

## X-RAY STUDY OF BARENYLMERCURY HALIDES. SPONTANEOUS SYMMETRIZATION OF PHENYLBARENYLMERCURY IODIDE IN THE CRYSTAL

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### SUMMARY

A crystallographic investigation of the structure of (methyl- and phenylborenyl)mercury bromide and (phenylborenyl)mercury iodide has been undertaken. The bond lengths of the Hg-Br and Hg-I bonds of these compounds are unchanged in comparison with those in compounds containing less electron-acceptor radicals. Only in the case of the (phenylborenyl)mercury iodide does the intermolecular contact Hg...I decrease (3.29 Å instead of the usual 3.81-4.2 Å).

In the crystal state (phenylborenyl)mercury iodide was observed to undergo spontaneous symmetrization. This effect has been explained in terms of the strong intermolecular coordination between the mercury and iodine atoms of the two molecules in the crystallographic dimer.

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### INTRODUCTION

Organomercury derivatives of barene\* show very unusual properties in comparison with classical organomercuric compounds, the reasons for such properties having been attributed to the unusual valency state of the barenic carbon atom bonded with a mercury atom, and to the strong electron-acceptor influence of the barene nucleus<sup>1,2</sup>. Each of the two barenic carbon atoms has a coordination number of six, and for this reason the formation of a transition complex involving an unprecedented increase of carbon coordination number up to seven is probably impossible. For the same reason, borenylmercury compounds are very stable under action of electrophiles but react easily with nucleophiles including complexing reagents. However borenylmercury salts show no tendency to symmetrization when treated by complexing agents<sup>1-3</sup>, as is typical for organomercury compounds.

In an attempt to explain this anomaly, a structural investigation of borenylmercury halides has been undertaken to establish their crystallochemical features. (Phenylborenyl)mercury bromide and iodide, and (methylborenyl)mercury bromide,

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\* Barene = 1,2-dicarbap-closo-dodecaborane (12) =  $\begin{array}{c} \text{HC}-\text{CH} \\ \diagdown \quad \diagup \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$

have been studied in this way, samples of these materials being obtained by the halogenation of methyl(phenylborenyl)mercury and methyl(methylborenyl)mercury as has been described earlier<sup>3</sup>.

#### RESULTS AND DISCUSSION

The investigation of the crystal structure of (phenylborenyl)mercury bromide was carried out employing unfiltered Mo-K radiation. Oscillation about *a* and *c* axes was undertaken and de-Young photographs (*hk0*, *hk1*, *hk2*, *hk3*, *hk4*, *hk5*, *hk6*, *0kl* indexes) were obtained. The dimensions of the orthorhombic cell as determined from these photographs were found to be *a* = 10.94 Å, *b* = 18.15 Å, *c* = 7.79 Å respectively, indicating that four molecules exist in the cell. The crystallographic space group was determined by analyses of the extinction of the X-ray reflections. The absence of extinction reflections with indexes *hkl* and the presence of only reflections with an even sum *k* + *l* = 2*n* in *0kl* and *h* + *l* = 2*n* in *h0l* require two possible space groups: *Pnmm* and *Pnn2*. After determination of the atom position in the structure the space group was unequivocally selected as *Pnn2*.

Two Patterson projections *P(uv)* and *P(vw)* were obtained, 68 independent non-zero X-ray reflections being used for *P(uv)* projection construction and 56 for *P(vw)* (projection construction.) These projections suggested the positions of "heavy" atoms (Hg and Br) and a three-dimensional electron density distribution  $\rho(xyz)$  was subsequently constructed, 460 independent non-zero reflections being used for the construction of this distribution. After four cycles of electron density refinement the atomic coordinates of mercury, bromine and carbon bonded with mercury were obtained as:

	<i>x</i>	<i>y</i>	<i>z</i>
Hg	0.079	0.112	0
Br	0.863	0.074	0
C <sub>1</sub>	0.267	0.165	0

The reliability factor *R* was 0.22 for all observed reflections.

