

Die vorliegende Übersicht stellt nur einen ersten Versuch einer gemeinsamen Sicht aller Schichtsilikate dar. Als ein nächster Schritt wäre die Berechnung des elektrostatischen Anteils der Gitterenergien der verschiedenen Kationen-Tetraederschicht-Anordnungen wünschenswert, um aus einem Vergleich dieser Werte für verschiedene Anordnungen auf deren Stabilität schliessen zu können. Für topologisch gleiche Kationen-Tetraederschicht-Anordnungen lassen sich diese elektrostatischen Potentiale noch ohne grössere Schwierigkeiten berechnen und vergleichen; für topologisch ungleiche Anordnungen sind solche Berechnungen dagegen schwieriger.

Der in der vorliegenden Arbeit gegebene rein qualitative Zusammenhang zwischen Grösse und Ladung der Kationen einerseits und der Struktur der Schichtsilikate andererseits zeigt jedoch dem Chemiker von welchen Kationen wasserfreie bzw. wasserhaltige noch nicht bekannte Schichtsilikate mit Aussicht auf Erfolg hergestellt werden können und erlaubt bei Berücksichtigung kürzlich (Liebau, 1962) beschriebener Gesetzmässigkeiten beim Bau von Silikaten dem Kristallographen Annahmen darüber zu machen, welche Form die Tetraederschichten eines Schichtsilikats unbekannter Struktur haben werden.

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The Crystal and Molecular Structure of Tetramethylbiphosphine-Bis(monoborane)

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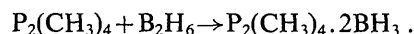
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Crystals of the 'lump' form of $P_2(CH_3)_4 \cdot 2BH_3$ are monoclinic with space group $P2_1/c$. The lattice constants are $a = 6.78$, $b = 11.64$, $c = 20.41$ Å and $\beta = 95^\circ$, with six molecules in the unit cell. The crystal structure was determined and refined from three-dimensional visual data. Least-squares refinement of the positional and anisotropic thermal parameters of the twelve non-hydrogen atoms using 1096 reflections of non-zero intensity yielded an R index of 7.7% with hydrogen positions included. There are three conformational isomers of $P_2(CH_3)_4 \cdot 2BH_3$ present in the 'lump' form in the ratio of 1:1:1. The average bond lengths are P–P 2.204 ± 0.005 , P–C 1.827 ± 0.010 , and P–B 1.951 ± 0.021 Å. The phosphorus atoms show essentially no thermal anisotropy while the terminal ligands show marked anisotropy best described as an oscillatory motion about the P–P bond. The bond lengths and angles are compared with those found in related compounds.

Introduction

Tetramethylbiphosphine reacts with excess diborane to yield the double addition product, tetramethylbiphos-

phine-bis(monoborane) (Burg, 1961). The reaction is:



The double addition product, $P_2(CH_3)_4 \cdot 2BH_3$, is an air-stable solid at room temperature and melts with decomposition at $190^\circ C$. It was reported by Burg (1961) that there are two different crystal forms, one

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having a vapor tension considerably higher than the other. The form having the lower vapor tension was called the 'lump' form since the crystals collected in clusters, while the other form was called the 'needle' form, since it formed very small, transparent needles. It was also noted that the needle form converted to the lump form through sublimation at room temperature. A highly speculative explanation of the existence of two forms was that they are different conformational isomers. Attempts to find structural differences between the two forms by the use of infrared spectroscopy proved fruitless since they gave almost identical infrared spectra (Burg, 1961).

To initiate the study of possible structural differences between the two forms of $P_2(CH_3)_4 \cdot 2BH_3$, the study of the 'lump' form by means of X-ray diffraction has been carried out in this laboratory.

