Molecular Structures of Cycloborataphosphonianes. Part I. Crystal Structure of 2,2,4,4-Tetraiodo-1,1,3,3-tetraphenylcyclodiborataphosphoniane

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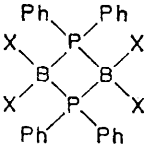
The crystal structure of the title compound has been determined by the heavy-atom method from *X*-ray diffractometer intensity data and refined by least-squares methods to *R* 0·064 for 3343 independent reflexions. The crystals are monoclinic with $a = 12{\cdot}34$, $b = 13{\cdot}80$, $c = 17{\cdot}56$ Å, $\beta = 111{\cdot}8°$, $Z = 4$, space-group $P2_1/c$. The dimeric molecules contain a non-planar, four-membered boron–phosphorus ring with approximate symmetry *mm*2 and a dihedral angle of 30°. The endocyclic bond angles are 88·2° at boron and 87·9° at phosphorus. Two different B–P bond lengths, 1·94 and 2·01 Å, are found. The mean B–I bond length is 2·21 Å. The complete molecule has an axis of approximate two-fold symmetry, in terms of which the tendency to form twinned crystals is explained.

DIMERIC phosphinoboranes may be prepared by the reaction of diphenylphosphine with boron trihalides to form adducts Ph_2PH,BX_3 (X = Br or I) from which hydrogen and halogen are eliminated to form $[(Ph_2P)BX_2]_2$ (I).[1,2]



(I)

Nöth and Schrägle[3] have also prepared dimeric derivatives by the reaction of phosphinosilanes with boron halides. They suggested that the dimers contain planar four-membered boron–phosphorus rings, by analogy with the dimer $[(Me_2N)BCl_2]_2$ which possesses a planar ring in the crystalline state.[4] Their observation that $[(Et_2P)BBr_2]_2$ has a dipole moment of 2·54 D is in conflict with this but they noted[3] that $[(Me_2N)BCl_2]_2$ also possesses a significant dipole moment (1·79 D) in benzene solution, which is unexpected in view of the high symmetry (*mmm*) of this molecule in the crystal.

In a preliminary crystallographic examination of the isomorphous compounds $[(Ph_2P)BBr_2]_2$ and $[(Ph_2P)BI_2]_2$ Gee *et al.*[1] found there to be eight Ph_2PBX_2 units in the

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[1] W. Gee, R. A. Shaw, B. C. Smith, and G. J. Bullen, *Proc. Chem. Soc.*, 1961, 432.

[2] W. Gee, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1964, 4180.

[3] H. Nöth and W. Schrägle, *Chem. Ber.*, 1965, **98**, 352.

[4] H. Hess, *Z. Krist.*, 1963, **118**, 361.

unit cell. Since the space-group is $P2_1/c$ the cell might contain either eight monomeric molecules, four dimers, or two tetramers, but ebullioscopic molecular-weight measurements favoured dimers. We have now carried out a full crystal-structure analysis of $[(Ph_2P)BI_2]_2$ to determine the size and shape of the boron–phosphorus ring. Preliminary results have already been reported.[5]

EXPERIMENTAL

Crystal Data.—$[(C_6H_5)_2PBI_2]_2$, $M = 899{\cdot}59$, Monoclinic, $a = 12{\cdot}34(2)$, $b = 13{\cdot}80(3)$, $c = 17{\cdot}56(8)$ Å, $\beta = 111{\cdot}8° \pm 0{\cdot}2°$, $U = 2777$ Å^3, $D_c = 2{\cdot}15$, $Z = 4$, $D_m = 2{\cdot}13$, $F(000) = 1664$. $\mu = 46{\cdot}2$ cm^{-1} for Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). Space-group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $h0l$ when l is odd, $0k0$ when k is odd.

The prismatic crystals (elongated along c) obtained by recrystallisation from benzene exhibit the forms {110} and {001}. Those examined in the earlier work[1] had shown a tendency to twinning, but this was not observed in the crystals considered for intensity measurements. 5522 Independent reflexions from a single crystal of dimensions $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}4$ mm were measured from the layers $hk0$—20 on a Philips PAILRED diffractometer by use of monochromatised Mo-K_α radiation. These comprised all possible reflexions with $\sin\theta/\lambda \leqslant 0{\cdot}61$ Å^{-1}. Of these 3343 had $I > 2\sigma(I)$ and were considered observed. The intensities were measured by the ω-scan method; Lorentz and polarisation factors were applied but no corrections were made for absorption. The unit-cell parameters were determined on the diffractometer.

