Acta Cryst. (1960). **13**, 535

The Crystal Structure of $(H_2N)_3PBH_3$*

By C. E. Nordman

Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

(*Received* 12 *October* 1959)

The compound $(H_2N)_3PBH_3$ crystallizes in the monoclinic space group $P2_1/c$. There are four molecules in the unit cell with

$$a = 9\cdot414 \pm 0\cdot010,\ b = 9\cdot492 \pm 0\cdot015,\ c = 6\cdot227 \pm 0\cdot008\ \text{Å};\ \beta = 100\cdot3 \pm 0\cdot15^\circ.$$

The molecule contains three NH_2 and one BH_3 group coordinated to the central phosphorus atom in approximately tetrahedral fashion. Average P–N and P–B bond lengths and standard deviations are, respectively, $1\cdot653 \pm 0\cdot005$ and $1\cdot887 \pm 0\cdot013$ Å. The nine hydrogen atoms in the molecule were located by means of Fourier difference syntheses following an approximate correction for anisotropy in the thermal motion of the heavier atoms. The BH_3 group is staggered relative to $P(NH_2)_3$. The amide hydrogen atoms are preferentially oriented in the directions of the shortest intermolecular $N \cdots N$ or $N \cdots B$ distances.

Introduction

Phosphorustrifluoride–borane, F_3PBH_3, is known to react with trimethylamine in the following way (Parry & Bissot, 1956):

$$F_3PBH_3 + N(CH_3)_3 \rightarrow (H_3C)_3NBH_3 + PF_3\ .$$

Recent work by Kodama & Parry (1960) has shown that the analogous reaction with ammonia proceeds in a different manner. Instead of the expected product ammonia–borane, H_3NBH_3, the reaction yields a new compound of the composition $(H_2N)_3PBH_3$:

$$F_3PBH_3 + 6\ NH_3 \rightarrow (H_2N)_3PBH_3 + 3\ NH_4F.$$

On chemical grounds Kodama & Parry have characterized the new compound as triamidophosphorus–borane. The present crystallographic study was initiated shortly after the compound was first isolated; its aim was to confirm the structure of the molecule and to obtain accurate molecular parameters.

Experimental

Crystals obtained by slow sublimation under vacuum were mounted in thin walled glass capillaries, the compound being quite hygroscopic. X-ray patterns showed the crystals to belong to the monoclinic space group $P2_1/c$ with

$$a = 9\cdot414 \pm 0\cdot010,\ b = 9\cdot492 \pm 0\cdot015,\ c = 6\cdot227 \pm 0\cdot008\ \text{Å},\ \beta = 100\cdot3 \pm 0\cdot15^\circ.$$

The calculated density is $1\cdot13$ g.cm.$^{-3}$ with four formula units per cell.

Intensity data were recorded as zero and upper level photographs on the Buerger precession camera using Mo $K\alpha$ radiation. A total of 639 reflections of measurable magnitude were recorded in the range $\sin\theta/\lambda \le 0\cdot704$. All reflections with $\sin\theta/\lambda < 0\cdot493$ were photographed; of these 379 were of measurable magnitude.

Reduction of data

Relative intensity readings were obtained by visual comparison of the diffraction spots with scales of timed exposures, and reduced to relative F^2 values in the usual way. Data from different nets were placed on a common scale, corresponding to the logarithmic average of the scales of the individual nets, by means of the following procedure which utilizes the readings of all reflections observed on two or more nets.

Let us assume that the data are contained in n zero or upper level nets which are interconnected in the sense that they cannot be divided into two groups having no reflections in common. There is no need for each net to intersect all others. Let f_{hi} and w_{hi} denote, respectively, the unscaled value and weight, or estimated reliability, of $F^2(hkl)$ as read on net i. The subscript h stands for (hkl), and $i = 1, 2, \ldots, n$. We shall find n scale factors k_i such as to minimize the n quantities

$$\sum_h w_{hi} (\sum_j w_{hj})^{-1} \sum_j w_{hj}\, [\log (k_i f_{hi}) - \log (k_j f_{hj})]^2$$
$$i = 1, 2, \ldots, n\ .$$

Differentiating with respect to $\log k_i$ and equating to zero one obtains the n equations

$$\sum_h w_{hi} (\sum_j w_{hj})^{-1} \sum_j w_{hj}\, [\log (k_i f_{hi}) - \log (k_j f_{hj})] = 0\ .$$

These may be solved by successive approximations. If a set of approximate $\log k_i$'s are known, the next

---

* This work was conducted, in part, under Contract AF 33(616)–3343 with the U.S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

approximation to each $\log k_i$ may be obtained by substituting $\log k_i + \Delta \log k_i$ for $\log k_i$ and solving for $\Delta \log k_i$:

$$\Delta \log k_i = (\sum_h w_{hi})^{-1} \sum_h w_{hi} (\sum_j w_{hj})^{-1} \sum_j w_{hj} \times [\log (k_j f_{hj}) - \log (k_i f_{hi})] \; . \quad (1)$$

Since $k_i f_{hi} \approx k_j f_{hj}$ and $\Delta \log k_i \ll 1$, at least in the later stages of the refinement, equation (1) can alternatively be written

$$\Delta k_i \approx 2k_i (\sum_h w_{hi})^{-1} \sum_h w_{hi} (\sum_j w_{hj})^{-1} \sum_j w_{hj} \times \left(\frac{k_j f_{hj} - k_i f_{hi}}{k_j f_{hj} + k_i f_{hi}} \right) \; . \quad (2)$$

Using a set of assumed initial k_i's—all may be taken as unity, if desired—the n values of Δk_i are computed. The k_i values are then corrected and a new set of Δk_i's calculated. This process is continued until the corrections become insignificantly small. While too cumbersome for hand calculation, and less elegant than the method recently described by Kraut (1958), this scaling procedure is more general in that it does not require every net to intersect all others. It is also well adapted for automatic computation.