Experimental

Crystals of the 'lump' form of $P_2(CH_3)_4 \cdot 2BH_3$ suitable for X-ray investigation were obtained by sublimation at $50^\circ C$. The crystals which previously appeared in clusters were now found to be colorless, transparent needles, elongated parallel to what was later found to be the a axis. Although the crystals were found to be needles, it is quite certain that they are the 'lump' form since the so-called 'needle' form was found to exist only at temperatures lower than room temperature (Burg, 1961).

Preliminary oscillation, rotation, and Weissenberg photographs taken about the needle axis showed the crystals to be monoclinic. The systematic absences are $0k0$ with k odd and $h0l$ with l odd; therefore the space group is $P2_1/c$ (C_{2h}^5 , No. 14). The values of the lattice constants were determined from rotation photographs and zero-level Weissenberg photographs about the a , b and c axes. The unit cell constants obtained are:

$$a = 6.78 \pm 0.02, b = 11.64 \pm 0.02, c = 20.41 \pm 0.02 \text{ \AA} \\ \beta = 95.0^\circ (\lambda \text{ Cu } K\alpha = 1.5418 \text{ \AA}).$$

The density was measured by flotation in a solution of ethanol and water and found to be $\sim 0.9 \text{ g.cm}^{-3}$. The density calculated for six molecules per unit cell is 0.93 g.cm^{-3} .

Since there are six $P_2(CH_3)_4 \cdot 2BH_2$ molecules per unit cell, and only four general positions in space group $P2_1/c$, at least two of the molecules must occupy one of the four sets of special positions, all of which are located on centers of symmetry. Thus, these two molecules must have the *trans* conformation. Nothing can be said at this point, of course, concerning the conformation of the remaining four molecules.

Intensity data

Two crystals were used to collect multiple-film, equi-inclination Weissenberg photographs. A needle measuring 1 mm in length and having a cross-section of

about $0.25 \times 0.25 \text{ mm}$ was used to record the levels 0–3 around the a axis, and a second crystal measuring $0.30 \times 0.25 \times 0.25 \text{ mm}$ was used to record the levels 0–6 about the c axis. $Cu K\alpha$ radiation was used throughout. The data were estimated by visual comparison with standard intensity strips. The recorded intensities ranged from 1 to 6000. Of the 1863 unique reflections within the $Cu K\alpha$ sphere for $0kl-3kl$ data, 900 were observed, and of the 962 reflections possible for $hk0-hk6$, 532 were observed. The combined Lorentz-polarization-Tunell correction was applied to obtain the values of the $|F_o|^2$. No absorption corrections were applied. The 336 reflections common to both the a - and c -axis data were then used to obtain the interlayer scale factors by the method of Heilbronner (1963). These computations were carried out with a scaling program written for this laboratory by Dr H.-C. Mez. The interlayer correlation initially had an agreement index, R , of 0.093, where

$$R = \frac{\sum |F(a) - F(c)|}{\sum \frac{1}{2} [|F(a) + F(c)|]}.$$

The same correlation was repeated in a later state of the refinement, after the data had been edited, with a resulting R of 0.064. The method of Wilson (1942) was then used to place the data on the absolute scale and to obtain the average crystal B of 3.32 \AA^2 .

Solution of the structure

In order to obtain a trial structure, a sharpened, origin-removed Patterson function was calculated. Two strong vectors were found at about 2.2 \AA from the origin, one having twice the weight of the other; it was presumed that the higher weight vector corresponded to the P-P interaction of four molecules occupying the general positions and the other peak to the twofold *trans* molecules. Coordinates of the three crystallographically different phosphorus atoms were determined from peaks elsewhere in the Patterson function. These co-

