Molecular Structure of Cycloborataphosphonianes. Part II.[1] Crystal Structure of 1,1,3,3,5,5-Hexaphenylcyclotriborataphosphoniane $[(Ph_2P)BH_2]_3$

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The title compound gives two crystalline modifications: α, m.p. 161 °C, triclinic, $a = 13{\cdot}96$, $b = 10{\cdot}27$, $c = 12{\cdot}54$ Å (all $\pm 0{\cdot}04$ Å), $\alpha = 108{\cdot}2$, $\beta = 96{\cdot}8$, $\gamma = 97{\cdot}7°$ (all $\pm 0{\cdot}2°$), space group $P\bar{1}$, $Z = 2$; and β, m.p. 179 °C, monoclinic, $a = 20{\cdot}23 \pm 0{\cdot}06$, $b = 9{\cdot}71 \pm 0{\cdot}02$, $c = 18{\cdot}65 \pm 0{\cdot}09$ Å, $\beta = 113{\cdot}9° \pm 0{\cdot}4°$, space group Ic or $I2/c$, $Z = 4$. The structure of the α-form was determined by the heavy-atom technique from X-ray diffractometer intensity data and refined by least-squares methods to R 0·075 for 5940 independent reflexions. The six-membered boron–phosphorus ring has the chair conformation with a close approach to symmetry C_s (m), the torsion angles in the ring lying in the range 40—55°. Mean bond lengths are: B–P 1·948, B–H 1·11, P–C 1·823 Å; and bond angles: B–P–B 114·3, P–B–P 112·6, H–B–H 112, and C–P–C 103·1°. The molecular dimensions differ only slightly from those of $[(Me_2P)BH_2]_3$ and $[(Me_2N)BH_2]_3$; they provide no evidence for B→P π bonding and are compatible with a simple cyclic structure based on P→B σ bonds.

Both phosphinoboranes R_2PBX_2 and aminoboranes R_2NBX_2 form cyclic trimers such as (I) and (II) in which the boron atoms achieve co-ordination saturation by the formation of dative P→B or N→B bonds. The cyclotriborataphosphonianes $[(R_2P)BH_2]_3$ are surprisingly stable compounds. For example, $[(Me_2P)BH_2]_3$ (I; R = Me) has great resistance to hydrolysis, which is exceptional for a compound containing B–H bonds,[2] and it is more stable than the analogous $[(MeHN)BH_2]_3$ (II; R^1 = Me, R^2 = H)[3] although one would expect the P→B to be weaker than the N→B dative bond. More surprising still is the stability of $[(CF_3)_2PBH_2]_3$ (I; R = CF_3) since phosphines substituted with CF_3 groups are very weak bases.[4] To account for this stability Burg and coworkers[2,4] suggested that the B–H bonding electrons are partially assigned to phosphorus $3d$ orbitals forming weak B→P π bonds, so tending to compensate the P^+ formal charges resulting from the P→B σ bonding and make the B–H groups more inert to protonic reagents.

Hamilton[5] concluded that the molecular geometry of $[(Me_2P)BH_2]_3$, found from crystal structure analysis, is consistent with some contribution to the bonding from Burg's B→P π bonds, but the fact that the positions of the hydrogen atoms in the BH_2 groups were not determined with any accuracy (and the final R, 0·169, is by present-day standards high) limits the conclusions which can be drawn from this work. As this has remained as the sole cyclotriborataphosphoniane whose molecular structure is known in detail and as the

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[1] Part I, G. J. Bullen and P. R. Mallinson, *J.C.S. Dalton*, 1972, 1143.

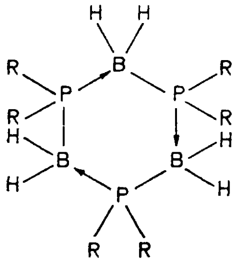
[2] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

[3] T. C. Bissot and R. W. Parry, *J. Amer. Chem. Soc.*, 1955, **77**, 3481.

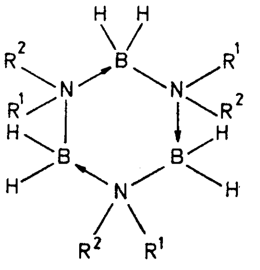
[4] A. B. Burg and G. Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198.

[5] W. C. Hamilton, *Acta Cryst.*, 1955, **8**, 199.

exceptional stability of this type of compound has still not been adequately explained we decided to examine the crystal structure of $[(Ph_2P)BH_2]_3$ (I; R = Ph),



(I)



(II)

which is prepared by pyrolysis of the adduct Ph_2PH,BH_3.[6] From the crystallographic point of view this compound has the added interest that it forms two crystalline modifications which we designate α (m.p. 161 °C) and β (m.p. 179 °C). We now report the crystal data for the two forms, and the complete crystal structure of the α form.