It is interesting to note that the position of these atoms belongs to the space group *Pnmm* with symmetry *m*. Analysis of the three-dimensional electron distribution  $\rho(xyz)$  does not lead to the same molecular symmetry *m* because seven other carbon atoms and ten boron atoms have a very large displacement from this symmetry.

A "topologic" search for icosahedral C<sub>2</sub>B<sub>10</sub> groups was made by searching for five neighbours of each atom at a 1.5–1.8 Å distance (the dispersion of distances was determined by allowing for the usual errors in the positions of "light" atoms in the presence of "heavy" mercury and bromine atoms). It was found out that there were some maxima resembling an icosahedron, but besides these maxima in the three-dimensional distribution  $\rho(xyz)$ , there were some "false" maxima, comparable in height to the "true" maxima. However, attempts to find the disposition of phenyl rings in the three-dimensional distribution  $\rho(xyz)$  led to an unexpected result, *viz.* a phenyl carbon atom bonded with the icosahedron is on equal distance (about 1.5–1.6 Å)

from two neighbouring isocahedral atoms.

It is difficult to understand this difference in the positions of phenyl ring carbon atoms obtained from two-dimensional projections  $\rho(xy)$  and three-dimensional distributions  $\rho(xyz)$ , although it may be related to "pseudo-symmetry" in the mercury and bromine atom disposition. A different synthesis of the  $\rho(xyz)$  distribution was made by crossing out the mercury and bromine atom positions, but no greater success in the localisation of the position of "light" atoms (other than C(1) atoms linked with mercury) was achieved. The reasons for this failure are not immediately apparent.

The unit cell of (phenylborenyl)mercury bromide includes one crystallographically independent Hg-Br group. Since Hg-Br groups are connected with each other by a two-fold symmetry axis, the disposition of Hg-Br bonds is antiparallel (Fig. 1).

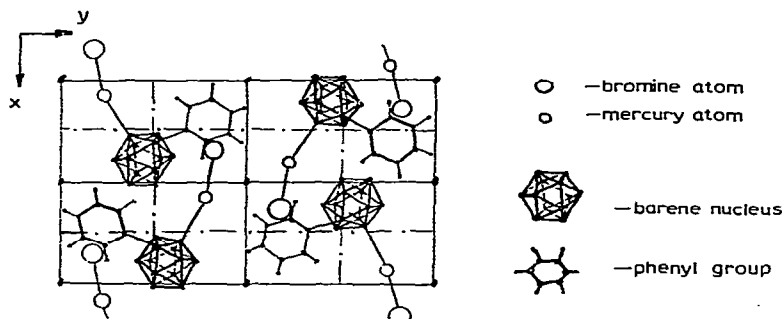


Fig. 1. Projection of the (phenylborenyl)mercury bromide structure on the  $xy$  plane.

The intramolecular Hg-Br distance was found to be 2.44 Å, while the intermolecular Hg...Br distance was 3.49 Å. (In the crystal of phenylmercury bromide,  $C_6H_5HgBr$ , the intramolecular Hg-Br distance was 2.43 Å and intermolecular Hg...Br distance 3.45 Å<sup>4</sup>.)

The "heavy" atoms (Hg and Br) positions were refined by a least-squares method and temperature factors ( $B_j$ ) obtained for the mercury and bromine atoms.

	$x$	$y$	$z$	$B_j$ (Å <sup>2</sup> )
Hg	0.079	0.112	0.973	-2.60
Br	0.868	0.073	0.995	-2.54

The discrepancy factor was found to be 0.19. Using these atomic positions the intramolecular Hg-Br distance was found to be 2.42 Å, and the intermolecular Hg...Br distance 3.42 Å in good agreement with the above values. It is interesting to note, however, that the Hg-C bond found from a  $\rho(xy)$  projection and a  $\rho(xyz)$  three-dimensional distribution is 2.27 Å, *i.e.* larger than the comparable distance in  $C_6H_5HgBr$  (2.10 Å)<sup>5</sup>. It is however very difficult to decide how relevant such a distance is in the context of these measurements since the accuracy in determining the carbon atom position is very small.