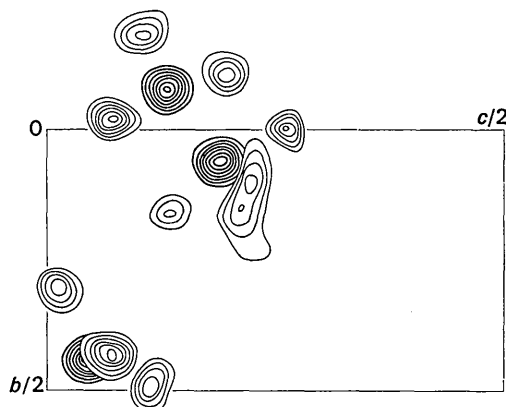


Fig. 1. Composite of the electron density of the initial Fourier synthesis. Contours of constant density are drawn at intervals of $0.5 \text{ e.}\text{\AA}^{-3}$ starting at $1.5 \text{ e.}\text{\AA}^{-3}$ for the non-phosphorus atoms, and at intervals of $2.5 \text{ e.}\text{\AA}^{-3}$ starting at $5.0 \text{ e.}\text{\AA}^{-3}$ for the phosphorus atoms.

ordinates, together with the form factor curve of Freeman & Watson (1961), were then used to calculate structure factors. R at this stage was 0.324. A three-dimensional electron density map was then calculated with 752 terms, the phases of which appeared to be governed by the phosphorus atom contributions. The resulting map showed, in addition to three large peaks corresponding to the phosphorus atoms, nine weaker peaks of density greater than $2.5 \text{ e.}\text{\AA}^{-3}$. These nine peaks were placed so that a chemically feasible trial structure resulted, but it was not possible to identify which peaks were due to carbon atoms and which were due to boron atoms. Fig. 1 is a composite of this initial electron density map.

Identification of boron and carbon atoms

In order to identify the nine terminal atoms, a least-squares treatment of three atomic coordinates and one thermal parameter per atom, plus the scale factor, was carried out. The form factor curve of Hoerni & Ibers

(1954) for carbon was used for the nine terminal atoms. All of the observed reflections were included, each being weighted according to the scheme suggested by Hughes (1949). This was: $w=1$, when $F_o \leq 4F_{\text{min}}$, and $w=4F_{\text{min}}/F_o$, when $F_o > 4F_{\text{min}}$, with $4F_{\text{min}}=19.6$.

Least-squares calculations at this stage were carried out with the UCLALS4 full-matrix least-squares program of Sparks, Long & Trueblood (1964) on the CSL Honeywell 800 computer at the University of Southern California. After four cycles of least squares, three of the terminal ligands were found to have anomalously high thermal parameters. This result may be attributed to the attempt of the least-squares procedure to compensate for the lower scattering power of boron by making the thermal parameters of the atoms anomalously high. These three terminal atoms were then assigned the boron scattering curve of Ibers (1957), and three additional cycles of isotropic least squares were carried out. The reliability index at this point was 0.139. Confirmation of the assignment of the boron atoms was later obtained from the bond lengths (see below).