EXPERIMENTAL

Crystal Data.—(i) *α-Form*. $C_{36}H_{36}B_3P_3$, $M = 594{\cdot}04$, m.p. 161 °C, Triclinic, $a = 13{\cdot}96$, $b = 10{\cdot}27$, $c = 12{\cdot}54$ Å (all $\pm 0{\cdot}04$ Å), $\alpha = 108{\cdot}2$, $\beta = 96{\cdot}8$, $\gamma = 97{\cdot}7°$ (all $\pm 0{\cdot}2°$), $U = 1668$ Å^3, $D_m = 1{\cdot}18$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1{\cdot}18$, $F(000) = 624$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) $= 2{\cdot}0$ cm^{-1}. Space group $P\bar{1}$ (No. 2).

(ii) *β-Form*. M.p. 179 °C, Monoclinic, $a = 20{\cdot}23 \pm 0{\cdot}06$, $b = 9{\cdot}71 \pm 0{\cdot}02$, $c = 18{\cdot}65 \pm 0{\cdot}09$ Å, $\beta = 113{\cdot}9° \pm 0{\cdot}4°$, $U = 3349$ Å^3, $Z = 4$ (D_m assumed the same as for α), $D_c = 1{\cdot}18$. Mo-K_α radiation. Space group Ic (No. 9) or $I2/c$ (No. 15), from systematic absences: hkl present for $h + k + l$ even, $h0l$ present for h and l even.

The α-modification was obtained by crystallisation from various combinations of solvents: diethyl ether–ethanol, acetone–ethanol, diethyl ether–light petroleum, and benzene–light petroleum, at room temperature. The most prominent forms exhibited are {100}, {010}, and {101}. The β-modification was first produced as opaque white, anhedral crystals when the compound was dried *in vacuo* at 140° at the time of preparation.[7] Single crystals of β were obtained by heating single crystals of α in contact with fragments of the β-form to between 161 and 179 °C, the m.p.'s of the two forms.

A single crystal of the α-form with dimensions $0{\cdot}4 \times 0{\cdot}3 \times 1$ mm was used for the measurement of 9763 independent *X*-ray reflexions at room temperature in 17 layers $hk0$—16 on a Philips PAILRED diffractometer with monochromatised Mo-K_α radiation. These comprised all possible reflexions with $\sin\theta/\lambda \leqslant 0{\cdot}72$ Å^{-1}. 5940 Reflexions gave statistically significant intensities, with $I > 2\sigma(I)$, and the remaining 3823 were considered unobserved. Intensities were corrected for Lorentz and polarisation effects but not for absorption. The unit-cell constants were determined from Weissenberg and precession photographs.

Least-squares refinement was carried out on the University of Essex I.C.L. 1909 computer, the I.B.M. 1130 computer at the A.R.C. Unit of Structural Chemistry (University College London), and the I.B.M. 360/65 computer at University College Computer Centre. Atomic scattering factors were taken from ref. 8 for boron, carbon, and phosphorus, and from ref. 9 for hydrogen. The principal programmes used are listed in ref. 10.

Structure Determination.—The space group was found to be the centrosymmetric $P\bar{1}$ by analysis of the *X*-ray intensity distribution.[11] The structure was solved by the heavy-atom method, after the three phosphorus atoms in the asymmetric unit had been located from the Patterson function. Structure factors calculated from the phosphorus positions for all reflexions with $|F_o| > 20$ (on absolute scale), and with overall scale and temperature factors estimated by Wilson plot,[12] gave R 0·51 for 1008 reflexions. This rather high value is attributable to phosphorus contributing only 15% of the total scattering power. The first Fourier synthesis, phased on the heavy atoms and containing 341 reflexions having $|F_o| > 25$ and $|F_c| > 0{\cdot}5|F_o|$, revealed the boron atomic positions only. These were used to estimate the positions of the six carbon atoms attached to phosphorus, assuming a tetrahedral co-ordination for each phosphorus atom. A further six carbon atoms, at the outer ends of the phenyl groups, were placed by assuming them to be collinear with the P–C bonds. A series of Fourier syntheses and difference syntheses revealed the remaining 24 carbon atom positions. 1177 Reflexions with $|F_o| > 15$ and $|F_c| > 0{\cdot}5|F_o|$ contributed to the last of these Fourier maps.