In a very recent communication Dickerson (1959) has described a general scaling procedure based on minimizing the quantity

$$E = \sum_{i=1}^{n} \sum_{j=1}^{n} (k_i J_{ij} - k_j J_{ji})^2,$$

where J_{ij} is proportional to the readings on net i of spots common to net j. In order to avoid the solution $k_i = 0$ for all i one of the scale factors, say k_p, is given an arbitrary, fixed value and the remaining $n-1$ scale factors adjusted so as to minimize E. This procedure will, in general, tend to slightly overestimate k_p relative to the rest of the scale factors and, consequently, lead to a set of values which is not entirely independent of the choice of the 'standard' net p. From a practical standpoint this ambiguity is probably insignificant, except perhaps in cases where, due to low measuring accuracy, the overall fit of the scaled nets is very poor.

In the present case 208 different reflections (hkl) were observed on two or more nets, comprising a total of 532 observations usable for scaling the fifteen nets. The individual readings were assigned weights of 3, 2 or 1 depending on the *a priori* estimated reliability of each value. The computation, performed on an IBM 650 computer, led to a set of essentially constant scale factors in less than thirty minutes.

Structure determination

Phosphorus and tentative nitrogen and boron coordinates, derived from Patterson projections, were refined by least squares using individual isotropic thermal parameters. The quantity

$$R' = \sum_{hkl} w(hkl) (\mathrm{k}F_o - F_c)^2 / \sum_{hkl} w(hkl) \mathrm{k}^2 F_o^2$$

was minimized, taking $w(hkl) = 4|F_{\mathrm{min.}}|/|F_o(hkl)|$ if $F_o \geq 4F_{\mathrm{min.}}$, and equal to unity otherwise. This refinement led to $R' = 0{\cdot}0195$ and $R = 0{\cdot}116$. A three-dimensional difference Fourier synthesis computed at this time showed peaks identifiable as eight of the nine hydrogen atoms, including those of the BH_3 group. Moderate anisotropy in the thermal motion of the phosphorus, nitrogen and boron atoms was also evident. An approximate correction for this effect was incorporated in the assumed model by computing the structure factors as

$$F_c(hkl) = 2 \sum_i^{N/2} f_i \exp \left[-B_i (\sin^2 \theta / \lambda^2) - \Delta B_i(hkl) \right] \cos 2\pi (hx_i + ky_i + lz_i) \; ,$$

where for each of the non-hydrogen atoms

$$\Delta B(hkl) = \Delta B_{11} h^2 + \Delta B_{22} k^2 + \Delta B_{33} l^2 + \Delta B_{12} hk + \Delta B_{13} hl + \Delta B_{23} kl \; .$$

Approximate values of the anisotropic correction parameters ΔB_{11}, etc., were derived from the Fourier difference synthesis. Including the eight hydrogen atoms, with temperature factors $\exp(-5 \sin^2 \theta / \lambda^2)$, the coordinates and overall thermal parameters B_i of the heavier atoms were further refined. Two more three-dimensional Fourier difference syntheses yielded improved coordinates of all nine hydrogen atoms as well as successively better values for the anisotropic corrections. The final agreement was $R = 0{\cdot}077$ and $R' = 0{\cdot}0090$. The final atomic coordinates for one molecule are given in Table 1 along with the estimated standard deviations of phosphorus, nitrogen and boron coordinates. The latter were arrived at by analyzing

Table 1. *Atomic coordinates*

Atom	x	y	z
P	0·2515 ± 0·0003	0·0464 ± 0·0002	0·1685 ± 0·0003
N_1	0·1286 ± 0·0006	0·1682 ± 0·0006	0·0852 ± 0·0015
N_2	0·2053 ± 0·0005	−0·0714 ± 0·0003	−0·0265 ± 0·0012
N_3	0·4009 ± 0·0007	0·1377 ± 0·0007	0·1626 ± 0·0008
B	0·2686 ± 0·0017	−0·0458 ± 0·0011	0·4405 ± 0·0019
H_1	0·137	0·253	0·177
H_2	0·033	0·140	0·100
H_3	0·200	−0·033	−0·163
H_4	0·230	−0·147	−0·008
H_5	0·392	0·195	0·027
H_6	0·458	0·087	0·267
H_7	0·340	−0·130	0·440
H_8	0·293	0·040	0·573
H_9	0·155	−0·058	0·433

Table 2. *Thermal parameters* (×10^4)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	119	97	226	0	44	8
N_1	168	95	446	− 7	7	16
N_2	168	119	283	−14	58	1
N_3	166	166	437	−98	34	179
B	191	148	238	6	93	25