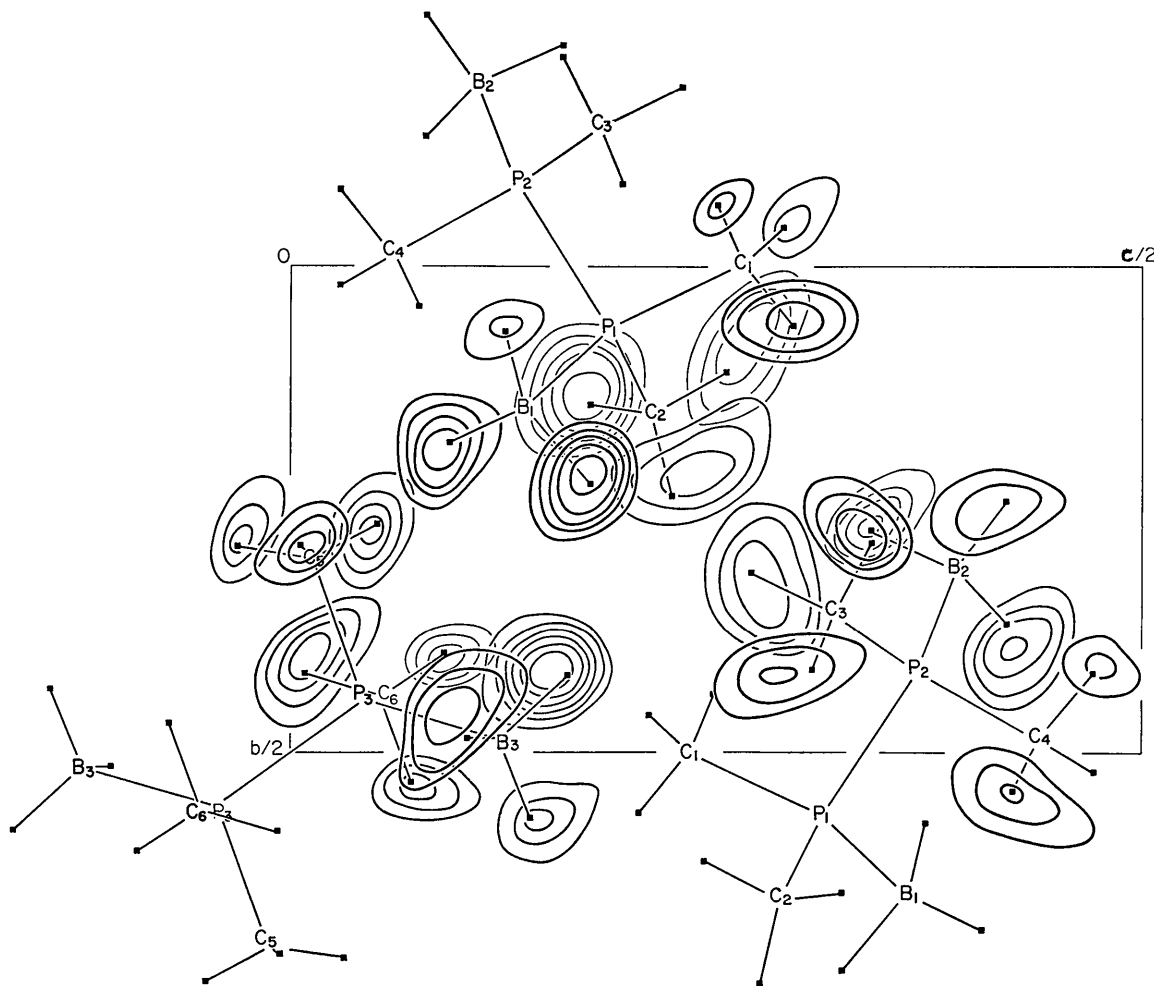


Fig. 2. Composite of the difference synthesis. The contours are drawn at intervals of $0.05 \text{ e.}\text{\AA}^{-3}$ beginning at $0.20 \text{ e.}\text{\AA}^{-3}$. The calculated hydrogen positions are denoted by the heavy black squares.

Refinement of the structure

After the data had been edited for incorrect indexing and mispunched intensities, six additional cycles of isotropic least squares were calculated with the result that R dropped to 0.105 and the quantity $\Sigma w(\Delta F)^2$ dropped to 21% of its initial value. The refinement was carried further by refining the anisotropic thermal parameters. After three cycles, the R index had dropped to 0.082 and $\Sigma w(\Delta F)^2$ was 12.4% of the initial value. At this point, all parameter shifts were less than 10% of their corresponding estimated standard deviations.

