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A Re-investigation of *o*-Phenylenemercurials (V) [1]: the Crystal and Molecular Structure of Monoclinic Tribenzo[b, e, h] [1, 4, 7] trimercuronin

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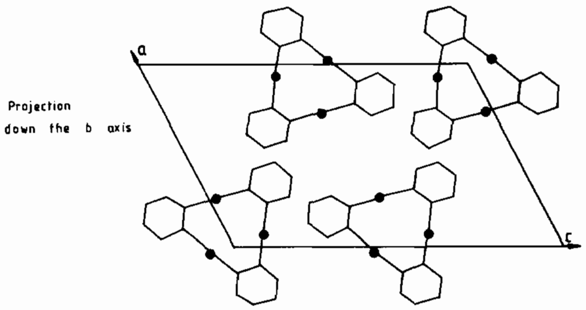
The reaction of 1,2-dihalobenzenes with either sodium or potassium amalgam produces polymeric *ortho*-phenylenemercury, $(C_6H_4Hg)_n$. On the basis of molecular weight determinations in solution [3] and a partial structure determination carried out on a monoclinic crystal [4] the mercurial was assumed to be hexameric. However, the mass spectrum suggested that *ortho*-phenylenemercury was a trimer [5] and this was verified by an X-ray study of an orthorhombic crystal modification [2]. We have now been able to isolate the original monoclinic form and report here the preliminary structural results on it.

The *ortho*-phenylenemercury was prepared by agitation of a dioxan solution of 1,2-dibromobenzene with 2% sodium amalgam and monoclinic crystals obtained from N,N-dimethylformamide solution. Crystal data: $C_{18}H_{12}Hg$, M = 830.1; monoclinic, a = 10.512(3), b = 8.116(2), c = 19.128(7) Å, β = 106.92 (3)°, U = 1561.2 Å^3, F(000) = 1440, Z = 4, D_c = 3.49 Mg m^{-3}; MoKα, λ = 0.71069 Å, μ = 8.53 mm^{-1}. Absences: 0k0 when k odd, h0l when l odd; Space group $P2_1/c$ (No. 14).

A crystal 0.2 × 0.05 × 0.6 mm was mounted about b and investigated photographically; final alignment, refined cell dimensions and data collection were then performed on an automatic 4-circle diffractometer. The 2856 observed reflections where $I \geqslant 3\sigma(I)$ were data reduced, corrected for Lorentz and polarisation effects and the structure refined using the XRAY 72 suite of programs [6] after initial solution for the heavy atoms using the MULTAN 74 package [7]. Least squares refinement of non-hydrogen atoms has led to a current conventional R of 11.2% for a *trimeric* molecule. The unit cell contents is shown in Fig. 1 and the atomic co-ordinates are given in Table I.



Monoclinic Tribenzo[b,e,h][1,4,7]trimercuronin

TABLE I. Atomic Co-ordinates × 10^3 (with Standard Deviations in Parentheses).

Atom	*x*	*y*	*z*
Hg(1)	−25(0)	289(0)	−82(0)
Hg(1)	271(0)	476(0)	21(0)
Hg(3)	73(0)	246(0)	109(0)
C(1)	283(4)	583(5)	−128(2)
C(2)	220(3)	490(4)	−91(2)
C(3)	241(4)	608(5)	−204(2)
C(4)	107(5)	426(6)	−129(2)
C(5)	128(3)	541(4)	−242(2)
C(6)	48(5)	445(6)	−210(2)
C(7)	242(3)	370(4)	168(1)
C(8)	275(3)	374(4)	246(2)
C(9)	313(3)	472(3)	134(1)
C(10)	382(3)	462(4)	284(1)
C(11)	422(3)	559(4)	175(2)
C(12)	462(3)	558(4)	254(2)
C(13)	−317(4)	−35(5)	−41(2)
C(14)	−282(4)	−44(5)	38(2)
C(15)	−261(3)	76(4)	−74(2)
C(16)	−175(3)	25(4)	78(2)
C(17)	−139(3)	154(3)	−32(2)
C(18)	−94(3)	131(3)	47(1)

TABLE II. Bond Lengths (Å) and Angles (°) Involving Mercury Atoms; atomic numbering as reference [2], standard deviations in parentheses.

Atoms	Interatomic Separations		Angle
C(17)–Hg(1)–C(4)	2.16(5)	2.05(3)	175.7(1.3)
C(2)–Hg(2)–C(9)	2.06(3)	2.07(2)	176.4(1.2)
C(7)–Hg(3)–C(18)	2.07(3)	2.04(2)	177.1(1.1)

Each mercury atom in the molecule possesses approximately linear geometry; C–Hg–C angles and C–Hg bond lengths are given in Table II. The mercury–mercury contact distances are 3.56(0), 3.52(0), 3.51(0) Å (bridged) and 3.67(0), 3.82(0) Å (non bridged). This implies the structural reason for the two crystal forms: the monoclinic form is dictated by van der Waals forces between the phenyl rings and between the rings and the metal atoms, whereas in the orthorhombic form the van der Waals forces between the metal atoms appear to be an important feature. The van der Waals radius [2, 8] for mercury is too small to explain the packing in the monoclinic form.

The monoclinic form of *o*-phenylenemercury may be converted into the orthorhombic form simply by recrystallisation from boiling quinoline. The two forms have only very minor spectral differences: the i-r band at about 74 mm^{-1} is split slightly differently in each; the orthorhombic modification has a more intense band in the far i-r (15–24 mm^{-1}) and fluoresces more strongly under laser Raman conditions.

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