Table 3. *Observed and calculated structure factors*

h	k	ℓ	KF_o	F_c
0	0	0	--	200.0
0	0	2	11.7	10.6+
0	0	4	9.5	10.4+
0	0	6	11.7	12.0+
0	0	8	4.7	4.2-
0	1	1	44.2	46.8+
0	1	2	41.1	43.5-
0	1	3	30.0	29.1-
0	1	5	12.1	12.2+
0	1	7	6.3	5.6+
0	2	0	52.7	53.0+
0	2	1	48.5	49.7-
0	2	3	5.6	7.7-
0	2	5	7.8	8.4+
0	2	6	10.0	9.6+
0	2	7	5.5	4.9-
0	3	1	15.7	16.9-
0	3	2	36.4	36.4-
0	3	3	10.2	10.9-
0	3	4	7.2	7.4+
0	3	5	10.0	7.5+
0	3	6	5.2	3.6-
0	3	7	4.2	3.4+
0	3	8	4.6	4.0-
0	4	0	9.3	8.1-
0	4	1	15.7	15.2-
0	4	2	5.2	5.9-
0	4	3	7.1	7.9+
0	4	5	10.8	11.3+
0	4	7	6.7	6.2-
0	5	2	15.1	14.9-
0	5	3	3.4	4.3-
0	5	4	9.2	9.4+
0	6	1	13.7	13.9-
0	6	5	8.5	8.5+
0	6	7	4.9	4.2-
0	7	1	3.3	3.3-
0	7	2	16.7	18.0-
0	7	4	5.4	5.6+
0	7	5	5.3	4.1-
0	8	0	16.0	16.7-
0	8	1	12.3	12.3-
0	8	5	6.7	5.9+
0	9	1	7.9	8.2-
0	9	2	6.2	6.2-
0	9	3	8.4	7.6+
0	9	4	4.2	4.4+
0	10	0	14.4	13.7-
0	11	3	7.4	6.8+
0	12	0	3.8	3.8-
1	0	6-	5.6	5.7-
1	0	4-	26.2	28.7-
1	0	2-	48.6	54.4+
1	0	2	22.7	22.0-
1	0	4	27.5	28.7+
1	1	7-	5.1	6.1+
1	1	5-	14.4	14.5-
1	1	4-	14.6	14.7+
1	1	3-	12.3	12.5+
1	1	2-	16.3	17.9+
1	1	1-	58.5	61.0+
1	1	0	28.2	26.8+
1	1	1	40.5	40.6-
1	1	2	14.6	12.6+
1	1	5	10.8	12.1+
1	1	7	5.1	6.7-
1	2	4-	18.6	20.7-
1	2	3-	32.9	34.1+
1	2	2-	8.1	8.5+
1	2	1-	26.6	26.8-
1	2	0	4.6	3.9-
1	2	1	12.7	12.3-
1	2	2	10.0	8.3-
1	2	3	18.2	17.4+
1	2	4	22.7	23.7+
1	2	5	4.2	4.6-
1	2	6	4.3	3.3+
1	3	7-	4.4	5.0+
1	3	6-	6.7	7.7-
1	3	5-	4.1	3.9-
1	3	4-	15.0	15.0+
1	3	3-	8.0	8.8-
1	3	2-	25.5	26.0+
1	3	0	5.4	4.3-
1	3	1	9.8	10.1-
1	3	2	33.8	32.9+
1	3	4	9.8	10.0+
1	3	5	9.0	9.2+
1	3	6	8.5	8.8-
1	4	4-	5.2	7.8-
1	4	3-	18.7	20.3+
1	4	2-	4.9	4.9-
1	4	0	4.9	5.1+
1	4	2	7.7	7.8-
1	4	3	26.1	26.0+
1	4	5	4.3	4.8-
1	5	6-	8.4	8.9-
1	5	4-	3.9	4.4
1	5	2-	19.9	22.1
1	5	1-	6.6	6.7
1	5	0	3.7	2.7-
1	5	2	19.5	20.2
1	5	3	6.1	6.1-
1	5	4	11.8	11.0
1	5	6	8.3	8.9-
1	6	5-	4.3	5.2-
1	6	4-	4.6	3.9
1	6	3-	14.8	16.4+
1	6	2-	5.9	6.1+
1	6	1-	5.3	6.1-
1	6	1	12.9	13.5-
1	6	3	13.5	14.0+
1	6	4	7.8	7.2-
1	7	6-	6.7	6.4-
1	7	4-	6.6	6.7+
1	7	3-	4.3	3.8+
1	7	2-	11.3	11.5+
1	7	1-	5.3	5.1-
1	7	0	16.8	17.6-
1	7	1	2.9	3.4+
1	7	2	5.0	4.8+
1	7	4	4.4	4.1+
1	7	5	4.4	4.6-
1	7	6	4.2	4.9-
1	8	4-	8.5	8.1+
1	8	3-	9.2	9.9+
1	8	2-	6.2	7.3-
1	8	1-	11.1	11.0-
1	8	0	4.1	4.5-
1	8	1	10.9	11.4-
1	8	2	5.1	5.2+
1	8	3	4.4	5.5+
1	8	4	5.8	6.0-
1	9	5-	4.3	4.5+
1	9	1-	14.1	13.8-
1	9	0	7.9	8.2-
1	9	1	8.1	7.8+
1	9	2	4.4	3.6+
1	9	5	4.1	2.6-
1	10	4-	7.0	6.4+
1	10	2-	8.2	8.2-
1	10	1-	3.2	3.7-
1	10	2	6.2	6.2+
1	10	4	7.1	6.0+
1	11	1-	5.7	5.5-
1	11	1	8.0	7.5+
1	12	2	3.2	3.6+
2	0	6-	11.5	12.2-
2	0	4-	10.7	11.3+
2	0	2-	10.9	9.8-
2	0	0	82.3	78.4-
2	0	2	3.4	4.2-
2	0	6	8.3	9.4-
2	0	8	3.7	4.4+
2	1	7-	7.8	7.0-
2	1	5-	10.3	12.1-
2	1	4-	3.4	3.8+