A three-dimensional difference synthesis was then calculated, using only those reflections for which $\sin \theta/\lambda$ was less than 0.45. Of the 27 hydrogen atoms to be located, 26 were found in the difference map. The expected hydrogen atom positions were also calculated for the 27 hydrogen atoms, assuming tetrahedral angles and C-H and B-H distances of 1.09 and 1.17 Å, respectively. Fig. 2 shows the composite of the difference synthesis and the calculated hydrogen atom positions. It may be seen that the calculated positions vary only slightly from the peaks in the difference map. Two more cycles of least squares were carried out with the hydrogen atom contributions included in the structure factors but with their parameters held constant. The hydrogen atoms were assigned isotropic B values equal to the B of the respective atoms to which they are bound. The hydrogen scattering curve of Stewart, Davidson & Simpson (1965) was used. The R index dropped to 0.077 and $\Sigma w(\Delta F)^2$ was lowered to 11.9% of its initial value. The least-squares refinement for the last eleven cycles was carried out using ACA Program 317 (Gantzel, Sparks & Trueblood, 1963).

The final coordinates of the non-hydrogen atoms are given in Table 1, and the assumed coordinates and isotropic thermal parameters of the hydrogen atoms are given in Table 2. The anisotropic thermal parameters of the non-hydrogen atoms are given in Table 3. Table 4 is the list of observed and calculated structure factors.

Table 1. The final coordinates of the non-hydrogen atoms and their standard deviations (in parentheses)

	All values $\times 10^4$		
	x	y	z
P(1)	0708 (4)	0638 (2)	1885 (1)
P(2)	1700 (4)	-0832 (2)	1319 (1)
P(3)	5403 (4)	4452 (2)	0432 (1)
B(1)	-1382 (26)	1457 (14)	1384 (8)
B(2)	-0526 (28)	-1872 (13)	1098 (9)
B(3)	4099 (25)	4874 (16)	1223 (7)
C(1)	-0017 (22)	-0012 (11)	2635 (5)
C(2)	2944 (19)	1486 (10)	2119 (7)
C(3)	3829 (19)	-1446 (11)	1816 (6)
C(4)	2733 (18)	-0160 (11)	0613 (5)
C(5)	4705 (23)	3023 (19)	0141 (6)
C(6)	8113 (15)	4476 (11)	0518 (6)

Table 2. Assumed hydrogen atom coordinates and isotropic thermal parameters of the terminal ligands

	x	y	z	B	Bonded to
H(1)	-0.188	0.223	0.170	6.1	B(1)
H(2)	-0.079	0.179	0.090		
H(3)	-0.272	0.083	0.126		
H(4)	-0.054	0.066	0.295	5.7	C(1)
H(5)	-0.120	-0.063	0.251		
H(6)	0.126	-0.045	0.289		
H(7)	0.254	0.223	0.240	6.0	C(2)
H(8)	0.400	0.095	0.242		
H(9)	0.359	0.177	0.168		
H(10)	0.002	-0.265	0.080	6.8	B(2)
H(11)	-0.113	-0.220	0.158		
H(12)	-0.177	-0.137	0.078		
H(13)	0.438	-0.218	0.156	5.6	C(3)
H(14)	0.498	-0.080	0.189		
H(15)	0.336	-0.172	0.229		
H(16)	0.327	-0.083	0.052	5.2	C(4)
H(17)	0.158	0.034	0.059		
H(18)	0.395	0.040	0.138		
H(19)	0.462	0.425	0.165	6.1	B(3)
H(20)	0.454	0.582	0.138		
H(21)	0.238	0.481	0.111		
H(22)	0.506	0.179	0.054	6.4	C(5)
H(23)	0.313	0.301	-0.001		
H(24)	0.555	0.281	-0.028		
H(25)	0.866	0.395	0.094	4.9	C(6)
H(26)	0.868	0.413	0.007		
H(27)	0.863	0.536	0.059		

Table 3. The final anisotropic thermal parameters of the non-hydrogen atoms and their standard deviation (in parentheses)