Five cycles of block-diagonal isotropic least-squares refinement, with use of reflexions for which $|F_c| > 0{\cdot}33|F_o|$ and unit weights, brought R to 0·144 for the 5940 observed reflexions. For the anisotropic refinement the positions of the phenyl hydrogen atoms were estimated from the molecular geometry and included in the calculations, but not refined. The hydrogen atoms of the BH_2 groups were located in a three-dimensional difference synthesis calculated after one cycle of anisotropic refinement of the boron, carbon, and phosphorus atoms. After this refinement C(14), C(15), C(17), and C(18) (for atom numbering see Figure 1) had high thermal vibration parameters (U_{jj} in the range 0·14—0·24 Å^2) suggesting that phenyl group (iii) might be disordered. This is in accord with the observation of diffuse scattering effects on the *X*-ray Laue photographs. The difference synthesis showed peaks corresponding to alternative positions of C(14), C(15), C(17), and C(18) equivalent to a new orientation of the phenyl group produced by rotation about the P(2)–C(13) bond.

The new phenyl group parameters [co-ordinates, isotropic temperature factors, and occupancies of the atoms, design-

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[8] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 202—206.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[10] X-RAY ARC, I.B.M. 1130 Program System for Crystallography, programmes by B. L. Vickery, D. Bright, P. R. Mallinson, A. Zalkin, M. E. Pippy, and F. R. Ahmed; Full-matrix least-squares program NUCLS by R. J. Doedens and J. A. Ibers; Interatomic distances and errors ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy; Programme XANADU (for librational analysis) by P. Roberts and G. M. Sheldrick.

[11] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

[12] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

ated C(14′), C(15′), C(17′), and C(18′)] were refined in two cycles of full-matrix least squares. The hydrogen positions for the new orientation of the disordered phenyl group were estimated at this stage from the molecular geometry. Seven further cycles of full-matrix refinement were carried out. Positional parameters of all atoms including the hydrogens of the BH_2 groups, together with the isotropic temperature factors of C(13)—(18), C(14′), C(15′), C(17′), and C(18′) and the hydrogen atoms, plus the site occupancies of the disordered atoms, were varied in alternate cycles between the anisotropic temperature factor refinement of boron, phosphorus, and carbon atoms of the ordered phenyl groups. The 5940 observed reflexions used in the refinement were assigned weights $w = (2{\cdot}1 - 0{\cdot}2|F_o| + 0{\cdot}008|F_o|^2)^{-1}$. These gave similar average values of $w\Delta^2$ (where $\Delta = |F_o| - |F_c|$) for ranges of increasing $|F_o|$ or $\sin\theta/\lambda$. Oscillations of the parameters were damped by halving the shifts. In the last five cycles of least squares $\Sigma w\Delta^2$ was reduced from 6740 to 6560 (on a relative scale) with a change of only 20 in the final cycle. At this point all co-ordinate shifts were $<0{\cdot}46\sigma$ and temperature factor shifts $<0{\cdot}54\sigma$, except for the disordered atoms, whose shifts were $<1{\cdot}9\sigma$ in the co-ordinates, $<0{\cdot}3\sigma$ in the isotropic temperature factors, and $<0{\cdot}9\sigma$ in the site occupancies. Since the change in $\Sigma w\Delta^2$ was small and only seven atoms out of a total of 52 had parameter shifts $>0{\cdot}5\sigma$, the refinement was concluded at this stage. A difference synthesis computed from the final structure factors for the observed reflexions weighted according to the least-squares weights showed no peaks or holes of magnitude $>0{\cdot}5$ eÅ^{-3}. The final R for the 5940 observed reflexions was 0·075 and R' 0·090 $[R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and site occupancies (for the disordered atoms) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	Occupancy
P(1)	4278(1)	887(1)	2736(1)	
P(2)	1953(1)	880(1)	2846(1)	
P(3)	2739(1)	1031(1)	604(1)	
B(1)	3283(3)	1274(4)	3698(3)	
B(2)	1820(3)	1653(5)	1617(4)	
B(3)	4091(3)	1434(5)	1373(3)	
H(1a) *	3340(34)	2452(49)	4065(39)	
H(1e)	3352(30)	739(44)	4329(36)	
H(2a)	2068(37)	2749(56)	2008(43)	
H(2e)	1020(34)	1417(48)	1132(39)	
H(3a)	4257(34)	2643(50)	1692(40)	
H(3e)	4615(31)	1051(44)	876(36)	
Phenyl group (i)				
C(1)	5444(2)	1958(4)	3584(3)	
C(2)	5527(3)	3408(4)	3947(4)	
C(3)	6414(4)	4244(5)	4577(4)	
C(4)	7197(3)	3657(6)	4856(4)	
C(5)	7122(3)	2235(6)	4502(5)	
C(6)	6246(3)	1379(5)	3865(4)	
Phenyl group (ii)				
C(7)	4488(2)	−893(3)	2458(3)	
C(8)	4628(3)	−1686(4)	1384(3)	
C(9)	4768(4)	−3048(5)	1194(4)	
C(10)	4771(4)	−3634(5)	2039(5)	
C(11)	4652(4)	−2843(5)	3112(5)	
C(12)	4506(3)	−1485(4)	3316(3)	
Phenyl group (iii)				
C(13)	1188(3)	1675(4)	3860(3)	
C(14)	361(10)	2100(15)	3502(11)	0·40(2)
C(15)	−270(11)	2603(17)	4255(12)	0·40(2)
C(16)	22(5)	2784(7)	5401(5)	
C(17)	756(14)	2316(25)	5706(13)	0·37(4)
C(18)	1361(11)	1709(18)	4956(11)	0·42(3)
C(14′)	807(9)	2887(14)	3818(10)	0·59(3)
C(15′)	216(11)	3481(18)	4622(13)	0·56(3)
C(17′)	454(13)	1739(23)	5528(11)	0·62(4)
C(18′)	1023(11)	1105(17)	4719(10)	0·53(3)
Phenyl group (iv)				
C(19)	1391(3)	−951(4)	2340(3)	
C(20)	399(3)	−1342(6)	1832(4)	
C(21)	−40(4)	−2715(7)	1407(5)	
C(22)	501(5)	−3724(6)	1464(5)	
C(23)	1482(5)	−3361(5)	1979(6)	
C(24)	1920(3)	−1961(5)	2426(4)	
Phenyl group (v)				
C(25)	2714(2)	2012(4)	−388(3)	
C(26)	2809(3)	3457(4)	28(4)	
C(27)	2808(4)	4230(5)	−699(4)	
C(28)	2732(4)	3573(5)	−1849(5)	
C(29)	2647(4)	2147(5)	−2275(4)	
C(30)	2622(3)	1356(4)	−1559(3)	
Phenyl group (vi)				
C(31)	2345(2)	−752(3)	−330(3)	
C(32)	2997(3)	−1481(4)	−927(3)	
C(33)	2671(3)	−2793(4)	−1728(4)	
C(34)	1694(4)	−3400(4)	−1921(4)	
C(35)	1045(3)	−2702(5)	−1329(4)	
C(36)	1354(3)	−1382(4)	−542(3)	

