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THE CRYSTAL AND MOLECULAR STRUCTURE OF *ortho*-TERPHENYLENEMERCURY DIMER, $(C_{18}H_{12}Hg)_2$

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Summary

$C_{36}H_{24}Hg_2$, hexabenzo[*b,d,f,i,k,m*][1,8] dimercuracyclotetradecene, $M_r = 857.768$, monoclinic, $P2_1/n$, a 17.315(3), b 16.576(2), c 10.545(6) Å, β 114.60(4)°, U 2751.65 Å^3, $Z = 4$, D_m 2.055, D_x 2.071 g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ 107.51 cm^{-1}, $F(000) = 1600$, T 293 K; Final $R = 0.041$ for 4290 observed reflections with $I > 3\sigma(I)$. The two C–Hg–C angles are 175.5(3) and 175.6(4)°; average C–Hg distance, 2.088(13) Å.

Introduction and discussion

The reaction of 1,2-$Br_2C_6H_4$ with sodium amalgam in basic ethers such as 1,2-dimethoxyethane gives a 10–15% yield of *ortho*-terphenylenemercury $\{C_6H_4C_6H_4C_6H_4Hg\}_n$; cryoscopic measurements of the molecular weight made by Wittig and his co-workers [1] suggested that the molecule was dimeric. Our mass spectral measurements confirmed the dimeric nature of the mercurial by showing the presence in the spectrum of a peak cluster around 858 m.u. corresponding to the parent ion $C_{36}H_{24}Hg_2^+$; however, the intensity of the parent ion is very weak because the molecule fragments very readily to give $C_{36}H_{24}^+$ and the base peak corresponding to what is probably ionized triphenylene $C_{18}H_{12}^+$. A weak ion cluster centred at 656 m.u. represents $(C_6H_4)_6Hg^+$ which must correspond to (P–Hg) and not an impurity since a strain-free model of such a heterocycle cannot be made; this ion, and Hg^+, are the only mercury-containing fragments which are detectable. Of the two prominent metastable peaks present, the one at 60.7 m.u. may correspond to the transition:

$$(C_{18}H_{12}Hg)_2^+ \rightarrow C_{18}H_{12}^+ + Hg_2C_{18}H_{12} \text{ (calc 60.7)}$$

whilst the second represents the loss of C_2H_2 from the base ion

$$C_{18}H_{12}^+ \rightarrow C_{16}H_{10}^+ + C_2H_2 \text{ obs. 179 (calc 179.0 m.u.).}$$

Presumably due partially to its high intensity, the base ion and its main fragment

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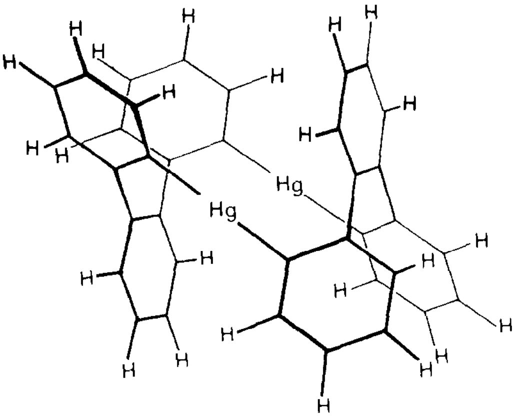
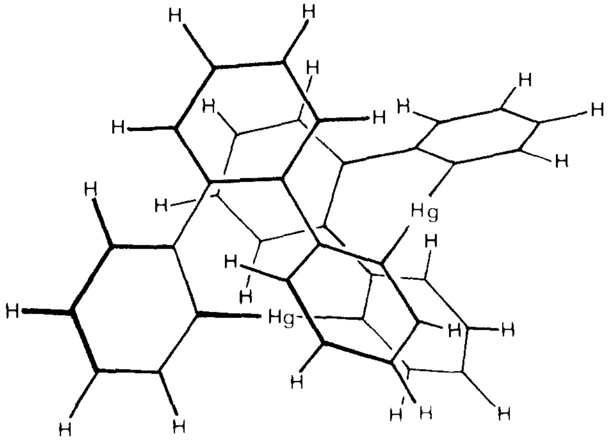
$C_{18}H_{10}^+$ also occur as doubly-charged and (weak) triply-charged ions at 113, 114, 75.3 and 75.7 m.u.

A study of Dreiding models shows that only the dimer for *ortho*-terphenylenemercury would be strain-free if the C–Hg–C bond angles are held at the normal value of 180°. Two structural isomers, I and II, appear to be possible of which I is the more symmetrical and gives rise to a rigid model; the Dreiding model of II is much less rigid and can be deformed readily into shapes which result in closer than Van der Waals contacts between some of the hydrogen and carbon atoms. Conceptually, isomer I would seem to be by far the more probable molecule.