2	1	3-	19.7	21.9+
2	1	2-	16.5	16.9-
2	1	1-	30.4	30.0-
2	1	1	11.3	11.3-
2	1	2	2.5	3.0
2	1	3	17.7	18.5+
2	1	5	10.3	11.1-
2	1	6	4.5	4.1+
2	2	6-	9.0	9.3-
2	2	5-	10.6	10.9+
2	2	2-	7.5	7.2-
2	2	1-	6.5	5.1-
2	2	0	58.3	55.6-
2	2	1	17.2	15.7+
2	2	2	9.9	9.3+
2	2	3	4.5	4.0-
2	2	4	7.9	7.9+
2	2	6	8.0	8.1-
2	2	7	4.5	4.8+
2	3	8-	4.1	3.4-
2	3	5-	8.3	9.7-
2	3	4-	6.5	6.7+
2	3	3-	9.6	11.0+
2	3	2-	22.1	23.4-
2	3	1-	8.9	7.4-
2	3	0	19.1	18.0+
2	3	1	11.3	10.4-
2	3	2	24.9	24.9+
2	3	3	23.9	24.4+
2	3	4	6.2	6.5-
2	3	6	4.5	4.7+
2	4	7-	6.9	6.5-
2	4	5-	9.3	9.5+
2	4	3-	6.1	6.6+
2	4	2-	10.0	10.8+
2	4	1-	9.8	9.1-
2	4	0	18.0	17.0-
2	4	1	36.8	34.5+
2	4	2	3.3	3.3+
2	4	4	7.7	8.0+
2	4	5	11.0	11.2-
2	4	7	4.4	5.1+
2	5	6-	4.4	4.2-
2	5	4-	9.4	11.2+
2	5	3-	9.7	11.0+
2	5	2-	17.5	17.6-
2	5	1-	6.9	7.6+
2	5	0	4.8	5.5+
2	5	2	32.6	32.7+
2	5	4	8.6	8.9-
2	6	7-	4.4	5.0-
2	6	5-	14.4	10.9+
2	6	4-	6.0	6.0+
2	6	3-	5.8	6.1+
2	6	2-	5.2	6.4+
2	6	1-	19.6	19.8-
2	6	0	9.0	9.3+
2	0	1	19.0	18.1+
2	6	4	4.4	3.3-
2	6	5	9.5	8.8-
2	7	5-	7.7	6.3+
2	7	4-	7.7	9.2+
2	7	2-	18.2	17.9-
2	7	1-	5.0	5.8+
2	7	0	5.1	5.2-
2	7	1	7.6	8.2+
2	7	2	11.7	12.0+
2	7	3	7.6	7.0-
2	7	4	4.6	5.1-
2	8	6-	4.4	4.6+
2	8	5-	8.2	7.1+
2	8	2-	5.4	4.6-
2	8	1-	10.5	11.0-
2	8	0	14.9	15.7+
2	8	1	4.7	5.4+
2	9	5-	4.4	3.7+
2	9	3-	10.5	10.0-
2	9	2-	6.3	6.1-
2	9	1-	4.3	4.2+
2	9	1	5.4	6.3+
2	9	3	5.5	5.1-
2	10	2-	3.9	3.0-
2	10	0	10.8	10.5+
2	11	3-	5.3	4.8-
2	11	1-	3.8	3.5+
2	11	3	6.0	6.2-
2	12	0	5.2	4.5+
3	0	4-	19.7	21.1+
3	0	2-	11.7	10.2-
3	0	0	21.4	18.4-
3	0	2	10.3	8.7-
3	0	4	23.2	22.8-
3	1	5-	9.4	10.2+
3	1	4-	4.9	5.1-
3	1	3-	4.4	5.8-
3	1	2-	15.4	14.8-
3	1	1-	39.1	35.2-
3	1	0	26.1	24.7-
3	1	2	3.5	4.3-
3	1	3	8.7	9.1-
3	1	5	8.7	9.3-
3	2	4-	13.9	15.6+
3	2	3-	20.1	17.8-
3	2	2-	24.9	23.0-
3	2	1-	18.8	16.8-
3	2	1	8.2	7.8-
3	2	2	18.8	18.0+
3	2	3	3.4	3.0-
3	2	4	18.0	18.5-
3	2	5	6.2	6.0+
3	3	6-	5.5	6.4+
3	3	5-	6.0	5.3+
3	3	4-	10.0	9.8-
3	3	3-	6.5	6.0-
3	3	2-	17.2	17.3-
3	3	1-	30.4	27.9-
3	3	1	33.1	30.8+
3	3	2	18.2	16.7-
3	3	3	5.4	5.4+
3	3	4	4.5	5.0-
3	3	5	7.5	7.8-
3	3	6	6.3	6.9+
3	4	4-	7.5	8.7+
3	4	3-	23.4	21.7-
3	4	2-	11.1	12.0-
3	4	1-	16.3	15.9+
3	4	0	2.5	2.4+
3	4	1	16.2	15.9+
3	4	2	19.4	17.5+
3	4	3	20.4	20.7-
3	4	4	5.0	6.0-
3	4	5	5.4	5.2+
3	5	6-	8.2	8.7+
3	5	4-	7.9	8.9-
3	5	2-	15.7	15.8-
3	5	1-	3.4	3.1-
3	5	0	27.2	26.4+
3	5	2	18.2	16.3-
3	5	4	9.7	10.3-
3	5	6	7.5	7.7+
3	6	3-	21.1	20.4-
3	6	2-	5.0	6.0+
3	6	1-	11.6	11.6+
3	6	1	13.8	13.6+
3	6	2	4.9	4.7-
3	6	3	13.8	14.5-
3	6	4	5.5	5.0+
3	6	5	4.6	4.8+
3	7	6-	7.2	7.0+
3	7	4-	6.3	6.1-
3	7	2-	11.1	11.0-
3	7	1-	12.9	12.4+
3	7	0	10.5	10.7+
3	7	1	7.6	7.4-
3	7	2	7.7	7.5-
3	7	5	4.6	4.5+
3	7	6	5.1	5.0+
3	8	4-	8.7	8.0-
3	8	3-	7.8	7.2-
