

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  $\text{Ph}_3\text{SnOH}$  (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  $\text{Ph}_3\text{SnOH}$ , 118.9 (10)° (Glidewell & Liles, 1978); this angle in compounds  $\text{Ph}_n\text{M}$  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,  $U = 1589.75$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.49$  g cm<sup>-3</sup>,  $F(000) = 1440$ ; 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  $\text{F}$ , 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  $\text{Hg}_1$ ,  $\text{Hg}_2$  and  $\text{Hg}_3$  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.

Stoe automatic Weissenberg diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) and a graphite monochromator. Of the 2513 reflections measured, 845 were classed as unobserved on the basis  $F < 3\sigma(F)$ . Lorentz and polarization corrections were applied to the net intensity counts, but no corrections were made for absorption [ $\mu(\text{Mo } K\alpha) = 85.3 \text{ cm}^{-1}$ ] or extinction.

A Patterson map gave the positions of two of the Hg atoms, and a difference Fourier map based on the refined positions of these atoms enabled the third Hg position to be determined. Full-matrix least-squares refinement, with anisotropic temperature factors, led to a conventional  $R$  value of 10.6%. A difference Fourier synthesis revealed the positions of all the C atoms. These atoms, with individual isotropic temperature factors, were included in block-diagonal least-squares refinement to converge at a final  $R$  of 7.8%. Unobserved reflections were omitted from the least-squares matrix, and unit weights were used.

Atomic scattering factors for C and Hg were those of Cromer & Mann (1968) and Thomas & Umeda (1957) respectively. All calculations were carried out using the XRAY system (1972), as implemented at the University of Manchester Regional Computer Centre.

Table 1. *Final positional parameters ( $\times 10^4$ ) with their standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Hg(1)	-116 (4)	-55 (1)	76 (1)
Hg(2)	5075 (4)	32 (1)	8317 (2)
Hg(3)	2095 (4)	1317 (1)	4197 (2)
C(1)	4325 (118)	1311 (26)	8597 (47)
C(2)	3181 (105)	755 (20)	8800 (38)
C(3)	3038 (87)	1821 (17)	8957 (32)
C(4)	1275 (86)	745 (18)	9528 (35)
C(5)	891 (91)	1789 (19)	9515 (37)
C(6)	91 (95)	1264 (18)	9878 (35)
C(7)	5832 (82)	8738 (18)	8094 (35)
C(8)	6942 (93)	8210 (18)	7771 (35)
C(9)	6905 (98)	9299 (18)	7786 (36)
C(10)	9070 (95)	8260 (20)	7094 (39)
C(11)	8999 (98)	9274 (19)	7185 (39)
C(12)	9861 (96)	8760 (18)	6792 (39)
C(13)	5893 (126)	8519 (25)	1648 (55)
C(14)	7145 (122)	8024 (23)	1248 (45)
C(15)	6530 (100)	9109 (20)	1346 (40)
C(16)	9176 (119)	8104 (25)	603 (51)
C(17)	8717 (82)	9136 (17)	647 (35)
C(18)	35 (87)	8653 (17)	269 (32)

Table 2. *Bond lengths ( $\text{\AA}$ ) with their estimated standard deviations in parentheses*

C(1)–C(2)	1.47 (8)	C(7)–C(8)	1.43 (6)	C(13)–C(14)	1.43 (8)
C(1)–C(3)	1.46 (7)	C(7)–C(9)	1.49 (6)	C(13)–C(15)	1.47 (8)
C(2)–C(4)	1.38 (7)	C(8)–C(10)	1.45 (7)	C(14)–C(16)	1.39 (9)
C(3)–C(5)	1.38 (7)	C(9)–C(11)	1.38 (7)	C(15)–C(17)	1.49 (7)
C(4)–C(6)	1.44 (6)	C(10)–C(12)	1.30 (6)	C(16)–C(18)	1.43 (7)
C(5)–C(6)	1.38 (6)	C(11)–C(12)	1.38 (6)	C(17)–C(18)	1.42 (6)
Hg(1)–C(4)	2.13 (4)	Hg(2)–C(2)	2.08 (5)	Hg(3)–C(7)	2.12 (4)
Hg(1)–C(17)	2.12 (4)	Hg(2)–C(9)	2.09 (5)	Hg(3)–C(18)	2.07 (5)

The final atomic positional parameters, together with their standard deviations, are listed in Table 1.\* The numbering scheme for the atoms is shown in Fig. 1, and bond lengths and angles are given in Tables 2 and 3.

**Discussion.** This structure analysis shows unequivocally that, for the crystal modification studied, *o*-phenylenemercury exists as a trimeric species, in contrast to the hexameric structure reported by Grdenić (1959). However, Grdenić's crystals were monoclinic with  $a = 10.40$ ,  $b = 8.16$ ,  $c = 19.28 \text{ \AA}$  and  $\beta = 105^\circ$ . Since the present work commenced we have been able to isolate the second (Grdenić) modification by reacting a solution of the reagents in dioxane, instead of ether, and recrystallizing from *N,N*-dimethylformamide as before.