(I)



(II)

As we have shown previously [2], *ortho*-terphenylenemercury dimer forms solvates with virtually every solvent from which it crystallizes, the dimer/solvent ratios being 1/0.5, 1/1, 1/1.5 and 1/2.0 depending on the size of the solvating molecule.

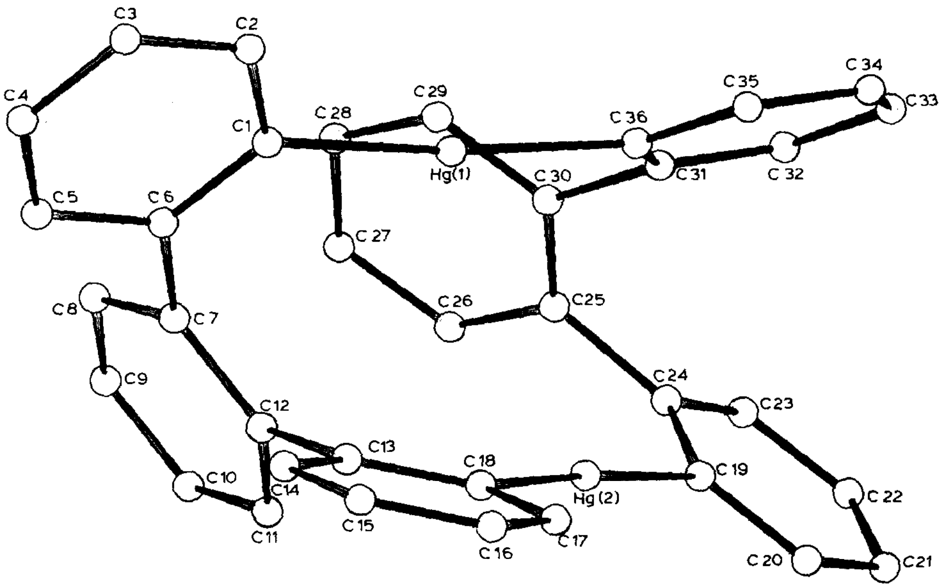


Fig. 1. ORTEP drawing of the *ortho*-terphenylenemercury dimer (hydrogens omitted).

Because of this solvate formation the crystal used in these X-ray studies was grown via sublimation in a sealed, evacuated tube heated under a temperature gradient. As can be seen from the ORTEP drawing of Fig. 1 the molecule, somewhat surprisingly, adopts the less-symmetrical structure II; the presence in the unit cell of two types of molecule related by a mirror plane shows the molecule exists in two enantiomeric forms. The bond lengths, bond angles, atom numbering and ring numbering are given in Fig. 2 whilst the angles between the various ring normals are

TABLE 1

ANGLES BETWEEN THE NORMALS TO THE AROMATIC RINGS IN *ortho*-TERPHENYLENEMERCURY DIMER

Rings	Angle between normals (°)
1–2	64.5
1–3	61.4
1–4	84.5
1–5	45.0
1–6	34.0
2–3	50.1
2–4	43.5
2–5	22.5
2–6	62.4
3–4	27.8
3–5	57.0
3–6	31.3
4–5	61.4
4–6	58.6
5–6	54.9