3	8	2-	8.3	9.1+
3	8	1-	4.5	4.6+
3	8	0	5.0	3.7+
3	8	1	4.5	4.8+
3	8	2	4.7	3.7-
3	8	4	7.5	7.5+
3	9	1-	10.6	10.7+
3	9	0	4.3	4.4+
3	9	1	4.3	4.1-
3	10	4-	6.6	5.1-
3	10	2-	4.8	5.4+
3	10	1-	4.1	4.0+
3	10	2	4.0	3.8-
3	10	4	5.0	4.8+
3	11	1-	4.5	4.7+
3	11	1	5.9	6.1-
4	0	6-	10.3	11.2+
4	0	2-	10.2	9.1-
4	0	0	18.8	19.1+
4	0	2	5.7	5.5-
4	0	4	4.2	4.2-
4	0	6	8.1	7.1+
4	1	7-	6.0	6.1+
4	1	5-	12.8	13.6+
4	1	4-	8.0	6.2-
4	1	3-	14.2	13.3-
4	1	2-	11.6	10.8-
4	1	1	7.0	7.0+
4	1	2	3.4	.4-
4	1	3	18.2	19.0-
4	1	5	5.4	5.2+
4	2	7-	4.4	3.6+
4	2	6-	7.2	8.2+
4	2	5-	7.3	7.2-
4	2	4-	6.8	7.0-
4	2	3-	15.3	14.8-
4	2	0	42.4	41.8+
4	2	1	6.7	8.0-
4	2	2	9.7	7.5-
4	2	4	7.1	5.6-
4	2	6	5.7	5.3+
4	3	5-	4.2	4.2+
4	3	4-	12.3	11.3-
4	3	3-	19.7	16.9-
4	3	2-	10.7	10.0+
4	3	0	5.2	5.0-
4	3	1	10.9	10.8+
4	3	2	22.8	21.0-
4	3	3	16.8	16.4-
4	3	4	4.3	3.9+
4	4	7-	5.1	5.1+
4	4	5-	11.7	11.7-
4	4	4-	9.3	7.9-
4	4	2-	6.1	.7-
4	4	1-	17.1	15.2+
4	4	0	19.7	18.2+
4	4	1	33.0	30.9-
4	4	2	4.6	6.3-
4	4	4	4.4	2.6-
4	4	5	4.7	5.9+
4	5	4-	10.6	9.8-
4	5	3-	6.6	5.1-
4	5	2-	19.9	24.2+
4	5	0	7.0	7.7-
4	5	2	25.0	24.1-
4	5	4	7.9	6.9+
4	6	7-	4.1	3.9+
4	6	5-	10.8	10.5-
4	6	2-	3.9	2.5-
4	6	1-	12.6	11.8+
4	6	0	10.6	12.6-
4	6	1	19.4	19.3-
4	6	5	7.3	6.9+
4	7	5-	4.4	3.5-
4	7	4-	6.9	8.1-
4	7	3-	5.3	5.1+
4	7	2-	11.6	10.5+
4	7	1-	7.1	8.7-
4	7	2	7.3	7.3-
4	7	3	7.1	6.7+
4	7	4	7.6	7.2+
4	8	5-	4.4	4.2-
4	8	1-	5.5	4.9+
4	8	0	8.9	9.7-
4	8	1	3.1	3.7-
4	8	2	5.7	4.9+
4	8	5	5.0	4.3+
4	9	5-	4.0	3.5-
4	9	3-	6.5	5.5+
4	9	2-	4.4	4.4+
4	9	3	6.7	6.5+
4	10	1-	4.4	3.3+
4	10	0	6.4	6.6-
4	11	3-	4.4	4.4+
5	0	4-	15.5	16.5-
5	0	2-	14.6	14.1+
5	0	0	9.2	9.8+
5	0	4	17.7	17.4+
5	1	7-	5.1	6.3+
5	1	5-	6.5	7.1-
5	1	3-	3.4	2.3+
5	1	2-	9.2	9.2+
5	1	1-	37.0	34.1+
5	1	1	9.9	8.7-
5	1	5	8.3	8.6+
5	2	4-	11.9	12.1-
5	2	3-	13.6	13.3+
5	2	2-	22.1	21.1+
5	2	1-	4.6	5.0+
5	2	1	5.8	6.9-
5	2	2	11.5	11.6-
5	2	3	8.4	8.4+
5	2	4	10.5	11.1+
5	3	6-	6.8	6.6-
5	3	5-	6.7	6.3-
5	3	4-	6.4	6.4+
5	3	3-	10.1	9.9+
5	3	2-	15.5	15.3+
5	3	1-	19.7	19.0+
5	3	0	15.7	16.3-
5	3	1	13.1	12.1-
5	3	2	6.8	7.2+
5	3	4	4.6	4.3+
5	3	6	4.7	5.3-
5	4	3-	21.3	21.4+
5	4	2-	6.9	7.1+
5	4	1-	13.1	13.3-
5	4	0	6.0	6.5-
5	4	1	15.2	14.4-
5	4	2	5.7	5.1-
5	4	3	7.7	8.0+
5	4	5	6.1	5.4-
5	5	6-	6.1	6.7-
5	5	4-	9.9	9.7+
5	5	2-	8.0	7.2+
5	5	1-	4.2	5.5-
5	5	0	18.0	18.2-
5	5	2	9.3	9.5+
5	5	6	4.3	5.0-
5	6	3-	13.1	12.2+
5	6	2-	9.6	9.6-
5	6	1-	9.9	11.0-
5	6	0	3.1	3.8-
5	6	1	5.5	6.0-
5	6	3	9.4	8.6+
5	6	5	5.3	4.8-
5	7	6-	4.8	5.1-
5	7	3-	4.4	5.1-
5	7	2-	4.7	3.9+
5	7	1-	7.9	8.6-
5	7	0	6.5	6.8-
5	7	2	9.4	8.9+
5	7	4	4.6	3.3+
5	8	3-	4.4	4.2+
5	8	2-	4.7	5.5-
5	8	3	5.4	5.4+
5	8	4	6.7	6.0-
5	9	1-	5.4	5.4-
5	9	1	5.3	4.9+
5	10	4-	4.0	4.2+
5	10	2-	4.3	3.4-