The structure of the present orthorhombic modification is shown projected down *a* in Fig. 2. The trimeric *o*-phenylenemercury units are linked together by van der Waals contacts, the bridged distances being 3.61 [Hg(1)–Hg(2)], 3.56 [Hg(1)–Hg(3)], and 3.54  $\text{\AA}$  [Hg(2)–Hg(3)] and the non-bridged distances being

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33343 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

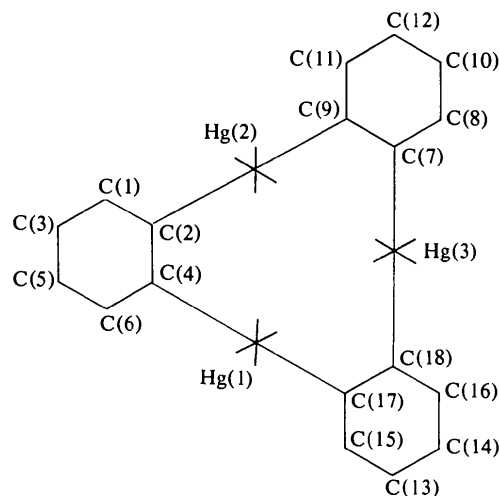


Fig. 1. Idealized molecular structure of tribenzol[*b,e,h*][1,4,7]trimercuronin showing the atomic numbering.

Table 3. Bond angles ( $^{\circ}$ ) with their estimated standard deviations in parentheses

C(4)—Hg(1)—C(17)	176.5 (1.8)	C(3)—C(5)—C(6)	119.3 (4.2)	Hg(2)—C(9)—C(11)	127.6 (3.3)
C(2)—Hg(2)—C(9)	178.1 (1.9)	C(4)—C(6)—C(5)	120.3 (4.4)	Hg(3)—C(18)—C(17)	125.2 (3.0)
C(7)—Hg(3)—C(18)	178.5 (1.6)	C(2)—C(1)—C(3)	117.4 (5.1)	C(8)—C(7)—C(9)	121.0 (4.1)
Hg(1)—C(4)—C(2)	119.6 (3.2)	C(13)—C(14)—C(16)	118.7 (5.2)	C(7)—C(8)—C(10)	116.0 (3.9)
Hg(1)—C(4)—C(6)	118.5 (3.2)	C(14)—C(16)—C(18)	123.7 (5.2)	C(7)—C(9)—C(11)	115.8 (3.9)
Hg(3)—C(7)—C(8)	117.0 (3.1)	C(16)—C(18)—C(17)	116.6 (4.4)	C(8)—C(10)—C(12)	120.7 (4.4)
Hg(3)—C(7)—C(9)	121.4 (3.1)	Hg(1)—C(17)—C(15)	118.6 (2.9)	C(9)—C(11)—C(12)	121.1 (4.4)
Hg(3)—C(18)—C(16)	118.0 (3.5)	Hg(1)—C(17)—C(18)	116.3 (3.1)	C(10)—C(12)—C(11)	124.4 (4.9)
C(1)—C(2)—C(4)	117.0 (4.4)	Hg(2)—C(2)—C(1)	116.9 (4.0)	C(14)—C(13)—C(15)	123.5 (5.7)
C(1)—C(3)—C(5)	122.0 (4.2)	Hg(2)—C(2)—C(4)	123.9 (3.3)	C(13)—C(15)—C(17)	112.5 (4.4)
C(2)—C(4)—C(6)	121.7 (4.0)	Hg(2)—C(9)—C(7)	116.5 (3.4)	C(15)—C(17)—C(18)	125.0 (3.8)

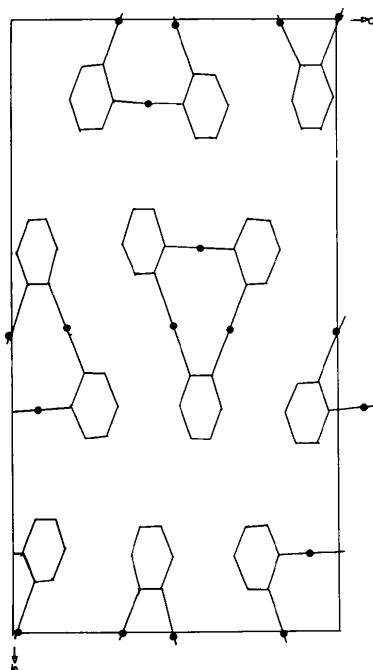
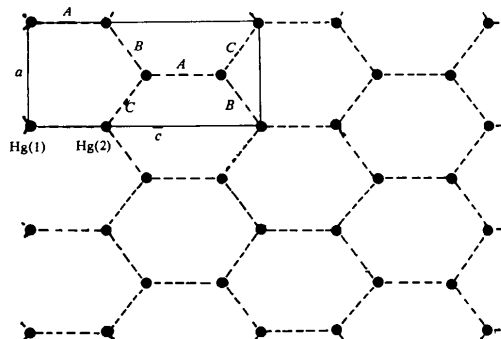

 Fig. 2. Unit-cell contents projected down *a*.


Fig. 3. Hexagonal array of Hg atoms in the (010) plane.

3.44 and 3.97 Å [both Hg(1)—Hg(2)]. Hg(1) and Hg(2) form an approximately hexagonal array in the (010) plane as shown in Fig. 3. There are three crystallographically unique Hg—Hg contacts in the array, *viz* *A* = 3.97 Å, *B* (bridged) = 3.61 Å and *C* =

3.44 Å, which suggest a van der Waals radius for Hg of about 1.72 Å, somewhat larger than that of 1.50 Å suggested by Grdenić (1965).

The Hg—C bond lengths fall in the range 2.06–2.15 Å found in other mercury—carbon compounds, *e.g.* 2.09 Å in diphenylmercury (Grdenić, Kamenar & Nagl, 1977), 2.09 and 2.10 Å in bis(pentafluorophenyl)mercury (Kunchur & Mathew, 1966) and 2.08 Å in bis(*p*-tolyl)mercury (Mathew & Kunchur, 1970). The C—Hg—C bond angles do not differ significantly from the 180° expected for the *sp* hybridization of the Hg orbitals.

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