The Stereochemistry of some Organic Derivatives of Ter- and Quinque-valent Group VB Elements

A Preliminary Note on the Crystal Structures of Triphenylbismuth Dichloride and Triphenylbismuth

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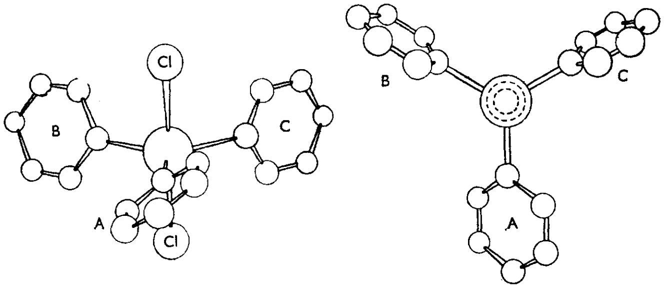
A DISTINCTIVE feature of the chemistry of bismuth is the relative lack of Bi^{V} compounds, although a few of general formula R_3BiX_2 (R = aryl group; X = halogen, acetate, *etc.*,) as well as bismuth pentaphenyl and pentafluoride are known. As part of a general study of organometallic halides of Group VB elements, Harris and co-workers[1,2] have made a conductance study of some triphenylbismuth–halogen systems from which it is evident that triphenylbismuth dihalides behave as molecular species in solvents of high dielectric constant, such as methyl cyanide. Jensen[3] found that triphenylbismuth dichloride has zero dipole moment in benzene and a trigonal bipyramidal structure has been suggested.



(I) (II)

Figure 1. *A general view (I) of an average molecule of triphenylbismuth dichloride and (II) a view down the Cl–Bi–Cl vector showing clearly the orientations of the benzene rings.*

Our cell data for this molecule are listed in the Table along with Stroganov's earlier values.[4] The crystal structure was solved and refined by Patterson and difference-Fourier methods using some 1300 three-dimensional data. The discrepancy factor, R, is now 11·2%.

The two molecules in the asymmetric unit, although crystallographically independent, adopt almost identical conformations. Two views of an "average" molecule are given in Figure 1, where the trigonal bipyramidal arrangement of the molecular species is evident. The bismuth atom and the carbon atoms to which it is bonded, lie in a plane with the Bi–Cl bonds on the plane normal. The inclination of the benzene rings A, B, and C to this plane are 31°, 70°, and 79° respectively. The mean Bi–Cl distance is 2·605 ± 0·010 Å which is significantly longer than that reported[5] for the Bi^{III}–Cl distance (2·48 ± 0·02 Å) in bismuth trichloride but comparable with those found[6] for the Bi–Cl distances (2·61—2·87 Å) in the $BiCl_5^{2-}$ ion. Because of the dominating effect of the bismuth and chlorine atoms on the scattering, the resolution of the carbon atoms leaves much to be desired. The mean Bi–C distance is 2·24 ± 0·10 Å.

At an early stage in the analysis of triphenylbismuth dichloride, it was hoped to compare the structure with that of the parent triphenylbismuth. Iveronova and Roitburd[7] report cell and space-group data for triphenylbismuth, but

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make no mention of Wetzel's work,[8] which as well as giving cell data, also describes the crystal structure. There is a discrepancy between Wetzel's and Iveronova and Roitburd's assignment of space group. The structure proposed by Wetzel is based on quantitative intensity data for 210 ($h0l$) planes with qualitative data for 324 ($h1l$) and ($h2l$) planes, and involves a planar distribution of Bi–C bonds with the planes of the benzene rings inclined at 60° to (010). Quite apart from the lack of a quantitative foundation, the proposed structure is inconsistent with the short b-axis, *e.g.*, in a diagram of the 5·8 Å projection there are overlapping benzene rings. Furthermore the $\mathrm{Bi^{III}}$–C distance (2·30 Å) reported in various tables,[5,9,10] is based on this erroneous structure.

TABLE

Various cell data for $\mathrm{Ph_3BiCl_2}$ *and* $\mathrm{Ph_3Bi}$

Molecule	Source	aÅ	bÅ	cÅ	β	Space Group	D_m	Z	D_c
$\mathrm{Ph_3BiCl_2}$	Hawley[11]	9·18	17·11	22·30		$P2_12_12_1$		8	
	Stroganov[4]	9·16	17·00	22·30		$P2_12_12_1$	1·955	8	1·955
	Hawley[11]	27·70	5·82	20·45	114° 29′	$C2/c$		8	
$\mathrm{Ph_3Bi}$	Wetzel[8]	26·74	5·78	20·44	109° 34′	$I2/c$	1·952	8	1·952
	Iveronova and Roitburd[9]	26·7	5·78	20·4	109° 24′	$C2/c$		8	

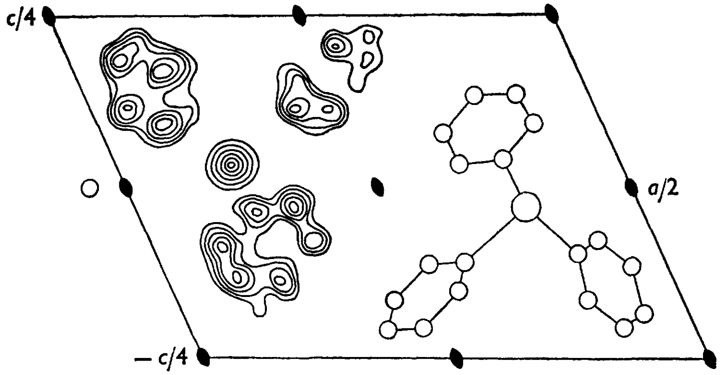

FIGURE 2. *The* (010) *projection of triphenylbismuth and its interpretation. Contour level at* 1e Å^{-2} *except around the bismuth atom where it is arbitrary.*

Our cell data[11] are given in the Table along with the earlier work for comparison. Wetzel's cell is consistent with his space-group assignment: Iveronova and Roitburd's cell is incorrect for $C2/c$ or Cc. We have solved this structure in projection on (010) using photographic data. A correct view of this projection is shown in Figure 2, where it is evident that the tilts of the benzene rings to (010) vary considerably from ring to ring. The present value of R for 274($h0l$) data is 11·4%.

Work on both compounds is being continued with diffractometer[12] data. Full details will be reported in due course.

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