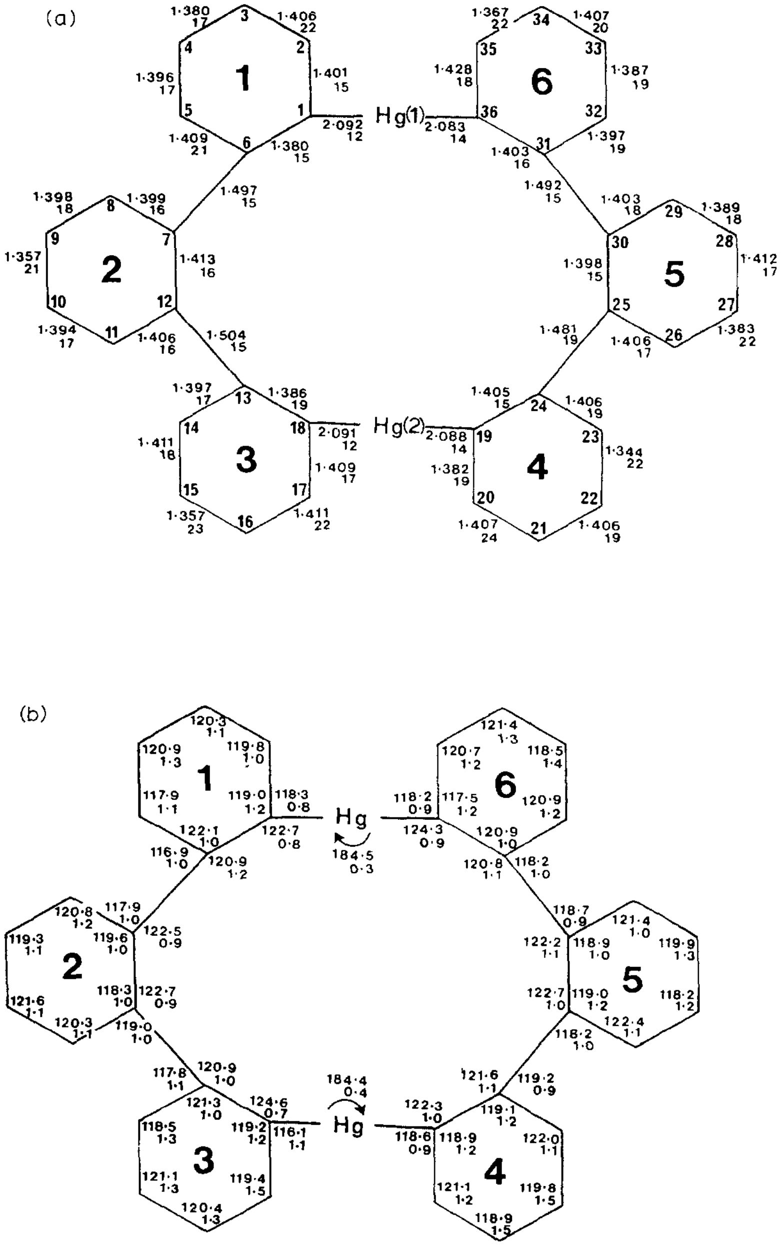
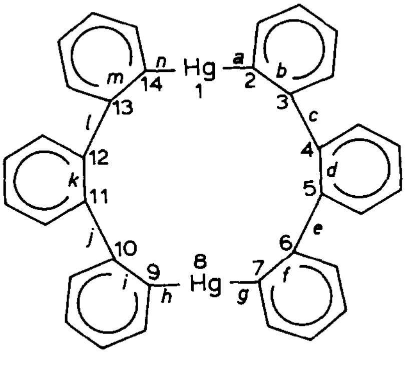


Fig. 2. (a) Bond lengths (Å) with e.s.d. given as sub-scripts. (b) Bond angles (°) with e.s.d. given as sub-scripts.

listed in Table 1. The C–Hg–C angles are only about 5° from linearity and are, like all the other atomic parameters, within the usual range found in similar organomercurials [3,4]. *Ortho*-terphenylenemercury dimer, like biphenylenemercury trimer [3] and the, as yet unknown, phenylenemercury hexamer can be visualized as being derived from *ortho*-hexaphenylene. The systematic name of the dimer is hexabenzo[*b,d,f,i,k,k,m*][1,8]dimercuracyclotetradecene:



Experimental

A solution of 1,2-dibromobenzene (20 mmol) in dry 1,2-dimethoxyethane (50 cm^3) was stirred vigorously under an atmosphere of nitrogen with sodium amalgam; an exothermic reaction occurred which appeared to be essentially complete after 30 min but stirring was continued for a further 2–3 h and water added until no more precipitate formed. The supernatant liquid was separated from the mercury and the precipitate, the latter being washed with distilled water before removal of the mercury. Terphenylenemercury was extracted from the dried precipitate using chloroform and dried in an oven at 80°C to drive off adhering chloroform (Found: C, 50.6; H, 2.7; $C_{36}H_{24}Hg_2$ calc: C, 50.4; H, 2.8%).

A single crystal, $0.62 \times 0.16 \times 0.09$ mm, was sealed in a Lindemann-glass capillary and preliminary cell dimensions were determined from oscillation and Weisenberg photographs taken with the crystal mounted about the c axis. Refined cell dimensions were obtained from a Stadi-2 two-circle diffractometer which was used for data collection. The intensities of 6,689 reflections were measured out to a maximum 2θ of 60°, using Mo-K_α radiation; 4,290 had $I > 3\sigma(I)$ and were classed as observed. A standard check reflection was measured for each layer and no significant variation in intensity was noted. Corrections were applied for Lp and absorption, but not for extinction. Mercury positions were found by direct methods using MULTAN 80 [5], and carbon positions by successive ΔF syntheses using SHELX [6]. The structure was refined by full-matrix least-squares with unit weights, omitting hydrogen atoms and allowing anisotropic motion for carbon and mercury atoms. The hydrogen atoms were placed in calculated positions after the last cycle of refinement, for which $\Delta/\sigma < 0.06$ and $R = 0.043$. Inclusion of the hydrogen atoms in the final difference synthesis reduced R to 0.041 and gave maximum and minimum difference electron densities of $+1.54$ and -2.18 e Å^{-3}, respectively, in the vicinity of the mercury atoms. Analytical scattering factors were taken from International Tables for Crystallography, Vol. 4 [7]. A copy of the list of structure factors and anisotropic temperature factors is available on request from J.B.J.