* Hydrogen atoms are numbered according to the boron atom to which they are attached; a = axial, e = equatorial.

TABLE 2

Fractional co-ordinates ($\times 10^4$) assigned to hydrogen atoms of the phenyl groups, numbered according to the carbon atom to which they are attached

	x/*a*	*y*/*b*	*z*/*c*
H(2)	4909	3865	3739
H(3)	6477	5363	4848
H(4)	7876	4319	5348
H(5)	7742	1770	4712
H(6)	6185	259	3581
H(8)	4639	−1244	708
H(9)	4861	−3668	358
H(10)	4866	−4709	1860
H(11)	4676	−3276	3792
H(12)	4413	−874	4157
H(14) *	223	2135	2665
H(15) *	−819	3165	4044
H(16)	−405	3285	6025
H(17) *	846	2188	6543
H(18) *	1903	1153	5214
H(14′) *	956	3308	3163
H(15′) *	16	4496	4697
H(17′) *	302	1304	6183
H(18′) *	1292	159	4727
H(20)	−24	−550	1779
H(21)	−809	−3006	1025
H(22)	153	−4808	1104
H(23)	1900	−4169	2026
H(24)	2687	−1667	2842
H(26)	2892	3986	936
H(27)	2880	5350	−369
H(28)	2726	4170	−2421
H(29)	2610	1632	−3186
H(30)	2524	233	−1904
H(32)	3765	−1017	−761
H(33)	3184	−3330	−2204
H(34)	1438	−4439	−2531
H(35)	275	−3177	−1481
H(36)	839	−833	−87

* Site occupancy 0·5.

RESULTS

The final atomic co-ordinates, site-occupancy factors and thermal vibration parameters, with their estimated standard deviations, are listed in Tables 1—3. For the phenyl hydrogen atoms an isotropic temperature factor with B 5·0 Å^2, equivalent to $\overline{u^2}$ 0·063 Å^2, was used. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20679 (27 pp., 1 microfiche).* Bond lengths are listed in Table 4 and bond angles in Table 5. Standard deviations were calculated from the estimated standard deviations of the co-ordinates in Table 1, with allowance for correlation and for the errors in unit-cell dimensions. The thermal vibration parameters were analysed in terms of a rigid-body motion for the central part of the molecule comprising the boron–phosphorus ring and the carbon atoms directly bonded to phosphorus, by the method of Schomaker and Trueblood.[13] The analysis showed the motion to be almost entirely translational with a very small librational tensor. The resultant corrections to bond lengths were only 0·002—0·003 Å and they have therefore been disregarded. Inspection of the vibration parameters of the carbon atoms (Table 3) suggests that the phenyl groups are vibrating as rigid bodies but independently of the boron–phosphorus ring and of each other. Their motion was not analysed further since the carbon–carbon bond lengths have not been listed individually in Table 4.

