1 (1)
4—5—6	120.1 (5)	120.6 (5)	120.3 (4)	119.9 (4)	119.6 (5)	120.5 (5)	120.2 (1)
5—6—1	120.7 (4)	121.6 (4)	120.7 (4)	121.1 (4)	121.7 (5)	120.0 (4)	121.0 (2)
2—1— <i>i</i>	121.4 (3)	119.5 (3)	122.2 (3)	121.6 (2)	121.4 (3)	120.7 (3)	120.8 (4)
6—1— <i>i</i>	120.3 (3)	123.3 (3)	119.2 (3)	120.0 (3)	121.4 (3)	120.4 (3)	120.8 (5)

distance, 3.641 (1) Å, is almost identical with the 3.655 Å determined for $(\text{Me}_3\text{Sn})_2\text{O}$, indicating a hard-atom radius for Sn of 1.82 Å. The SnOSn angles in these two oxo compounds are 137.3 (1) and 140.8° respectively; these values indicate that the changes in the SnOSn bridge occasioned by changes of the substituent or of phase are negligible. The mean Sn—C distance, 2.135 (3) Å, is identical with that in Ph_3SnOH (Glidewell & Liles, 1978).

Within the phenyl rings C(*ij*3)—C(*ij*4) and C(*ij*4)—C(*ij*5) are, as usual, apparently shorter than the remainder. The internal angle at C(*ij*1), mean 118.1 (3), is comparable with that in Ph_3SnOH , 118.9 (10)° (Glidewell & Liles, 1978); this angle in compounds Ph_nM is related to the electronegativity of *M* (Domenicano, Vaciano & Coulson, 1975).

There are no short intermolecular non-bonded distances; in particular there are no significant intermolecular contacts involving O atoms.

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Structure of Tribenzo[*b,e,h*][1,4,7]trimercuronin*

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Abstract. $\text{C}_{18}\text{H}_{12}\text{Hg}_3$, FW 830.07, orthorhombic, $P2_12_12_1$ (absent reflections: $h00$ when h odd, $0k0$ when k odd, $00l$ when l odd), $a = 5.56$ (2), $b = 23.36$ (2), $c = 12.24$ (2) Å, $U = 1589.75$ Å³, $Z = 4$, $D_x = 3.49$ g cm⁻³, $F(000) = 1440$; analysis: found: C 26.1, H 1.47%; calculated: C 26.0, H 1.45%. *o*-Phenylenemercury, $(\text{C}_6\text{H}_4\text{Hg})_n$, has been shown to be a trimer in the crystal modification studied. Patterson and trial-and-error methods for the 1668 observed reflections refined the structure to a conventional *R* of 7.8%.

Introduction. Initial interest in the structure of *o*-phenylenemercury, $(\text{C}_6\text{H}_4\text{Hg})_n$, began because it appeared to provide an exception to the general rule that perfluoro derivatives have the same molecular structure as their hydrogen analogues (Awad, Brown, Cohen, Humphries & Massey, 1977). Wittig & Bickelhaupt (1958) described *o*-phenylenemercury as a hexamer, their formulation being supported by a partial X-ray study (Grdenić, 1959). Perfluoro-*o*-phenylenemercury

(dodecafluorotribenzo[*b,e,h*][1,4,7]trimercuronin) is thought, however, to be a trimer (Sartori & Golloch, 1968; Cookson & Deacon, 1973; Woodard, Hughes & Massey, 1976). Dreiding models indicate that mercurials of the formula $(\text{C}_6\text{X}_4\text{Hg})_n$, where $X = \text{H}$ or F , give molecules free from steric strain for values of n of 3, 4, 6, 8, 10, etc. Spectral evidence cannot distinguish between those oligomers with total certainty (albeit our title compound had only Hg_1 , Hg_2 and Hg_3 species in its mass spectrum) and solution molecular-weight determinations are hampered by the low solubility of *o*-phenylenemercury in all organic solvents.

The title compound was prepared by Dr S. B. Awad from the reaction of ethereal 1,2-dibromobenzene and sodium amalgam; crystals elongated along the crystallographic *a* axis were grown from *N,N*-dimethylformamide. XRF showed Hg to be the only heavy element present, and both infrared spectroscopy and differential thermal analysis showed the absence of solvent of crystallization.

The intensities and refined cell dimensions were obtained from a crystal 0.05 × 0.05 × 0.5 mm on a

* A Reinvestigation of *o*-Phenylene Mercurials. II.