The least-squares refinement was carried out on the University of Essex I.C.L. 1909 computer and at the Atlas Computer Laboratory, Chilton, Didcot, Berkshire. Atomic scattering factors were taken from ref. 6. The principal computer programmes used are listed in ref. 7.

Structure Determination.—The intensity data were placed on an approximate absolute scale determined from the observed height of the Patterson origin peak. At this stage it was assumed that the same scale-factor could be applied to all reflexions as they had been measured under constant experimental conditions.

The structure was solved by means of the heavy-atom technique. The unit cell contains 16 iodine atoms, four in each asymmetric unit, which were located from the three-dimensional Patterson function and were found to lie approximately in planes parallel to (100), the twin plane of the crystals previously examined by Gee *et al.*[1] Structure-factors calculated from the iodine positions gave R 0·35 for the 3343 observed reflexions. All the other atoms (except hydrogen) were located from a Fourier synthesis phased on the heavy atoms, to which 2946 reflexions with $|F_c| > 0{\cdot}5\ |F_o|$ contributed.

Five cycles of block-diagonal isotropic least-squares refinement, using reflexions for which $|F_c| > 0{\cdot}33\ |F_o|$ and unit weights, brought R to 0·12. The positions of the hydrogen atoms were estimated from the molecular geometry and were included but not refined. Since the boron and phosphorus atoms are formally B^- and P^+ as a consequence of the dative nature of the B–P bond in this molecule, modified scattering curves for these charged species were estimated by comparing the available curves[6] for N and N^-, and Al and Al^+. However, their use had no appreciable effect on the refinement or on either the boron or phosphorus temperature factors, and so scattering factors for the neutral atoms were used subsequently.

During the isotropic refinement the scale-factors for the 21 layers of reflexions were refined individually, but the values produced differed from each other by no more than 8%. These individual scale-factors were kept fixed, once the anisotropic temperature factor refinement had commenced and only an overall scale-factor was varied, together with the positional parameters and anisotropic temperature factors. Weights were chosen according to the conditions $w = x.y$, where $x = 110/|F_o|$ if $|F_o| \geqslant 110$ (on an absolute scale) but otherwise $x = 1$, and $y = \sin\theta/0{\cdot}15\lambda$ if $\sin\theta/\lambda \leqslant 0{\cdot}15$ but otherwise $y = 1$. These gave similar average values of $w\Delta^2$ for ranges of increasing $|F_o|$ or $\sin\theta/\lambda$. Also w was put equal to zero if $|F_o| > 3|F_c|$. A limitation on the number of variables in the full-matrix least-squares computer programme precluded the refinement of all 288 positional and anisotropic thermal parameters simultaneously. At first only the iodine atoms were refined anisotropically and subsequently the carbon atoms in groups of five. In the final two cycles all positional parameters plus the phosphorus and iodine temperature factors were varied. Oscillations of the parameters were damped by halving the shifts. The three reflexions $\bar{3},0,4$, $\overline{12},7,8$, and $\bar{3},0,14$ showed unusually large Δ values which did not decrease as the refinement progressed. Since extinction was not a satisfactory explanation their intensity measurements were presumed to be at fault and so these observations were excluded from the last stages of refinement. The refinement was taken to a point where all co-ordinate shifts were $<0{\cdot}14\sigma$ and temperature-factor shifts $<0{\cdot}10\sigma$. The final R for the 3343 observed reflexions is 0·064.

RESULTS

The final atomic co-ordinates and thermal parameters with their estimated standard deviations are listed in Tables 1—3. For the hydrogen atoms an isotropic temperature factor with B 5·0 Å^2, equivalent to $(\overline{u^2})^{\frac{1}{2}}$ 0·25 Å, was used. Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20343 (18 pp., 1 microfiche).* Of the 2179 unobserved reflexions, 16 gave $|F_c|$ values greater than the $|F_o|$ corresponding to the minimum significant intensity, and two of these had $|F_c|$ slightly greater than twice this quantity.

Bond lengths are listed in Table 4 and bond angles in Table 5 (see Figure 1 for labelling of the atoms). The standard deviations were calculated from the co-ordinate estimated standard deviations in Table 1 (assumed uncorrelated) with allowance for the errors of the unit-cell parameters. To obtain accurate bond lengths it is necessary, where possible, to correct the atomic positions for the effect of rotational oscillations of the molecule, by analysing the directions of the principal vibration axes for each atom.[8]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[5] G. J. Bullen and P. R. Mallinson, *Chem. Comm.*, 1969, 132.

[6] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 202, 203, 211.

