The Structure of *BB*-Di-iodo-*PP*-diphenylphosphinoborine $(Ph_2PBI_2)_2$

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ALTHOUGH examples of dimeric phosphinoborine derivatives have been reported,[1,2] their molecular structures have hitherto been uncertain. It has been assumed that they contain a four-membered boron–phosphorus ring which, it has been suggested, is planar, in spite of the possession of a dipole moment by the symmetrically substituted derivative $(Et_2PBBr_2)_2$.[2] Gee *et al.*[1] made a preliminary crystallographic examination of the isomorphous compounds $(Ph_2PBBr_2)_2$ and $(Ph_2PBI_2)_2$ which together with ebullioscopic measurements suggested that the molecules are dimeric, although the evidence was not conclusive. We have carried out a full crystal-structure analysis of the iodo-derivative which confirms that the molecules are dimeric with a non-planar four-membered ring.

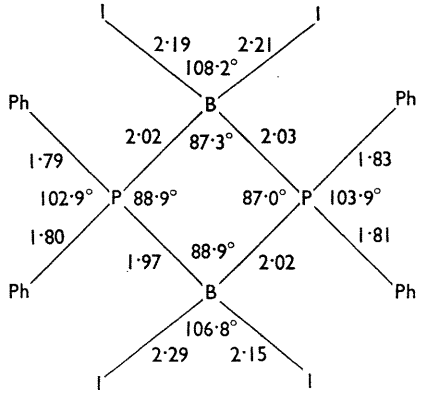

FIGURE 1. *Bond lengths (Å) and bond angles. Average standard deviations are 0·02 Å for the lengths and 0·7° for the angles.*

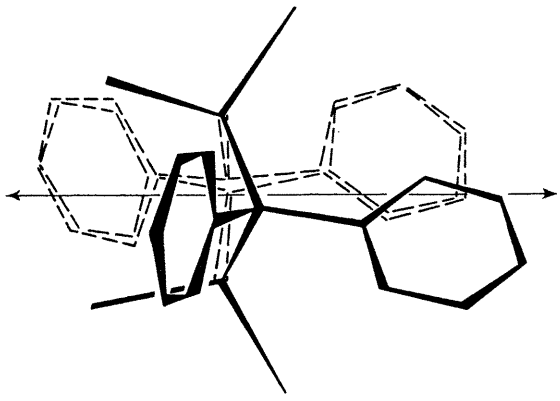

FIGURE 2. *Molecular shape. The arrow is the axis of two-fold symmetry.*

The unit-cell parameters quoted previously[1] were redetermined more accurately from diffractometer measure-measurements. *BB*-Di-iodo-*PP*-diphenylphosphinoborine, $C_{24}H_{20}B_2I_4P_2$, $M = 899{\cdot}59$, monoclinic, $a = 12{\cdot}32$, $b = 13{\cdot}93$, $c = 17{\cdot}50$ Å, $\beta = 110{\cdot}5°$, $U = 2813$ Å^3, $Z = 4$, $D_c = 2{\cdot}12$ g. cm.$^{-3}$, $D_m = 2{\cdot}13$ g. cm.$^{-3}$, space group $P2_1/c$ (C_{2h}^5, No. 14). 3343 *X*-Ray reflections with statistically significant intensities were measured on a Philips PAILRED automatic diffractometer with Mo-K_α radiation. The structure was solved by the heavy-atom technique and refined to $R = 0{\cdot}064$ by least squares by using anisotropic temperature factors for phosphorus, iodine, and carbon atoms and isotropic factors for boron and hydrogen. The hydrogen atoms were included in the calculations by placing them at positions estimated from the molecular geometry.

The bond lengths and bond angles calculated at this stage of the refinement are given in Figure 1. The boron–phosphorus ring is non-planar with the approximate symmetry $mm2$ (C_{2v}) or, if the distinction between boron and phosphorus is disregarded, $\bar{4}2m$ (D_{2d}). The differences between the lengths of the four P–B bonds and between the four endocyclic bond angles are not significant at this stage. The P–B–B–P and B–P–P–B torsion angles are both 30°. This ring shape is similar to that found in $(PCF_3)_4$,[3] where the torsion angles are 34°. As a dipole moment of 2·54 D has been observed[2] for $(Et_2PBBr_2)_2$ it is probable that this compound also has a non-planar ring. The co-ordination of the phosphorus and boron atoms is tetrahedral though very much distorted by having angles of only 87—89° between the P–B bonds. The phenyl groups are orientated in such a way that the whole molecule has a two-fold axis of symmetry along the perpendicular bisector of the P···P and B···B lines (Figure 2). This two-fold symmetry is not perfect but the deviations from it are small. The presence of this symmetry axis, which is nearly parallel to [012], would seem to be responsible for the tendency of the crystals to twinning which was reported previously.[1] The refinement of the structure is being continued.

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[1] W. Gee, R. A. Shaw, B. C. Smith, and G. J. Bullen, *Proc. Chem. Soc.*, 1961, 432.
[2] H. Nöth and W. Schrägle, *Chem. Ber.*, 1965, **98**, 352.
[3] G. J. Palenik and J. Donohue, *Acta Cryst.*, 1962, **15**, 564.