OXOBIS[TRIPHENYL Tin(IV)] distance, 3.641 (1) Å, is almost identical with the 3.655 Å determined for (Me$_3$Sn)$_2$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$_3$SnOH (Glidewell & Liles, 1978).

Within the phenyl rings C(ij3)–C(ij4) and C(ij4)–C(ij5) are, as usual, apparently shorter than the remainder. The internal angle at C(ij1), mean 118.1 (3), is comparable with that in Ph$_3$SnOH, 118.9 (10)° (Glidewell & Liles, 1978): this angle in compounds Ph$_3$M is related to the electronegativity of M (Domenicano, Vaciago & 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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References


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

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Abstract. C$_{18}$H$_8$Hg$_9$, FW 830.07, orthorhombic, P2$_1$2$_1$2$_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$^3$, 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-Phenylene-mercury, (C$_6$H$_4$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-phenylene-mercury, (C$_6$H$_4$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-phenylene-mercury as a hexamer, their formulation being supported by a partial X-ray study (Grdenič, 1959). Perfluoro-o-phenylene-mercury (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 (C$_6$X$_4$Hg)$_n$, where X = 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-phenylene-mercury 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 x 0.05 x 0.5 mm on a
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 \( a = 10.40, \ b = 8.16, \ c = 19.28 \) Å 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 Å |\( Hg(2)-Hg(3) \)| 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.
Table 3. Bond angles (°) with their estimated standard deviations in parentheses

\[
\begin{array}{cccc}
\text{Bond} & \text{Bond angles (°)} & \text{Estimated standard deviations} \\
\text{C(4)}-\text{Hg(1)}-\text{C(17)} & 176.5 (1.8) & \\
\text{C(2)}-\text{Hg(2)}-\text{C(9)} & 178.1 (1.9) & \\
\text{C(7)}-\text{Hg(3)}-\text{C(18)} & 178.5 (1.6) & \\
\text{Hg(1)}-\text{C(4)}-\text{C(2)} & 119.6 (3.2) & \\
\text{Hg(1)}-\text{C(4)}-\text{C(6)} & 118.7 (5.1) & \\
\text{Hg(3)}-\text{C(7)}-\text{C(8)} & 123.7 (5.2) & \\
\text{Hg(3)}-\text{C(7)}-\text{C(9)} & 116.6 (4.4) & \\
\text{Hg(3)}-\text{C(18)}-\text{C(16)} & 126.3 (2.9) & \\
\text{C(1)}-\text{C(2)}-\text{C(4)} & 116.3 (4.0) & \\
\text{C(1)}-\text{C(3)}-\text{C(5)} & 116.6 (4.4) & \\
\text{C(2)}-\text{C(4)}-\text{C(6)} & 119.0 (3.1) & \\
\text{Hg(1)}-\text{C(17)}-\text{C(15)} & 120.7 (4.4) & \\
\text{Hg(1)}-\text{C(17)}-\text{C(18)} & 121.4 (4.4) & \\
\text{Hg(2)}-\text{C(2)}-\text{C(4)} & 122.0 (4.2) & \\
\text{Hg(2)}-\text{C(9)}-\text{C(7)} & 125.7 (3.2) & \\
\text{Hg(2)}-\text{C(13)}-\text{C(15)} & 123.5 (5.7) & \\
\text{Hg(2)}-\text{C(16)}-\text{C(18)} & 123.3 (5.4) & \\
\text{Hg(2)}-\text{C(17)}-\text{C(18)} & 123.5 (4.4) & \\
\text{Hg(2)}-\text{C(17)}-\text{C(19)} & 117.0 (3.1) & \\
\text{Hg(2)}-\text{C(18)}-\text{C(17)} & 121.4 (4.4) & \\
\text{Hg(2)}-\text{C(19)}-\text{C(20)} & 122.0 (4.2) & \\
\text{Hg(2)}-\text{C(20)}-\text{C(22)} & 122.0 (4.2) & \\
\text{Hg(2)}-\text{C(22)}-\text{C(24)} & 122.0 (4.2) & \\
\text{Hg(2)}-\text{C(24)}-\text{C(26)} & 122.0 (4.2) & \\
\end{array}
\]

3.44 Å, which suggests 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 $sp^3$ hybridization of the Hg orbitals.

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References