The crystal structure of (methylbarynyl)mercury bromide has also been examined. Crystals of this compound were not so well-formed as those of (phenylbarynyl)mercury bromide and their photographs were obtainable only by the use of Cu-K radiation ( $hk0$ ,  $hk1$ ,  $hk2$  reflections). These crystals were found to exhibit orthorhombic symmetry with lattice parameters:

$$a = 13.42 \text{ \AA}, b = 13.97 \text{ \AA}, c = 6.83 \text{ \AA}$$

There are four molecules in the unit cell. Systematic absences confirm the space group to be  $Pbnm$  or  $Pbn2_1$ , the former space group being selected for "heavy" atom (Hg and Br) positions after a Patterson  $P(uvw)$  synthesis. The refinement of the bromine and mercury atoms positions was carried out by the synthesis of a section of the  $\rho(xyz)$  function using a least-squares procedure (final discrepancy factor 0.15). The following positions of the bromine and mercury atoms and the individual temperature factors were obtained:

Atom	$x^a$	$y^a$	$z^a$	$B_j (\text{\AA}^2)$
Hg	0.030 0.026	0.101 0.100	0.250 0.250	-5.89
Br	0.574 0.573	0.455 0.457	0.250 0.250	-5.37

<sup>a</sup> Second values obtained by least-squares procedure.

From the section of  $\rho(xyz)$  synthesis the intramolecular Hg-Br distance was found to be 2.47 Å, the intermolecular Hg...Br distance 3.55 Å, the least-squares procedure leading to mean values of 2.43 Å and 3.56 Å respectively.

Dimers are formed through Hg-Br bonding in the crystal of (phenylbarynyl)mercury bromide, but in (methylbarynyl)mercury bromide a chain of antiparallel Hg-Br bonds extends along the  $c$  axis. [Hg-I bonds have a similar disposition in crystals of  $(\text{CH}_3)_2\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)_2\text{CH}_2\text{HgI}^6$ .]

Crystallographic of (phenylbarynyl)mercury iodide was carried out using Mo-K radiation. Two photographs involving crystal oscillation, and nine de-Young photographs with  $hk0$ - $hk5$ ,  $0kl$ ,  $1kl$  and  $2kl$  indexes, were obtained. These crystals were found to belong to an orthorhombic symmetry with lattice dimensions resembling those of (phenylbarynyl)mercury bromide crystals:

$$a = 11.03 \text{ \AA}, b = 18.29 \text{ \AA}, c = 7.69 \text{ \AA}$$

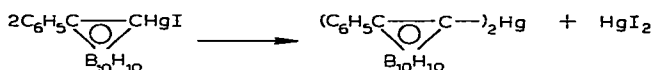
Four molecules again exist in the unit cell. Systematic absences of X-ray reflections lead to the space groups  $Pmmm$  and  $P2_1nm$  and  $Pmn2_1$  respectively.  $P(uv)$  and  $P(vw)$  projections of Patterson functions lead to the space group  $Pmn2_1$  for mercury and iodine. The refinement of these atoms positions was carried out from  $\rho(xy)$  projection and least-squares procedures (discrepancy factor 0.19).

Atom	$x$	$y$	$z$	$B_j (\text{\AA}^2)$
Hg(1)	0.015	0.142	0.000	-0.88
Hg(2)	0.844	0.366	0.000	-1.18
I(1)	0.784	0.164	0.000	-1.05
I(2)	0.067	0.319	0.000	-1.05

Intramolecular distances Hg(1)–I(1) and Hg(2)–I(2) were found to be 2.58 Å and 2.59 Å respectively, but intermolecular Hg(1)...I(2) and Hg(2)...I(1) distances were very different (3.29 Å and 3.75 Å respectively).