TABLE 3

(a) Components U_{ij} of thermal vibration tensors (Å^2, $\times 10^3$), with estimated standard deviations

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	27·3(4)	33·8(4)	33·3(4)	−0·1(3)	4·4(3)	5·8(3)
P(2)	30·1(4)	45·7(5)	35·3(4)	2·0(3)	10·0(3)	6·1(4)
P(3)	31·7(4)	35·8(4)	35·7(4)	5·2(3)	7·8(3)	11·5(3)
B(1)	33(2)	44(2)	36(2)	1(1)	7(1)	1(2)
B(2)	44(2)	53(2)	47(2)	16(2)	16(2)	14(2)
B(3)	33(2)	46(2)	44(2)	1(2)	6(1)	18(2)
C(1)	35(2)	49(2)	38(2)	−3(1)	8(1)	3(1)
C(2)	51(2)	47(2)	63(2)	−6(2)	15(2)	−2(2)
C(3)	69(3)	59(3)	71(3)	−22(2)	17(2)	−17(2)
C(4)	47(2)	103(4)	71(3)	−21(3)	−1(2)	−7(3)
C(5)	41(2)	102(4)	78(3)	−5(2)	−12(2)	13(3)
C(6)	40(2)	67(3)	55(2)	1(2)	1(2)	13(2)
C(7)	33(2)	39(2)	39(2)	1(1)	4(1)	9(1)
C(8)	52(2)	46(2)	44(2)	9(2)	9(2)	7(2)
C(9)	78(3)	48(2)	65(3)	17(2)	12(2)	2(2)
C(10)	70(3)	42(2)	92(3)	6(2)	8(3)	18(2)
C(11)	75(3)	66(3)	88(3)	16(2)	20(3)	43(3)
C(12)	64(2)	55(2)	54(2)	12(2)	15(2)	22(2)
C(19)	41(2)	53(2)	42(2)	−9(2)	13(1)	7(2)
C(20)	48(2)	96(4)	58(2)	−20(2)	2(2)	24(2)
C(21)	79(4)	117(5)	64(3)	−53(3)	0(3)	17(3)
C(22)	120(5)	74(4)	68(3)	−52(3)	28(3)	−7(3)
C(23)	115(5)	50(3)	104(4)	−6(3)	41(4)	7(3)
C(24)	61(3)	51(2)	76(3)	−6(2)	20(2)	9(2)
C(25)	38(2)	44(2)	51(2)	8(1)	8(1)	21(2)
C(26)	61(2)	44(2)	63(2)	5(2)	2(2)	16(2)
C(27)	71(3)	46(2)	87(3)	0(2)	0(2)	32(2)
C(28)	74(3)	74(3)	85(3)	16(2)	15(3)	52(3)
C(29)	101(4)	74(3)	60(3)	31(3)	23(3)	36(2)
C(30)	79(3)	52(2)	51(2)	20(2)	17(2)	20(2)
C(31)	38(2)	41(2)	36(2)	1(1)	6(1)	15(1)
C(32)	48(2)	41(2)	50(2)	8(2)	9(2)	13(2)
C(33)	70(3)	41(2)	60(2)	14(2)	11(2)	10(2)
C(34)	76(3)	40(2)	74(3)	−1(2)	−1(2)	6(2)
C(35)	54(2)	59(3)	81(3)	−14(2)	−2(2)	16(2)
C(36)	43(2)	58(2)	54(2)	−4(2)	8(2)	15(2)

(b) Mean square amplitudes of isotropic vibration $\overline{u^2}$ (Å^2), with estimated standard deviations

	$10^3\overline{u^2}$		$10^3\overline{u^2}$
C(13)	49(1)	C(17′)	89(5)
C(14)	64(5)	C(18′)	70(4)
C(15)	75(6)	H(1a)	67(13)
C(16)	90(2)	H(1e)	56(12)
C(17)	61(6)	H(2a)	84(16)
C(18)	58(5)	H(2e)	68(13)
C(14′)	89(5)	H(3a)	72(14)
C(15′)	107(7)	H(3e)	55(12)

Figure 1 shows the shapes of molecules having alternative orientations of the disordered phenyl group. A projection of the structure viewed along the b axis is shown in Figure 2.

TABLE 4

Bond lengths (Å) with estimated standard deviations in parentheses

B(1)–P(1)	1·947(4)	B(1)–H(1a)	1·14(5)
B(1)–P(2)	1·953(5)	B(1)–H(1e)	1·10(4)
B(2)–P(2)	1·944(5)	B(2)–H(2a)	1·07(5)
B(2)–P(3)	1·940(4)	B(2)–H(2e)	1·16(5)
B(3)–P(3)	1·942(4)	B(3)–H(3a)	1·16(5)
B(3)–P(1)	1·959(4)	B(3)–H(3e)	1·05(4)
P(1)–C(1)	1·836(4)	P(2)–C(19)	1·816(5)
P(1)–C(7)	1·822(4)	P(3)–C(25)	1·830(4)
P(2)–C(13)	1·824(4)	P(3)–C(31)	1·807(4)

The C–C lengths are in the range 1·259(14)—1·430(12) for the disordered and 1·368(8)—1·404(5) for the other phenyl groups.

