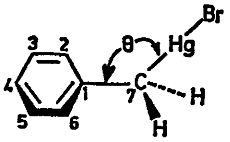
Benzyltriphenylmethylthiomercury; Crystal Structure Determination

By ROBERT D. BACH, A. THOMAS WEIBEL, WILLIAM SCHMONSEES, and MILTON D. GLICK
(*Department of Chemistry, Wayne State University, Detroit, Michigan* 48202)

Summary The crystal structure of $PhCH_2HgSCPh_3$ reveals a linear C–Hg–S bond, a Ph–C–Hg bond angle of 112° and a dihedral angle of 87° between the plane of the benzyl carbons and the plane formed by the mercury atom, the methylene carbon and C-1 on the phenyl group.

IT has been firmly established that the R_3MCH_2 group (M = Si, Ge, Sn, Pb) and the $-CH_2HgX$ group[1] exhibit an unusual electron-releasing capacity.[2] Experimental[1,2] and theoretical[3] evidence indicate that this enhanced reactivity is derived from hyperconjugation of the CH_2-M bond (σ–π conjugation). Vibrational spectral data[4] and extended Huckel MO calculations[3c] suggest that benzylmercuric halides are most stable in conformation (**1**) in which the polarizable C–Hg bond can interact with the π system of the aromatic ring. The hybridization at C-7 in (**1**) is also of theoretical interest. The crystal structures[5] of a series of tetrabenzyl derivatives [$M(CH_2Ph)_4$] of Zr, Hf, Ti, and Sn have established a unique distortion of the M–C–C bond angle [θ in (**1**)] from a tetrahedral value of 109·5°. The average M–C–C angles of 92°, 94°, 103° and 111°, respectively suggest that the small angle at the methylene carbon atoms in transition-metal derivatives may be due to bonding with the vacant *d* orbitals. We have, therefore, carried out an *X*-ray analysis on a benzylmercury compound to resolve its ground-state structure.



(**1**)

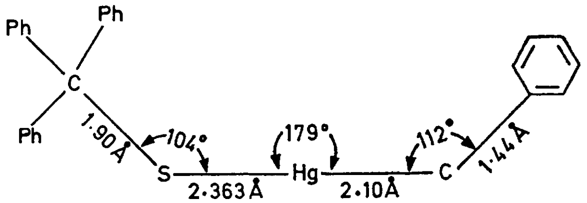


FIGURE 1

After examining a variety of benzylmercury compounds, we found that benzyltrimethylthiomercury (**2**) was sufficiently stable to light and *X*-rays to allow its structure determination. This compound is also of interest because alkyl mercury sulphides are biologically important and their structural parameters have not been extensively studied. The compound was prepared by the treatment of benzylmercuric chloride with triphenylmethanethiol in methanolic NaOH. Recrystallization from benzene-pentane gave white opaque crystals, m.p. 120° (decomp.).

The crystals were monoclinic, space group $P2_1/a$ with lattice constants $a = 11{\cdot}862(7)$, $b = 18{\cdot}137(15)$, $c = 12{\cdot}932(8)$ Å and $\beta = 128{\cdot}93(3)°$. The structure was solved by Patterson and Fourier methods from diffractometer data collected with Nb-filtered MoK_α radiation. Refinement of the structure yielded discrepancy factors of $R = 0{\cdot}069$ and $wR = 0{\cdot}084$ for the 1538 data with $I > \sigma(I)$. Only the CH_2 group adjacent to the mercury showed strongly anisotropic thermal motion.

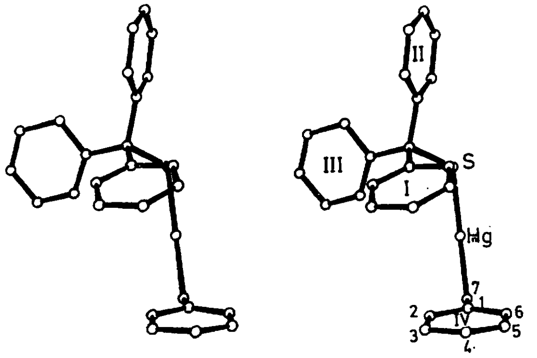


Figure 2

The compound is found to exist as a discrete monomer with a linear C–Hg–S bond (Figure 1). The Hg–C-7–C-1 bond angle is 112° suggesting that the hybridization at the benzyl carbon is essentially tetrahedral. Thus, the compounds of tin and mercury, both of which have filled inner *d* orbitals, have tetrahedral bond angles. Significantly the C=C–C–Hg dihedral angle (Figure 2) is 87° which approaches the predicted[3c] dihedral angle of 90° for benzylmercuric bromide (**1**).

Finally, the conformation of the molecule suggests that a weak intramolecular interaction exists between one of the aromatic rings and the mercury atom. The carbon–mercury bond distance of 3·30 Å is comparable to that estimated by Kiefer[6] who has also reported an intramolecular π-complex to mercury. The dihedral angle between the planes of phenyl (I) and phenyl (IV) is 78° and the projection angle between the C-1–C-4 bond in phenyl (I) and the S–C bond is 46°.

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