5	11	1-	4.7	5.6-
6	0	6-	10.3	8.9-
6	0	4-	4.5	4.8+
6	0	2-	7.2	7.5+
6	0	0	25.5	26.4-
6	0	4	8.3	8.0+
6	0	6	5.6	5.2-
6	1	7-	4.5	4.7-
6	1	5-	9.9	9.7-
6	1	4-	5.1	5.5+
6	1	3-	15.0	14.7+
6	1	1-	11.7	11.8-
6	1	0	5.0	5.4+
6	1	1	5.8	5.4-
6	1	2	9.8	9.7+
6	2	6-	5.9	6.0-
6	2	5-	6.7	6.9+
6	2	4-	6.8	7.6+
6	2	3-	6.3	6.5+
6	2	2-	7.6	7.2+
6	2	1-	4.5	4.5-
6	2	0	17.2	17.5-
6	2	2	4.5	5.2+
6	2	5	5.4	5.0-
6	3	4-	10.1	11.3+
6	3	3-	11.0	10.1+
6	3	2-	10.7	11.0-
6	3	1-	4.0	3.9-
6	3	2	13.7	14.4+
6	3	3	8.4	5.3+
6	3	4	4.6	4.8-
6	4	5-	11.1	10.6+
6	4	4-	4.2	4.0+
6	4	1-	7.7	8.3-
6	4	0	3.8	4.1-
6	4	1	17.8	14.5+
6	5	4-	6.8	7.4+
6	5	2-	12.0	12.6-
6	5	2	8.4	8.5+
6	5	4	4.6	4.3-
6	6	5-	6.9	6.1+
6	6	1-	4.1	4.9-
6	6	1	10.3	11.1+
6	6	5	4.2	3.9-
6	7	2-	6.8	6.8-
6	7	2	7.3	6.8+
6	7	4	5.1	4.8-
6	8	1-	4.1	4.6-
6	8	1	5.4	6.1+
6	9	5-	3.7	3.1+
6	9	2-	4.1	4.9-
6	11	3-	5.3	4.5-
7	0	4-	8.7	8.4+
7	0	2-	20.9	20.2-
7	0	0	7.1	4.4+
7	0	2	13.5	13.8+
7	1	7-	5.0	4.5-
7	1	5-	5.4	5.6+
7	1	1-	20.1	20.6-
7	1	0	10.6	10.3+
7	1	1	11.9	12.9+
7	1	2	5.1	4.7-
7	1	5	5.2	5.0-
7	1	4-	8.3	8.0+
7	2	2-	9.7	10.2-
7	2	1-	11.5	11.9+
7	2	1	6.3	6.7+
7	2	2	5.5	6.0+
7	2	3	10.4	7.0-
7	3	6-	4.5	5.1+
7	3	5-	4.4	3.9+
7	3	4-	4.7	4.7-
7	3	2-	4.3	4.3-
7	3	1-	8.1	9.8-
7	3	0	11.8	12.5+
7	3	2	5.7	5.8-
7	4	3-	14.2	12.1-
7	4	1-	3.8	5.2+
7	4	1	6.3	7.0+
7	4	5	4.8	4.5+
7	5	6-	4.4	5.1+
7	5	2-	5.5	6.0-
7	5	0	6.6	7.8+
7	5	2	3.3	3.8-
7	6	3-	11.1	7.9-
7	6	1-	5.0	4.9+
7	6	1	5.1	6.0+
7	7	1-	4.3	4.8+
7	7	0	7.7	8.0+
7	7	2	4.0	4.5-
7	8	3-	5.4	4.6-
7	8	1-	5.2	4.3+
7	9	1-	5.1	5.3+
7	9	1	4.1	4.5-
7	11	1-	2.3	3.4+
8	0	6-	5.1	4.5+
8	0	0	15.6	15.8+
8	0	2	7.3	8.1-
8	1	5-	4.3	3.9+
8	1	3-	11.5	9.7-
8	1	2-	5.5	5.5+
8	1	1-	7.8	8.2+
8	1	0	3.6	3.9-
8	1	3	12.7	10.8-
8	2	6-	4.4	3.7+
8	2	5-	4.3	4.8-
8	2	2-	5.2	5.9-
8	2	0	7.5	7.5+
8	2	1	9.7	10.7-
8	2	2	4.3	4.6-
8	3	5-	4.3	3.7+
8	3	3-	7.8	5.7-
8	3	2-	5.1	6.9+
8	3	2	6.1	6.0-
8	3	3	6.1	5.0-
8	4	5-	5.5	6.1-
8	4	3-	4.9	4.3-
8	4	1-	3.0	3.4+
8	4	1	6.9	7.7-
8	5	2-	4.3	5.4+
8	5	2	5.1	5.1-
8	6	1-	4.3	5.7+
8	6	1	6.0	6.7-
8	7	2-	6.8	7.2+
8	7	2	4.0	5.0-
8	8	1-	3.5	3.9+
8	8	1	3.9	4.4-
9	0	2-	8.9	10.0+
9	0	2	5.1	5.5-
9	1	3-	6.1	4.1+
9	1	1-	8.5	10.1+
9	1	1	4.7	6.0-
9	2	3-	5.3	3.9+
9	2	1-	5.2	5.4-
9	2	2	3.9	4.7-
9	3	1-	4.7	5.6+
9	3	0	5.0	6.5-
9	3	1	3.6	4.0-
9	4	3-	8.4	5.5+
9	4	1-	3.6	4.0-
9	4	1	3.2	3.9-
9	5	0	5.7	6.9-
9	5	2	4.0	3.5+
9	6	3-	9.2	6.3+
9	6	1-	3.2	3.8-
9	6	1	3.4	4.1-
9	7	1-	3.1	3.4-
9	7	0	4.9	5.5-
9	8	1-	3.8	2.5-
10	0	2-	5.1	4.9+
10	1	3-	8.6	5.9+
10	2	0	5.1	5.1-
10	3	2-	3.4	3.4-
10	3	3	5.4	4.2+
10	4	1	5.1	5.7+
10	5	2-	5.3	4.8-
10	6	1-	4.0	3.5-
10	6	1	3.8	4.4+
11	1	1-	4.8	5.0-
11	3	1	3.7	3.6+
11	4	3-	4.8	3.2-
11	6	3-	4.6	2.9-
12	1	3-	4.8	3.4-