TABLE 2

ATOMIC COORDINATES OF THE BONDED ATOMS AND THEIR ESD'S

Atom	*x*	*y*	*z*
Hg(1)	0.4337(0)	0.8457(0)	0.0979(0)
Hg(2)	0.5228(0)	0.7887(0)	0.4785(0)
C(1)	0.5154(6)	0.8646(6)	0.0001(10)
C(2)	0.4930(7)	0.9228(6)	−0.1055(12)
C(3)	0.5458(8)	0.9359(7)	−0.1750(12)
C(4)	0.6195(7)	0.8918(7)	−0.1395(12)
C(5)	0.6426(7)	0.8329(7)	−0.0356(13)
C(6)	0.5893(7)	0.8211(6)	0.0337(11)
C(7)	0.6133(7)	0.7550(6)	0.1399(11)
C(8)	0.6152(8)	0.6760(7)	0.0945(13)
C(9)	0.6337(8)	0.6111(7)	0.1872(14)
C(10)	0.6541(8)	0.6256(7)	0.3241(14)
C(11)	0.6548(7)	0.7036(7)	0.3740(12)
C(12)	0.6341(6)	0.7698(6)	0.2824(11)
C(13)	0.6369(6)	0.8533(6)	0.3399(11)
C(14)	0.6846(7)	0.9116(7)	0.3086(12)
C(15)	0.6906(8)	0.9895(8)	0.3659(13)
C(16)	0.6522(8)	1.0075(8)	0.4513(14)
C(17)	0.6041(9)	0.9486(8)	0.4831(13)
C(18)	0.5970(7)	0.8705(6)	0.4266(11)
C(19)	0.4511(7)	0.7120(7)	0.5444(12)
C(20)	0.4513(8)	0.7248(8)	0.6740(12)
C(21)	0.4065(10)	0.6734(9)	0.7259(15)
C(22)	0.3651(9)	0.6054(8)	0.6472(14)
C(23)	0.3660(8)	0.5923(7)	0.5220(13)
C(24)	0.4080(6)	0.6445(6)	0.4664(12)
C(25)	0.4050(6)	0.6275(6)	0.3265(12)
C(26)	0.4400(8)	0.5546(7)	0.3067(13)
C(27)	0.4417(8)	0.5342(7)	0.1807(14)
C(28)	0.4046(8)	0.5880(8)	0.0676(12)
C(29)	0.3697(7)	0.6602(6)	0.0857(12)
C(30)	0.3694(6)	0.6810(6)	0.2145(11)
C(31)	0.3248(6)	0.7563(6)	0.2238(10)
C(32)	0.2590(7)	0.7499(7)	0.2671(12)
C(33)	0.2124(8)	0.8171(8)	0.2713(13)
C(34)	0.2331(8)	0.8922(8)	0.2315(14)
C(35)	0.2976(7)	0.8997(7)	0.1896(13)
C(36)	0.3447(7)	0.8307(7)	0.1813(11)

Geometry calculations were carried out using XRAY 72 [8]. Table 2 lists the atomic coordinates of the bonded atoms.

References

1 G. Wittig, E. Hahn and W. Tochtermann, Chem. Ber., 95 (1962) 431.

2 A.G. Massey, N.A.A. Al-Jabar, R.E. Humphries and G.B. Deacon, J. Organomet. Chem., 316 (1986) 25.

3 N.A.A. Al-Jabar, J. Bowen Jones, D.S. Brown and A.G. Massey, Acta Cryst., C42 (1986) 425; K. Stender, W. Hinrichs, J. Kopf and G. Klar, Cryst. Struct. Commun., 10 (1981) 613.

4 D.S. Brown, A.G. Massey and D.A. Wickens, Acta Cryst., B34 (1978) 1695; Inorg. Chim. Acta, 44 (1980) L193.

5 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M.M. Woolfson, MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction.
6 G.M. Sheldrick, SHELX, Program for crystal structure determination, University of Cambridge, England, 1976.
7 International Tables for X-ray Crystallography (1974) Vol. IV. Birmingham, Kynoch Press (Present distribution: D. Reidel, Dordrecht.).
8 J.M. Stewart, G.J. Kruger, H.L. Ammon, C.W. Dickinson and S.R. Hall, The XRAY72 system-version of June 1972. Tech. Rep. TR-192. Computer Science Center, University of Maryland, College Park, Maryland, 1972.