[7] Computer programmes used: (*a*) '*X*-Ray '63 System,' compiled by J. M. Stewart and D. F. High: programmes FOURR for Fourier synthesis, ORFLS for least-squares refinement, and BOND67 for bond lengths and angles; (*b*) A PAILRED Data Reduction Programme, by P. R. Mallinson.

[8] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757; 1961, **14**, 896; Conference on Accuracy and Automation in *X*-Ray Analysis, Institute of Physics and Physical Society, 1968, Abstracts, Paper IV 4.

The vibration ellipsoids for the iodine atoms are shown in Table 6. For each iodine atom the direction of minimum vibration points approximately towards the molecular centre; the angles between these directions and the radius vectors are respectively **11**, **7**, **8**, and **3°** for I(1)—I(4).

TABLE 1

Atomic co-ordinates (as fractions of unit-cell edges) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
I(1)	0·31366(10)	0·35424(8)	−0·03979(6)
I(2)	0·27518(11)	0·52383(7)	0·10120(7)
I(3)	0·29518(10)	0·09030(8)	0·03208(7)
I(4)	0·29633(12)	0·08192(8)	0·23589(7)
P(1)	0·1699(3)	0·2809(3)	0·0907(2)
P(2)	0·4120(3)	0·2847(3)	0·1605(2)
B(1)	0·2925(15)	0·1782(12)	0·1370(10)
B(2)	0·2973(15)	0·3640(11)	0·0787(10)
Phenyl group (I)			
C(1)	0·0462(13)	0·2476(10)	0·0013(9)
C(2)	−0·0113(17)	0·1612(15)	0·0013(14)
C(3)	−0·1093(18)	0·1384(17)	−0·0689(15)
C(4)	−0·1459(16)	0·1980(17)	−0·1349(13)
C(5)	−0·0887(17)	0·2809(17)	−0·1344(11)
C(6)	0·0067(15)	0·3097(14)	−0·0671(10)
Phenyl group (II)			
C(7)	0·5472(13)	0·2621(11)	0·1457(8)
C(8)	0·6016(14)	0·3410(13)	0·1229(10)
C(9)	0·7087(16)	0·3251(18)	0·1156(12)
C(10)	0·7635(16)	0·2362(18)	0·1322(12)
C(11)	0·7098(14)	0·1596(15)	0·1542(11)
C(12)	0·5989(14)	0·1709(12)	0·1622(10)
Phenyl group (III)			
C(13)	0·4575(13)	0·3177(10)	0·2661(8)
C(14)	0·5443(16)	0·2619(14)	0·3217(9)
C(15)	0·5751(17)	0·2780(16)	0·4043(11)
C(16)	0·5245(16)	0·3511(13)	0·4315(11)
C(17)	0·4415(16)	0·4072(13)	0·3778(10)
C(18)	0·4061(15)	0·3943(11)	0·2951(8)
Phenyl group (IV)			
C(19)	0·1048(12)	0·3349(10)	0·1590(9)
C(20)	0·1420(16)	0·3131(13)	0·2382(10)
C(21)	0·0956(19)	0·3636(16)	0·2886(11)
C(22)	0·0135(17)	0·4346(14)	0·2567(12)
C(23)	−0·0242(15)	0·4562(13)	0·1771(11)
C(24)	0·0198(17)	0·4065(13)	0·1266(10)

TABLE 2

Co-ordinates (fractional) of hydrogen atoms used for final structure-factor calculations, each numbered according to the carbon atom to which it is attached

	x/*a*	*y*/*b*	*z*/*c*
H(2)	0·0140	0·1186	0·0520
H(3)	−0·1519	0·0672	−0·0712
H(4)	−0·2226	0·1785	−0·1863
H(5)	−0·1166	0·3304	−0·1894
H(6)	0·0518	0·3776	−0·0667
H(8)	0·5602	0·4116	0·1087
H(9)	0·7621	0·3828	0·1097
H(10)	0·8433	0·2273	0·1193
H(11)	0·7620	0·0919	0·1725
H(12)	0·5487	0·1120	0·1746
H(14)	0·5903	0·2069	0·3012
H(15)	0·6370	0·2304	0·4515
H(16)	0·5555	0·3652	0·4973
H(17)	0·4014	0·4670	0·4010
H(18)	0·3389	0·4398	0·2541
H(20)	0·2005	0·2530	0·2631
H(21)	0·1279	0·3557	0·3548
H(22)	−0·0190	0·4750	0·2992
H(23)	−0·0915	0·5104	0·1538
H(24)	−0·0098	0·4243	0·0612