TABLE 5

Bond angles (°) with estimated standard deviations in parentheses

B(1)–P(1)–B(3)	114·8(2)	P(3)–C(31)–C(32)	120·8(3)
B(1)–P(2)–B(2)	114·3(2)	P(3)–C(31)–C(36)	120·2(3)
B(2)–P(3)–B(3)	113·7(2)		
		P(1)–B(1)–H(1a)	108(2)
P(1)–B(1)–P(2)	113·7(2)	P(1)–B(1)–H(1e)	110(2)
P(2)–B(2)–P(3)	109·8(2)	P(2)–B(1)–H(1a)	96(2)
P(3)–B(3)–P(1)	114·4(2)	P(2)–B(1)–H(1e)	113(2)
		P(2)–B(2)–H(2a)	106(3)
H(1a)–B(1)–H(1e)	115(3)	P(2)–B(2)–H(2e)	113(2)
H(2a)–B(2)–H(2e)	111(3)	P(3)–B(2)–H(2a)	105(3)
H(3a)–B(3)–H(3e)	109(3)	P(3)–B(2)–H(2e)	112(2)
		P(3)–B(3)–H(3a)	102(2)
C(1)–P(1)–C(7)	103·7(2)	P(3)–B(3)–H(3e)	117(2)
C(13)–P(2)–C(19)	102·9(2)	P(1)–B(3)–H(3a)	106(2)
C(25)–P(3)–C(31)	102·8(2)	P(1)–B(3)–H(3e)	107(2)
P(1)–C(1)–C(2)	118·3(3)	B(1)–P(1)–C(1)	106·7(2)
P(1)–C(1)–C(6)	122·5(3)	B(1)–P(1)–C(7)	111·0(2)
P(1)–C(7)–C(8)	120·6(3)	B(3)–P(1)–C(1)	105·2(2)
P(1)–C(7)–C(12)	120·5(3)	B(3)–P(1)–C(7)	114·2(2)
P(2)–C(13)–C(14)	120·6(6)	B(1)–P(2)–C(13)	106·6(2)
P(2)–C(13)–C(18)	120·9(5)	B(1)–P(2)–C(19)	113·9(2)
P(2)–C(13)–C(14′)	121·0(5)	B(2)–P(2)–C(13)	107·6(2)
P(2)–C(13)–C(18′)	118·1(5)	B(2)–P(2)–C(19)	110·6(2)
P(2)–C(19)–C(20)	119·1(4)	B(2)–P(3)–C(25)	107·2(2)
P(2)–C(19)–C(24)	121·5(3)	B(2)–P(3)–C(31)	112·7(2)
P(3)–C(25)–C(26)	119·8(3)	B(3)–P(3)–C(25)	105·7(2)
P(3)–C(25)–C(30)	121·7(3)	B(3)–P(3)–C(31)	113·7(2)

C–C–C angles are in the range 116·2(11)—124·8(9)° for the disordered and 118·4(4)—121·7(4)° for the other phenyl groups.

DISCUSSION

Bond Lengths and Bond Angles.—The molecular geometry of $[(Ph_2P)BH_2]_3$ is similar to that of $[(Me_2P)BH_2]_3$ [5] and $[(Me_2N)BH_2]_3$ (II; $R^1 = R^2 = Me$),[14] all

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[13] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

[14] L. M. Trefonas, F. S. Mathews, and W. N. Lipscomb, *Acta Cryst.*, 1961, **14**, 273.