All values $\times 10^4$. The temperature factor is of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)	203 (8)	65 (2)	21 (1)	23 (6)	0 (5)	0 (2)
P(2)	211 (9)	63 (2)	22 (1)	-4 (7)	-3 (5)	-5 (2)
P(3)	202 (8)	64 (2)	17 (1)	-14 (6)	-3 (4)	3 (2)
B(1)	397 (55)	125 (15)	44 (5)	267 (47)	-70 (31)	-5 (14)
B(2)	474 (63)	102 (13)	52 (6)	-198 (46)	49 (35)	-40 (14)
B(3)	309 (51)	204 (20)	25 (4)	152 (54)	83 (26)	25 (15)
C(1)	475 (51)	137 (14)	25 (3)	41 (42)	89 (23)	28 (10)
C(2)	346 (44)	94 (11)	53 (5)	-142 (35)	-26 (25)	-61 (12)
C(3)	277 (38)	130 (12)	32 (4)	126 (36)	-62 (22)	2 (11)
C(4)	314 (39)	136 (12)	22 (3)	-54 (37)	42 (20)	-1 (9)
C(5)	597 (57)	62 (9)	39 (4)	-70 (35)	-54 (26)	3 (9)
C(6)	122 (26)	131 (2)	43 (4)	-17 (30)	-20 (21)	39 (12)

Table 4. List of F₀ and F_c for 1096 observed reflections

Table with 48 columns and 1096 rows, listing crystallographic data for various reflections. Columns are organized into groups of four: (h, k, l, F0), (h, k, l, Fc), (h, k, l, F0), (h, k, l, Fc), (h, k, l, F0), (h, k, l, Fc), (h, k, l, F0), (h, k, l, Fc). Each row represents a unique reflection.

Discussion

As has been pointed out, two of the six molecules of $P_2(CH_3)_4 \cdot 2BH_3$ must have the *trans* conformation while the other four molecules may be either *trans* or *D* and *L gauche*. This investigation shows that the latter is the case, so that crystals of the 'lump' form of $P_2(CH_3)_4 \cdot 2BH_3$ are a 1:1:1 mixture of three conformational isomers.

The bond distances and angles are presented in Table 5, while Fig. 5 shows the intermolecular distances shorter than 4.0 Å. The shortest distance of 3.66 Å occurs between C(6) atoms in adjacent cells and is not shown in the diagram. Also not shown is a C(2)–C(3) distance of 3.80 Å which occurs between molecules related by the *c* glide. All of the remaining short intermolecular distances between non-hydrogen atoms are shown. The closest intermolecular distance which occurs between hydrogen atoms is 2.36 Å between H(13) and H(20).

The root mean square vibration amplitudes and the direction cosines of the principal axes of the vibration ellipsoids were computed with ACA Program 232 of Gantzel, Coulter & Trueblood (1961). The results of this calculation are presented in Table 6.

It can be seen from Table 6 that the thermal motions of the phosphorus atoms are approximately isotropic, while the thermal motions of the nine terminal atoms are anisotropic. Figs. 3 and 4 show the vibration ellipsoids of the terminal atoms in the *trans* and *gauche* conformations, respectively. It is evident that the terminal atoms are oscillating about the P–P bonds in both cases.

The P–P bond

The phosphorus–phosphorus bond lengths found for the two conformations of $P_2(CH_3)_4 \cdot 2BH_3$ are the same, the average being 2.205 ± 0.004 Å. This value is in excellent agreement with the distance of 2.20 Å predicted by the phosphorus single-bond covalent radius of Pauling (1960). The value of the P–P bond distance obtained in this study is also in good agreement with

other previously reported values for the P–P single bond (Table 7), where the phosphorus is either a tri- or tetra-coordinate species.