TABLE 3

Components U_{ij} ($\times 10^3$) of thermal vibration tensors and their estimated standard deviations (in Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	53·4(6)	55·5(7)	31·9(5)	3·5(6)	18·6(5)	7·5(5)
I(2)	68·4(7)	28·7(5)	50·9(7)	1·2(5)	19·6(6)	4·1(5)
I(3)	56·8(7)	42·1(6)	47·8(5)	−0·9(6)	20·4(5)	−8·4(5)
I(4)	80·8(9)	40·0(6)	50·0(7)	0·7(5)	26·6(6)	16·2(5)
P(1)	31(2)	28(2)	26(2)	1(2)	10(2)	5(2)
P(2)	32(2)	27(2)	21(2)	2(2)	6(2)	4(1)
B(1)	36(9)	38(9)	24(8)	4(8)	7(7)	−8(7)
B(2)	40(10)	20(8)	35(9)	−9(7)	10(8)	−1(7)
C(1)	31(8)	28(7)	36(8)	−1(7)	−3(7)	−11(7)
C(2)	53(12)	62(13)	85(15)	3(10)	37(11)	−2(11)
C(3)	51(12)	76(15)	85(16)	−23(12)	17(11)	−14(13)
C(4)	33(10)	83(15)	64(13)	3(10)	0(10)	−13(12)
C(5)	53(12)	91(16)	39(10)	23(11)	8(9)	−17(10)
C(6)	50(11)	61(11)	36(9)	18(9)	13(8)	6(8)
C(7)	36(8)	37(8)	18(6)	4(7)	10(6)	7(6)
C(8)	36(9)	56(10)	41(9)	−21(8)	6(7)	3(9)
C(9)	32(10)	115(19)	62(13)	−11(11)	18(9)	17(12)
C(10)	38(11)	104(18)	53(11)	9(11)	14(9)	−10(12)
C(11)	30(9)	73(13)	59(11)	12(9)	9(9)	−25(10)
C(12)	41(9)	45(9)	35(8)	−3(8)	6(7)	−13(7)
C(13)	38(8)	32(8)	24(7)	−4(7)	10(6)	4(6)
C(14)	62(12)	59(11)	25(8)	26(9)	−1(14)	−3(8)
C(15)	61(12)	90(15)	35(9)	35(12)	17(9)	18(10)
C(16)	61(12)	52(11)	48(10)	−17(10)	24(9)	4(9)
C(17)	62(12)	44(10)	42(9)	5(9)	18(9)	−9(8)
C(18)	60(11)	38(9)	20(7)	9(8)	8(7)	8(7)
C(19)	31(8)	31(7)	31(8)	−1(6)	12(6)	−1(6)
C(20)	54(11)	50(10)	41(10)	13(8)	19(9)	11(8)
C(21)	77(14)	85(15)	35(10)	15(12)	27(10)	18(10)
C(22)	60(12)	61(12)	59(12)	13(10)	40(10)	−4(10)
C(23)	43(10)	59(11)	51(10)	12(8)	31(9)	6(9)
C(24)	66(12)	48(10)	40(9)	4(10)	24(9)	6(8)

TABLE 4

Bond lengths (Å) with estimated standard deviations in parentheses

B–P		C–C	
B(1)–P(1)	2·01(2)	C(4)–C(5)	1·34(3)
B(1)–P(2)	2·01(2)	C(5)–C(6)	1·38(2)
B(2)–P(1)	2·02(2)	C(6)–C(1)	1·41(2)
B(2)–P(2)	1·94(2)	C(7)–C(8)	1·41(2)
		C(8)–C(9)	1·39(3)
B–I		C(9)–C(10)	1·38(3)
B(1)–I(3)	2·22(2)	C(10)–C(11)	1·38(3)
B(1)–I(4)	2·17(2)	C(11)–C(12)	1·44(3)
B(2)–I(1)	2·17(2)	C(12)–C(7)	1·39(2)
B(2)–I(2)	2·28(2)	C(13)–C(14)	1·39(2)
		C(14)–C(15)	1·38(3)
P–C		C(15)–C(16)	1·36(3)
P(1)–C(1)	1·80(2)	C(16)–C(17)	1·35(2)
P(1)–C(19)	1·83(2)	C(17)–C(18)	1·36(2)
P(2)–C(7)	1·81(2)	C(18)–C(13)	1·42(2)
P(2)–C(13)	1·78(2)	C(19)–C(20)	1·33(2)
		C(20)–C(21)	1·41(3)
C–C		C(21)–C(22)	1·37(3)
C(1)–C(2)	1·39(3)	C(22)–C(23)	1·33(3)
C(2)–C(3)	1·41(3)	C(23)–C(24)	1·38(3)
C(3)–C(4)	1·35(3)	C(24)–C(19)	1·40(2)