the spread of six sets of coordinates obtained by dividing the available data (*hkl*) into six sets and refining each set separately (Nordman & Reimann, 1959). The final values of the six thermal parameters in the conventional temperature factor

$$\exp\left(-\sum_{ij=1}^{3} B_{ij}h_ih_j\right)$$

of each of the five non-hydrogen atoms of Table 1 are given in Table 2. Observed and final calculated structure factors are listed in Table 3.

Discussion

Fig. 1 shows the electron-density distribution in an $(H_2N)_3PBH_3$ molecule, viewed down the crystallographic *b* axis, and a schematic representation of the same molecule. Molecular parameters and their standard deviations are given in Table 4; the labeling of the atoms is that of Fig. 1 and Table 1.

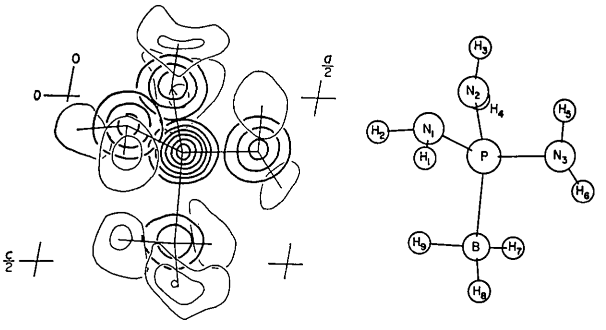

Fig. 1. Left: Electron-density distribution in the $(H_2N)_3PBH_3$ molecule. Heavy contours are at intervals of 2 e.Å^{-3} (N and B) or 4 e.Å^{-3} (P). Light contours showing the hydrogen atoms as given by a difference synthesis are at intervals of 0·25 e.Å^{-3}. Zero contour omitted in all cases. Right: Schematic drawing of the same molecule and key to the numbering of atoms.

The nitrogen and boron atoms surround the phosphorus atom in a nearly tetrahedral arrangement. The hydrogen atoms of the BH_3 group are staggered relative to the NH_2 groups. The three NH_2 groups are undoubtedly chemically equivalent; their P–N distances are equal within experimental error. The average value of this distance, $1·653 \pm 0·005$ Å is rather shorter than would be expected on the basis of the few previously reported values for phosphorus–nitrogen bond lengths. The value $1·785 \pm 0·03$ Å has been found in the $H_3NPO_3^-$ ion (Hobbs, Corbridge & Raistrick, 1953). Brockway & Bright (1943) found a P–N distance of $1·65 \pm 0·03$ Å in the cyclic compound $(NPCl_2)_3$, whose structure however suggests about 50% double bond character in the N–P bonds.

Table 4. *Interatomic distances and bond angles in the* $(H_2N)_3PBH_3$ *molecule*

(*a*) Bond distances (Å)

$P–N_1$	$1·652 \pm 0·005$	P–B	$1·887 \pm 0·013$
$P–N_2$	$1·650 \pm 0·005$	N–H	0·8 – 1·0
$P–N_3$	$1·658 \pm 0·009$	B–H	1·1 – 1·2
P–N (average)	$1·653 \pm 0·005$		

(*b*) Bond angles

N_1PN_2	$99·6 \pm 0·3°$	N_1PB	$123·3 \pm 0·6°$
N_1PN_3	$100·1 \pm 0·3$	N_2PB	$108·4 \pm 0·4$
N_2PN_3	$116·8 \pm 0·4$	N_3PB	$109·0 \pm 0·5$
PNH	100–120°	PBH	95–111°
HNH	99–145	HBH	100–124

A phosphorus–boron bond distance has previously been determined in the trimer of dimethyl phosphinoborine, $[(H_3C)_2PBH_2]_3$, where Hamilton (1955) found the value $1·935 \pm 0·009$ Å. The difference between this and the value $1·887 \pm 0·013$ Å found in the present study agrees qualitatively with Hamilton's conclusion, based on an analysis of the bond angles, that the P–B bond in the dimethyl phosphinoborine trimer molecule is slightly weaker than a normal single bond.

While the bond angles in the triamidophosphorus–borane molecule deviate appreciably from tetrahedral values, there is no clearcut difference between NPN and NPB angles. The variations within each of the two types of angle are quite considerable, and tend to mask any systematic difference between NPN and NPB angles. There is every reason to believe that the N–P–B skeleton of the free molecule possesses threefold symmetry, and that the observed distortions are due to crystal packing effects. Some support for this may be gained from considering the short intermolecular contacts (Fig. 2). The two shortest non-hydrogen contacts both involve N_1; the repulsion would tend to bend N_1 away from B and toward N_2 and N_3, in agreement with the observed distortion in the angles.