having a central six-membered ring with the chair conformation. Mean bond lengths and angles in these three compounds are compared in Table 6. In making the comparison, it should be noted that in $[(Me_2N)BH_2]_3$ the hydrogen atoms were not located and in $[(Me_2P)BH_2]_3$ they were located only approximately, so that the accuracy of the H–B–H angle is not known and that of the B–H bond length is merely estimated from the spread of lengths obtained. The differences between $[(Ph_2P)BH_2]_3$ and $[(Me_2P)BH_2]_3$ are scarcely significant, with the possible exception of the angles B–P–B and H–B–H, both of which are nearer the tetrahedral value in the phenyl derivative. Hamilton[5] concluded that for the methyl derivative the large B–P–B angle indicates a contribution to the bonding from B$\rightarrow$P π bonds as postulated by Burg and co-workers.[2,4] As this should lead to C–P–C and H–B–H angles smaller than the tetrahedral value Hamilton explained the large observed H–B–H angles by adding in a contribution from the no-bond structure (III). It is doubtful whether the accuracy of the hydrogen-atom positions justified this. A comparison of the bond angles in $[(Ph_2P)BH_2]_3$ and $[(Me_2N)BH_2]_3$ leads to a different conclusion. There are no significant differences between the bond angles in these two molecules and this would seem to indicate no great difference between their bonding. Since π bonding analogous to the B$\rightarrow$P bonding proposed by Burg and co-workers cannot occur in $[(Me_2N)BH_2]_3$ because the nitrogen atom does not have suitable *d* orbitals available, we must conclude that if B$\rightarrow$P π bonding occurs at all in $[(Ph_2P)BH_2]_3$ it has no significant effect on the molecular geometry, the latter being very much what one would expect for structure (I). Indeed, the bond angles in the ring of $[(Ph_2P)BH_2]_3$, although larger than the tetrahedral value, are not greatly different from those found in cyclohexane derivatives (*e.g. trans*-1,2-cyclohexanedicarboxylic acid,[15,16] 110·0—112·6°).

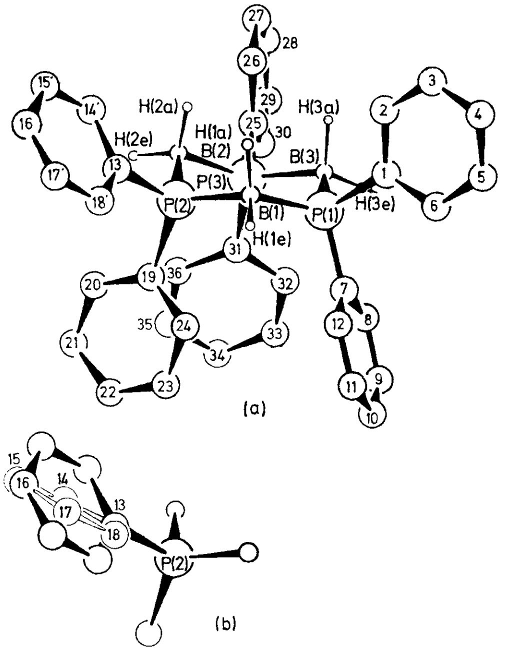


FIGURE 1 (a) Molecular shape and labelling of the atoms. Only one orientation of the disordered phenyl group is shown. Carbon atoms are labelled by numbers only. (b) Superposition of the alternative orientations of the disordered phenyl group

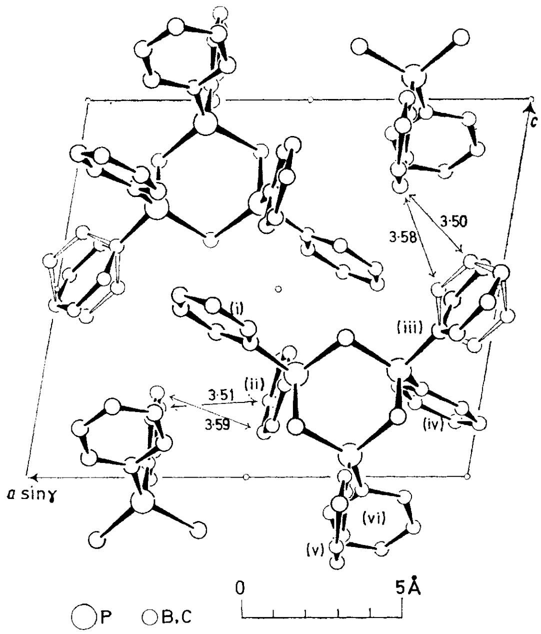


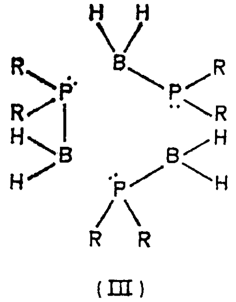
FIGURE 2 Projection of the crystal structure down the *b* axis, showing some of the shortest intermolecular distances (Å). Phenyl group numbers are given in parentheses

TABLE 6

Comparison of mean bond lengths (Å) and angles (°)

	$[(Ph_2P)BH_2]_3$ [a] (M = P)	$[(Me_2P)BH_2]_3$ [b] (M = P)	$[(Me_2N)BH_2]_3$ [c] (M = N)
B–P	1·948(2)	1·935(9)	
B–N			1·59(3)
B–H	1·11(2)	1·20(8)	*d*
B–M–B	114·3(1)	118(1)	113(1)
M–B–M	109·8—114·4	112·2(9)	114(2)
H–B–H	112(2)	119	*d*
C–M–C	103·1(1)	100·4(9)	104(2½)

[a] This work. [b] Ref. 5. [c] Ref. 14. [d] Not given.