This suggests strongly that there is a rigid-body oscillation of the molecule. Ideally all atoms in the molecule should be analysed in this way but in this structure analysis the estimated standard deviations of the U_{ij} components for atoms other than iodine are too large for the orientations of the ellipsoids derived from them to be reliable. For this reason the ellipsoids of the other atoms have not been included in Table 6. The vibration amplitudes corresponding to the parameters in Table 3 lie within the ranges 0·14—0·19 Å for phosphorus, 0·13—0·22 Å for boron, and 0·12—0·35 Å for carbon.

An approximate estimate of the size of the rotational

TABLE 5

Bond angles (°) with estimated standard deviations in parentheses

P(1)–B(1)–P(2)	87·2(7)	B(1)–P(1)–B(2)	86·8(7)
P(1)–B(2)–P(2)	89·1(7)	B(1)–P(2)–B(2)	89·0(7)
I(3)–B(1)–I(4)	109·1(8)	C(1)–P(1)–C(19)	103·8(8)
I(1)–B(2)–I(2)	106·7(7)	C(7)–P(2)–C(13)	104·0(7)
P(1)–B(1)–I(3)	106·9(7)	C(1)–C(2)–C(3)	118(2)
P(1)–B(1)–I(4)	123·0(11)	C(2)–C(3)–C(4)	121(2)
P(2)–B(1)–I(3)	109·5(10)	C(3)–C(4)–C(5)	120(2)
P(2)–B(1)–I(4)	119·1(7)	C(4)–C(5)–C(6)	122(2)
P(1)–B(2)–I(1)	114·8(7)	C(5)–C(6)–C(1)	118(2)
P(1)–B(2)–I(2)	112·6(9)	C(6)–C(1)–C(2)	121(1)
P(2)–B(2)–I(1)	112·0(10)	C(7)–C(8)–C(9)	118(2)
P(2)–B(2)–I(2)	121·3(8)	C(8)–C(9)–C(10)	122(2)
		C(9)–C(10)–C(11)	120(2)
B(1)–P(1)–C(1)	116·2(7)	C(10)–C(11)–C(12)	121(2)
B(1)–P(1)–C(19)	117·9(8)	C(11)–C(12)–C(7)	117(2)
B(2)–P(1)–C(1)	119·8(8)	C(12)–C(7)–C(8)	122(2)
B(2)–P(1)–C(19)	112·7(7)	C(13)–C(14)–C(15)	120(2)
B(1)–P(2)–C(7)	119·3(8)	C(14)–C(15)–C(16)	121(2)
B(1)–P(2)–C(13)	108·9(8)	C(15)–C(16)–C(17)	121(2)
B(2)–P(2)–C(7)	116·7(8)	C(16)–C(17)–C(18)	122(2)
B(2)–P(2)–C(13)	119·2(8)	C(17)–C(18)–C(13)	118(1)
		C(18)–C(13)–C(14)	120(1)
P(1)–C(1)–C(2)	119(1)	C(19)–C(20)–C(21)	119(2)
P(1)–C(1)–C(6)	120(1)	C(20)–C(21)–C(22)	121(2)
P(1)–C(19)–C(20)	122(1)	C(21)–C(22)–C(23)	120(2)
P(1)–C(19)–C(24)	118(1)	C(22)–C(23)–C(24)	120(2)
P(2)–C(7)–C(8)	118(1)	C(23)–C(24)–C(19)	120(2)
P(2)–C(7)–C(12)	120(1)	C(24)–C(19)–C(20)	120(2)
P(2)–C(13)–C(14)	117(1)		
P(2)–C(13)–C(18)	124(1)		

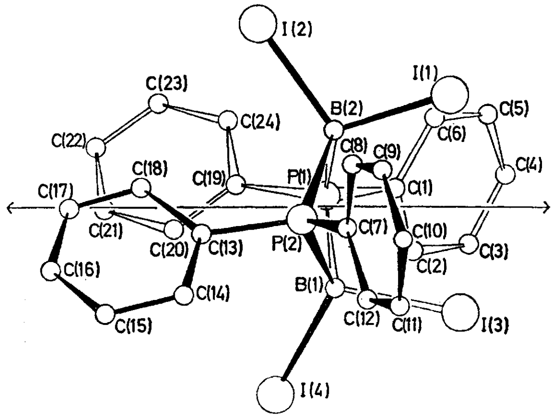

FIGURE 1 Molecular shape and labelling of the atoms. The arrow is the axis of approximate two-fold symmetry