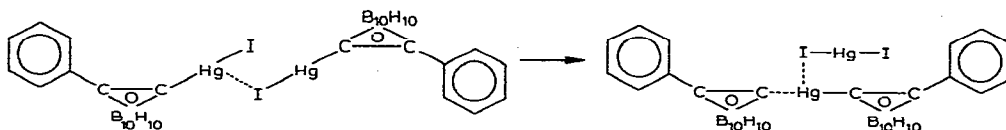
The above results indicate that the crystal chemistry of (phenylbarenyl)-mercury bromide does not differ from that of other related organomercury derivatives<sup>4</sup> and its chemical behaviour cannot be explained by any anomaly in its molecular structure. The deviation from the antiparallel structure of the dimer observed in the crystal structure of the iodide may be attributed to strong coordination interaction I→Hg in this compound.

Such intermolecular coordination is probably the reason of spontaneous symmetrization of (phenylbarenyl)mercury iodide observed when the crystal samples are stored;



Colourless crystals of iodide become red when stored in the absence of light for several months (temp. 20°) and yield mercuric iodide. This phenomenon is all the more interesting in that barenylmercury salts do not undergo symmetrization *in solution* under the action of such strong complexing agents as KI, NaCN, NH<sub>3</sub><sup>1-3</sup>. This reaction proceeds, apparently only in the crystalline state, *i.e. in solid*.

The above data concerning the crystal structure of (phenylbarenyl)mercury iodide allow an understanding of the molecular mechanism for this reaction. Mercury and iodine atoms are arranged in the crystal so that they form two crystallographic independent Hg–I groups which are located in a mirror plane of symmetry and are described by the *Pmn* space group. The disposition of these groups is almost antiparallel as in (phenylbarenyl)mercury bromide, but the difference in intermolecular distances leads to a distortion of the dimer structure. The intramolecular Hg–I distances (2.58 Å and 2.59 Å) correspond to similar distances in other organomercuric compounds (2.60 Å and 2.61 Å)<sup>6,7</sup>. The intermolecular distance Hg(2)...I(1) (3.75 Å) is also similar to the usual Hg...I distances in compounds of RHgI type<sup>6,7</sup>. But the Hg(1)...I(2) distance (3.29 Å) is essentially different from the usual values for such distances. The magnitude of the Hg(1)–I(2) distance lies between that of the Hg–I distance in the HgI<sub>3</sub><sup>-</sup> triangle (2.7 Å) and that of the usual contact Hg...I distance (3.81–4.28 Å). This iodine atom is probably the initiator of the symmetrization reaction because of its closeness to the mercury atom of the next molecule. Combination between these two atoms probably initiates the reaction, although a four-center transition state<sup>8</sup> is probably not realized in this case. It is suggested that the first stage of this reaction is separation of a HgI<sub>2</sub> molecule, and the next stage the connection of mercury and carbon atoms according to the scheme:



It was observed during these studies that the size of the crystals influences the rate of the symmetrization reaction; the smaller the size of the crystal, the faster the reaction state. The reason of this phenomenon must be related to the fact that the solid-state reactions involved in this case must proceed at the interface between reactant and product phases<sup>9</sup>. Hence, the larger the surface of the initial phase, the faster such reaction proceeds.

An explanation for the absence of (phenylborenyl)mercury halides symmetrization in the presence of the usual symmetrizing agents (NH<sub>3</sub>, KCN, KI, etc.) in solution probably lies in the stability of such complexes (with NH<sub>3</sub>, for example)<sup>10</sup> which are formed at the beginning of the reaction and which exhibit only a slow rate of change. The stability of such complexes is confirmed by the formation of stable complexes of borenylmercury halides with bipyridine<sup>1</sup>. In the "selfsymmetrization" of (phenylborenyl)mercury iodide in the solid state, the increase in the strength of the intermolecular Hg...I bond leads to the simultaneous weakening of the intramolecular Hg-I bond of the next molecule. For this reason the reaction is not slowed down at the stage of complex formation, as occurs in solution.

It is interesting to note that the strong electron-acceptor properties of phenyl- and methylborenyl groups have little influence on the lengths of the Hg-Br and Hg-I bonds.

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