(III)

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[15] E. Benedetti, P. Corradini, C. Pedone, and B. Post, *J. Amer. Chem. Soc.*, 1969, **91**, 4072.

[16] E. Benedetti, P. Corradini, and C. Pedone, *J. Amer. Chem. Soc.*, 1969, **91**, 4075.

The B–P bond length is also as expected for a single bond.

The mean P–C bond length (1·823 Å) is similar to that in $[(Me_2P)BH_2]_3$ (1·837 Å), the slight shortening possibly arising from the difference in size between trigonally and tetrahedrally co-ordinated carbon. In both cases the bond is longer than P–C bonds in analogous phosphazene molecules: $N_3P_3Ph_6$ 1·804,[17] and $N_4P_4Me_8$ 1·805 Å.[18] This is possibly attributable to slight differences in electronic structure arising from the different electronegativities of boron and nitrogen.

Molecular Shape.—The boron–phosphorus ring in $[(Ph_2P)BH_2]_3$ has the chair conformation with the torsion angles shown in Figure 3(a). There is a close approach to C_s (m) symmetry in the ring but failure to achieve the ideal C_{3v} ($3m$) symmetry. In this respect there is considerable similarity to the ring conformations in crystalline $[(Me_2P)BH_2]_3$ [5] and $[(Me_2N)BH_2]_3$,[14] since in both these methyl derivatives the molecules are situated on crystallographic mirror planes. The ring is more puckered in $[(Ph_2P)BH_2]_3$ than in $[(Me_2P)BH_2]_3$ [*cf.* torsion angles in Figures 3(a) and 3(b)]. In $[(Me_2N)BH_2]_3$ the torsion angles are −46, 50, and −50°. The mirror symmetry does not extend to the whole molecule of $[(Ph_2P)BH_2]_3$. Although phenyl group (i) lies almost in the pseudo-mirror plane of the ring, the mirror relationship fails between phenyl groups (iv) and (vi), and (iii) and (v). The orientation of the phenyl groups in axial positions is probably controlled largely by steric interactions between them, some of the inter-group distances being quite short, *e.g.* C(20) · · · C(36) 3·39 Å. The orientation of the phenyl groups in equatorial positions is probably influenced by the need to equalise contacts with the axial hydrogen atoms in the BH_2 groups, *e.g.* C(25) · · · H(2a) 3·13, and C(25) · · · H(3a) 3·02 Å. However, although phenyl groups (i) and (v) are symmetrically placed with respect to these axial hydrogen atoms (see Figure 1), both orientations of the disordered ring (iii) are far from symmetrical. In this case intermolecular contacts are probably the overriding factor (see next paragraph).

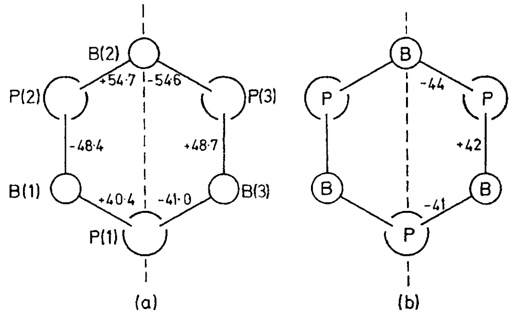

FIGURE 3 Torsion angles (°) in boron–phosphorus rings: (a) $[(Ph_2P)BH_2]_3$, and (b) $[(Me_2P)BH_2]_3$. Broken lines mark planes of mirror symmetry, approximate in (a) and exact in (b)

Intermolecular Distances.—The closest intermolecular contacts (disregarding hydrogen atoms) are between phenyl groups. Most of the C · · · C distances range from 3·50 Å upwards, some of the shortest being marked in Figure 2, but there are some exceptionally short contacts involving the disordered phenyl group (iii), *e.g.* C(15′)(x, y, z) · : · C(15′)$(-x, 1-y, 1-z)$ 3·13, and C(17′)(x, y, z) · · · C(18′)$(-x, -y, 1-z)$ 3·25 Å. These short distances result from contact between molecules across centres of symmetry and can be avoided if one or both of the molecules in contact adopts the alternative orientation of phenyl group (iii), then giving C(15′)(x, y, z) · · · C(15)$(-x, 1-y, 1-z)$ 3·81, and C(17′)(x, y, z) · · · C(18)$(-x, -y, 1-z)$ 3·90 Å. This may be the reason for the disorder. The C(14)(x, y, z) · · · C(35)$(-x, -y, -z)$ distance (3·43 Å) is also rather short for a van der Waals contact.

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[2/2846 *Received*, 18*th December*, 1972]

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[17] F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Cryst.*, 1969, **B25**, 316.

[18] M. Dougill, *J. Chem. Soc.*, 1961, 5471.