TABLE 6

Root-mean-square amplitudes (Å) of thermal vibration of the iodine atoms along the principal axes of their vibration ellipsoids. The direction of each principal axis is specified by the angles which it makes with the crystallographic axes *b* and *c* and a third axis *a′* perpendicular to these two

		a′	*b*	*c*			*a′*	*b*	*c*
I(1)	0·243	60°	32°	80°	I(3)	0·239	4°	92°	93°
	0·228	30	118	101		0·231	89	127	37
	0·167	95	76	165		0·188	93	143	127
I(2)	0·266	20	90	110	I(4)	0·285	8	92	97
	0·227	71	80	22		0·248	83	51	40
	0·167	93	10	100		0·162	87	141	51

oscillation of the molecule may however be obtained from the vibrations of the iodine atoms, as follows. The mean-square amplitude of vibration U in tangential directions is given by $U = T + r^2\omega$, where r is the distance of the atom from the molecular centre, and T and ω are respectively the mean-square amplitudes of the translational and rotational vibrations of the molecule as a whole. In a radial direction clearly $U = T$, so that T can be estimated from the minimum vibration amplitudes. Taking a mean for atoms I(1), I(2), and I(4) gave $T = 0{\cdot}165^2$ Å^2. ω Could then be calculated for the two tangential vibrations of each iodine atom; six of the eight values obtained lay within the range 0·0027—0·0037 radian^2, the other two being 0·0021 and 0·0047 radian^2. The mean was 0·0032 radian^2, equivalent to a root-mean-square amplitude of 3·2°. The resulting correction to the distance r is +0·010 Å for I(1) and I(3) and +0·011 Å for I(2) and I(4). If it is assumed that the boron atoms are experiencing the same angular oscillations, all the B–I bond lengths are increased by 0·007 Å. The corrections to the other bond lengths are likely to be of similar size or less. In any case the validity of applying them is questionable since the ellipsoids have not been analysed.

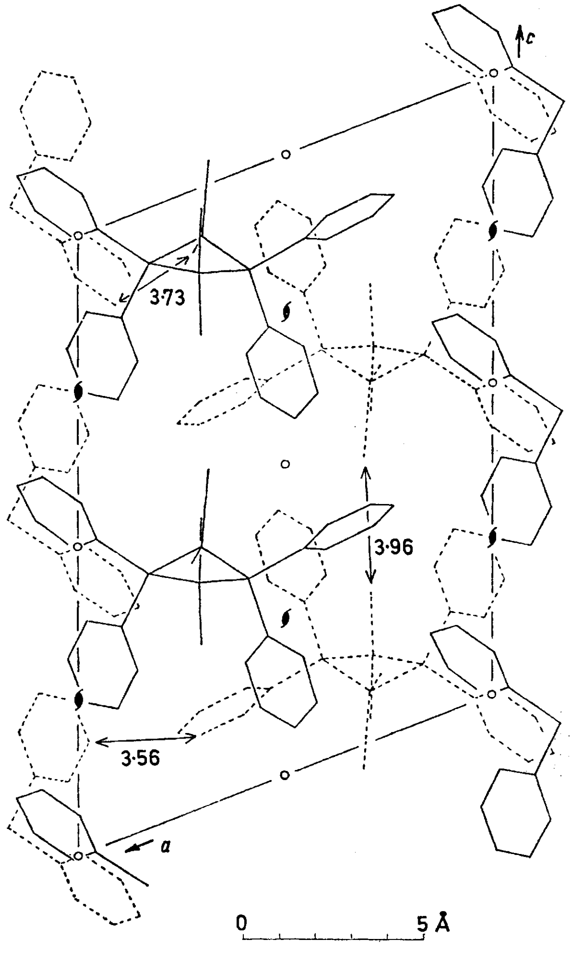

FIGURE 2 The crystal structure projected on (010). Molecules whose centres are near $y/b = \frac{1}{4}$ are shown by broken lines and those with centres near $y/b = \frac{3}{4}$ by full lines. Some of the shortest intermolecular distances are marked (in Å)

A projection of the structure on (010) is shown in Figure 2.