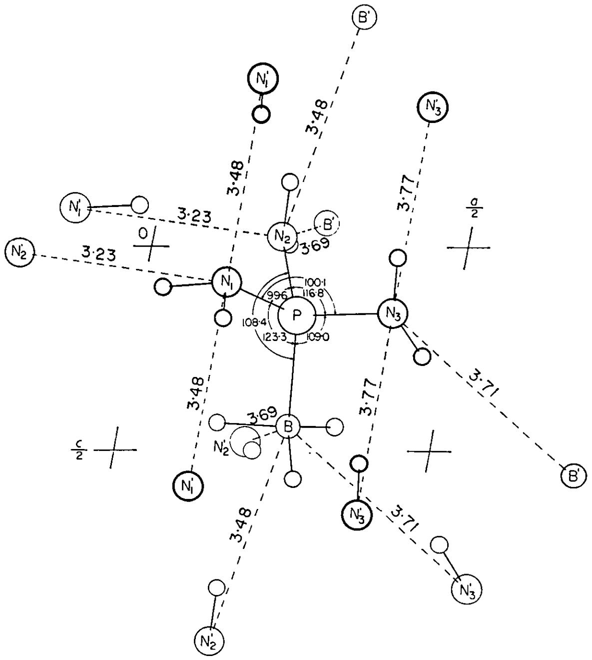

Fig. 2. A portion of the $(H_2N)_3PBH_3$ structure viewed along the *b* axis, showing the intermolecular contacts.

Another noteworthy feature shown in Fig. 2 is the fact that the six N–H bonds in the molecule are directed very nearly along the six shortest intermolecular non-hydrogen contacts. These are three N–H · · · N (3·23, 3·48, 3·77 Å) and three N–H · · · B (3·48, 3·69, 3·71 Å) contacts. While only the shortest one of these would conventionally be regarded as a hydrogen bond, it seems clear that the orientation of the amide groups is governed by electrostatic intermolecular forces acting on the protonic hydrogens. No such preferential orientation is observed in the hydrogens of the BH_3 group.

The author is indebted to Dr Goji Kodama for preparing the sample of $(H_2N)_3PBH_3$, to Miss Elfreda Chang for assistance in data preparation, and to Miss Joyce Joity for drawing the figures.

References

Brockway, L. O. & Bright, W. M. (1943). *J. Amer. Chem. Soc.* **65**, 1551.

Dickerson, R. E. (1959). *Acta Cryst.* **12**, 610.

Hamilton, W. C. (1955). *Acta Cryst.* **8**, 199.

Hobbs, E., Corbridge, D. E. C. & Raistrick, B. (1953). *Acta Cryst.* **6**, 621.

Kodama, G. & Parry, R. W. (1960). To be published.

Kraut, J. (1958). *Acta Cryst.* **11**, 895.

Nordman, C. E. & Reimann, C. (1959). *J. Amer. Chem. Soc.* **81**, 3538.

Parry, R. W. & Bissot, T. C. (1956). *J. Amer. Chem. Soc.* **78**, 1524.

Acta Cryst. (1960). **13**, 539

X-ray Scattering Factors of Two-Electron Ions from Radially and Angularly Correlated Wave Functions*†

By J. N. Silverman, O. Platas and F. A. Matsen

Departments of Chemistry and Physics, The University of Texas, Austin, U.S.A.

(*Received* 26 *October* 1959)

The X-ray scattering factors for helium and helium-like ions are calculated with radially and angularly correlated wave functions. If the energy criterion for quality of wave functions is used, these new factors are more reliable than those previously derived from radially correlated and restricted Hartree-Fock functions. In parallel trend with the relative magnitude of the electronic correlation energy, the correlation effects on the scattering factors are most pronounced for the lowest member of the isoelectronic series, H^-, and diminish rapidly with increasing nuclear charge. The calculations can be extended to polyelectronic ions without great difficulty.

Introduction

In earlier papers from this laboratory (Hurst, Miller & Matsen, 1958; Hurst & Matsen, 1959), there have been presented X-ray scattering factors, f, for two-, three- and four-electron ions calculated with single configuration functions constructed from antisymmetrized products of Slater orbitals with optimized orbital exponents.‡ These calculations have been made for S ground states and have used s orbitals. The configurations used have fallen in two classes: *SODE*, i.e. same orbitals for different (paired) electrons and *DODE*, i.e. different orbitals for different electrons. In this language, the conventional or 'restricted' Hartree–Fock functions (see Pratt, 1956) are *SODE* calculations which employ self-consistent field (SCF) orbitals. Restricted Hartree–Fock functions have been used to derive most of the Hartree–Fock f values published (Hoerni & Ibers, 1954; Berghuis *et al.*, 1955; Freeman, 1959; Veenendaal *et al.*, 1959). The analytical wave functions constructed from products of hydrogenic or Slater orbitals which were used for f calculation by Pauling & Sherman (1932) McWeeny (1951) and Tomiie & Stam (1958) are also of the *SODE* type. *SODE* wave functions do not permit electronic correlation while *DODE* wave functions contain some radial correlation (see for example, Löwdin, 1959, for a discussion of correlation in wave functions). The *DODE* functions yield more accurate energies than the restricted Hartree–Fock functions (Taylor & Parr, 1952; Shull & Löwdin, 1956; Brigman & Matsen, 1957; Hurst, Gray, Brigman & Matsen, 1958; Brigman, Hurst, Gray & Matsen, 1958) while the *DODE* f values differ from the corresponding Hartree–Fock results particularly for low atomic numbers in a given isoelectronic series.

In the present paper, the effect of correlation on the scattering factors for two-electron ions is further studied by the use of the *DODEAC* function which adds some angular correlation to the radial correlation of the *DODE*. The angular correlation is obtained by mixing an additional configuration constructed with angularly dependent orbitals. It has been shown by Silverman, Platas & Matsen (1959) (hereafter abbreviated SP&M) that the *DODEAC* wave functions yield expectation values for the energy and several other operators which are superior to those calculated from *DODE* and restricted Hartree–Fock functions and which are quite close to those obtained from more

---

* Briefly reported on at the Southwestern Meeting of the American Physical Society, March 1959, Austin, Texas.

† This research was supported by the Robert A. Welch Foundation of Houston, Texas, and the Office of Ordnance Research, U.S. Army.

‡ Determined from energy minimization.