DISCUSSION

Ring Shape and Molecular Symmetry.—The cyclodiborataphosphoniane ring is non-planar. The dihedral angle between the two halves of the ring which meet in the P · · · P line is 29·8° (for the two halves meeting in the B · · · B line the angle is slightly different, 29·7°, because the B–P bonds are not all of equal length but the difference is not significant). The symmetry of the ring is very close to *mm*2, there being only slight differences between the dihedral angles of the ring bonds: B(1)–P(2) 21·2, P(2)–B(2) 21·1, B(2)–P(1) 21·1, and P(1)–B(1) 20·3°.

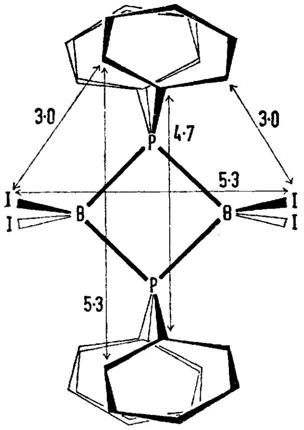

FIGURE 3 Interatomic distances (in Å) in a hypothetical $(Ph_2PBI_2)_2$ molecule with the ideal symmetry *mmm*

Although the four-membered ring in dimeric dichloro(dimethylamino)borane is planar,[4] non-planar rings are not uncommon for cyclobutane derivatives. In these molecules the bending of the ring is slightly less than in the present compound, *e.g.* the dihedral angles are 20° for C_4H_8 [9] and C_4F_8,[10] and 22° for C_4Cl_8.[11] It has been suggested that in C_4F_8 and C_4Cl_8 the ring is bent so as to allow greater clearance between the exocyclic atoms [10,11] and it seems probable that the diborataphosphoniane ring is bent for the same reason. If the diborataphosphoniane molecule had a planar ring and the full molecular symmetry *mmm* the distances between exocyclic atoms would be as shown in Figure 3. The pairs of iodine atoms and of phenyl groups are widely separated while the iodine–carbon contacts (3·0 Å) are far too close. These close contacts cannot be avoided by twisting the phenyl groups about the P–C bonds unless the twist is so great that the phenyl groups themselves interfere. The packing is inefficient as there is empty space over the centre of the ring but close contact above and below the periphery. By having the ring bent there is a simultaneous movement together of iodine atoms I(1) and I(3) to fill the central space on one side of the ring and of the phenyl groups (III) and (IV) to fill the space on the other side (Figure 1), while the iodine–carbon contacts are lengthened to 3·64 Å or more. Even so there is still some overcrowding in the molecule. There is one abnormally short contact between phenyl rings (III) and (IV), *viz.* C(18) · · · C(20) 3·23 Å, although other contacts between the carbon atoms of these rings are 3·69 Å or more. The I(1) · · · I(3) distance is only 3·89 Å. Although van der Waals distances between iodine atoms do vary over a considerable range (*e.g.* 3·98 Å in iodoform,[12] 4·30 Å in SnI_4 [13]) this is unusually short. Each of the four iodine atoms makes three I · · · C contacts in the range 3·64—3·80 Å, again close for a van der Waals contact between iodine and carbon, although the iodine atoms do tend to lie in regions between the phenyl groups where they can avoid the hydrogen atoms. If, as suggested, the diborataphosphoniane ring is bent for steric reasons, $[(Ph_2P)BBr_2]_2$, although isomorphous [1] with $[(Ph_2P)BI_2]_2$, might be expected to possess a more nearly planar diborataphosphoniane ring as bromine atoms are smaller than iodine. On the other hand the dipole moment [3] of $[(Et_2P)BBr_2]_2$ suggests that in this bromo-derivative the ring is again non-planar.

The phenyl groups are oriented in such a way that the symmetry of the molecule as a whole is approximately 2, the diad axis being the perpendicular bisector of the P · · · P and B · · · B lines (Figure 1). The degree of attainment of this symmetry is illustrated by the stereogram in Figure 4. The directions plotted are: the perpendicular bisector of P(1) · · · P(2) and B(1) · · · B(2), *i.e.* the diad axis of the diborataphosphoniane ring [pole (A)]; the bisector of the angle between the normals to the phenyl rings (I) and (II), *i.e.* the diad axis relating these rings [pole (B)]; the corresponding diad axis for rings (III) and (IV) [pole (C)]; and the bisector of the angle between the lines I(1) · · · I(2) and I(3) · · · I(4), *i.e.* the diad axis relating I(1) and I(2) with I(3) and I(4) [pole (D)]. The angular spread of these four poles gives some impression of the departure of various parts of the molecule from ideal symmetry. Poles (B) and (D) are 4°, and pole (C) as much as 14°, away from pole (A), the diad axis of the

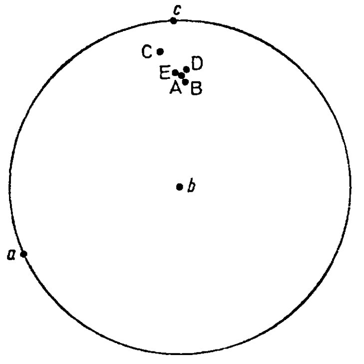

FIGURE 4

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central ring. The two-fold symmetry of the molecule is therefore not perfect although the deviations from it are small. The various poles are close to the lattice direction [012] [pole (E)]. This special alignment of the molecular symmetry axis is probably responsible for the occurrence of twinned crystals.

Bond Lengths and Angles.—Three of the B–P bonds are equal in length within experimental error, mean 2·01(1) Å, but the fourth, B(2)–P(2), is significantly shorter. The value 2·01 Å is significantly greater than the B–P bond length found[14] in the trimeric compound $[(Me_2P)BH_2]_3$ (1·94 Å). To account for the high stability of $[(Me_2P)BH_2]_3$ and $[(CF_3)_2PBH_2]_3$ Burg and co-workers[15,16] suggested that, in addition to P→B σ-bonding, there is B→P π-bonding resulting from the B–H bonding electrons entering hybrid orbitals involving 3*d* (and perhaps partly 4*s*) states of the adjacent phosphorus atoms. It may be that the B–P bonds in $[(Ph_2P)BI_2]_2$ are longer than those in $[(Me_2P)BH_2]_3$ because the inductive effect of the electronegative iodine atoms will reduce such donation of electrons to phosphorus orbitals and so reduce the B→P π-bonding. Alternatively the lengthening might be ascribed to a weakness of the B–P bonds caused by the lack of alignment of sp^3 atomic orbitals along the bond directions in a four-membered ring. Several cyclobutane derivatives[9–11,17] exhibit abnormally long C–C bonds (1·56—1·60 Å) which may be accounted for in this way. An even longer B–P bond length (2·08 ± 0·05 Å) has been quoted for the tetramer $[(Me_2P)BH_2]_4$,[18] but its reliability is open to question because it was obtained from an incomplete refinement, final *R* 0·18.

The mean length of the B–I bonds is 2·21(1) Å or, if the atomic vibration correction is applied, 2·22(1) Å. Previous measurements of the B–I length are 2·10 (±0·04) in BI_3,[19] 2·17 in iododecaborane,[20] 2·20 (±0·03) in iodopentaborane,[21] and 2·16 and 2·2 Å in two isomers of the carborane $C_2B_{10}H_{12}I$,[22] but none of these compounds is strictly comparable with the present structure as regards chemical-bond type. One would expect the bond to be shorter in BI_3 because of π-bonding but nevertheless 2·21—2·22 Å is long for a single covalent bond. Taking the covalent radius of boron as 0·80—0·88 Å (ref. 23) and applying the Schomaker–Stevenson formula for bond length,[24] gives 2·07—2·15 Å. Carbon–iodine bonds involving tetrahedrally co-ordinated carbon are also longer than expected (obs. 2·14,[25] calc. 2·09 Å). The dimer $[(Me_2N)BCl_2]_2$ similarly contains unusually long B–Cl bonds.[4]

The mean P–C length [1·81(1) Å] is similar to that found in phenylphosphazenes[26] and in $[(Me_2P)BH_2]_3$ (1·84 Å).[14] The mean C–C length is 1·38 Å (with σ 0·03 Å calculated from the deviations from the mean).

The tetrahedral co-ordination of the phosphorus and boron atoms is highly distorted because of the small size of the diborataphosphoniane ring and its lack of planarity. The P–B–P angles average 88·2(5)° and the B–P–B angles, which differ from each other with a 95% degree of confidence, average 87·9(5)°. The difference between the I–B–I angles [mean 107·9(5)°] is also significant at the 95% confidence level. The mean C–P–C angle is 103·9(5)°. Similarly small values have been found for the cyclic trimers $[(Ph_2P)BH_2]_3$ (103·0°)[27] and $[(Me_2P)BH_2]_3$ (100·4°).[14] In compensation for these small angles both the B–P–C (with one exception) and the P–B–I angles are larger than the tetrahedral value. Neither the individual C–C–C nor the P–C–C (except two) angles differ significantly from the ideal 120°.

Intermolecular Distances.—The shortest intermolecular distances up to 4 Å are: CH · · · CH 3·56, CH · · · I 3·73 Å, and I · · · I 3·96 Å (see Figure 2). Like the intramolecular non-bonded distances, these are somewhat short for van der Waals approaches.

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