Table 6. Principal axes of thermal ellipsoids (g_i in Å) and their direction cosines relative to *a*, *b* and *c**

	<i>i</i>	g_i	q_{ia}	q_{ib}	q_{ic}^*
P(1)	1	0.2285	0.7939	0.4813	−0.3716
	2	0.2104	0.0525	−0.6632	−0.7466
	3	0.1994	0.6058	−0.5732	0.5517
P(2)	1	0.2312	0.7892	0.1346	−0.5992
	2	0.2134	0.4849	−0.7352	0.4136
	3	0.2001	0.3768	0.6643	0.6455
P(3)	1	0.2248	−0.8416	0.4558	0.2896
	2	0.2056	−0.4623	−0.8853	0.0497
	3	0.1850	−0.2791	0.0920	−0.9559
B(1)	1	0.3959	−0.7259	−0.5654	0.3916
	2	0.2964	−0.0672	−0.5083	−0.8586
	3	0.1755	−0.6845	0.6496	−0.3310
B(2)	1	0.3777	−0.6814	0.5207	−0.5147
	2	0.3184	−0.5714	0.0614	0.8184
	3	0.2064	−0.4577	−0.8516	−0.2557
B(3)	1	0.3939	−0.3605	−0.9070	−0.2178
	2	0.2655	−0.6933	0.4167	−0.5880
	3	0.1843	−0.6240	0.0610	0.7790
C(1)	1	0.3501	−0.8060	−0.4298	−0.4070
	2	0.3019	−0.4874	0.8720	0.0444
	3	0.1957	−0.3359	−0.2342	0.9123
C(2)	1	0.3628	0.1150	0.4419	−0.8897
	2	0.3160	0.8657	−0.4839	−0.1284
	3	0.1645	0.4872	0.7554	0.4382
C(3)	1	0.3345	0.6325	0.6807	−0.3696
	2	0.2818	0.2883	−0.6498	−0.7034
	3	0.1838	0.7190	−0.3383	0.6072
C(4)	1	0.3127	0.4012	−0.9115	0.0909
	2	0.2649	0.8459	0.4067	0.3450
	3	0.2021	0.3515	0.0615	−0.9342
C(5)	1	0.3927	0.9332	−0.1237	−0.3375
	2	0.2692	0.3269	−0.0982	0.9399
	3	0.2013	0.1494	0.9874	0.0512
C(6)	1	0.3403	−0.1674	0.6799	0.7139
	2	0.2601	−0.1565	−0.7333	0.6617
	3	0.1638	−0.9734	0.0009	−0.2292

Table 5. Bond distances and angles with their standard deviations (in parentheses)

P(3)–P(3')	2.208 (0.005) Å	P(3')–P(3)–B(3)	114.4 (0.6)°
P(3)–B(3)	1.968 (0.016)	P(3')–P(3)–C(5)	103.2 (0.5)
P(3)–C(5)	1.816 (0.011)	P(3')–P(3)–C(6)	104.1 (0.5)
P(3)–C(6)	1.831 (0.011)	B(3)–P(3)–C(5)	112.0 (0.8)
P(1)–P(2)	2.202 (0.004)	B(3)–P(3)–C(6)	115.9 (0.7)
P(1)–B(1)	1.927 (0.016)	C(5)–P(3)–C(6)	106.0 (0.7)
P(2)–B(2)	1.957 (0.017)	P(1)–P(2)–B(2)	109.7 (0.6)
P(1)–C(1)	1.813 (0.012)	P(2)–P(1)–B(1)	110.5 (0.6)
P(1)–C(2)	1.836 (0.013)	P(1)–P(2)–C(3)	105.9 (0.5)
P(2)–C(3)	1.835 (0.013)	P(1)–P(2)–C(4)	103.7 (0.5)
P(2)–C(4)	1.833 (0.012)	P(2)–P(1)–C(1)	103.7 (0.5)
		P(2)–P(1)–C(2)	105.7 (0.5)
		B(1)–P(1)–C(1)	114.4 (0.8)
		B(1)–P(1)–C(2)	115.1 (0.8)
		B(2)–P(2)–C(3)	116.1 (0.8)
		B(2)–P(2)–C(4)	115.0 (0.8)
		C(1)–P(1)–C(2)	106.5 (0.7)
		C(3)–P(2)–C(4)	105.4 (0.7)

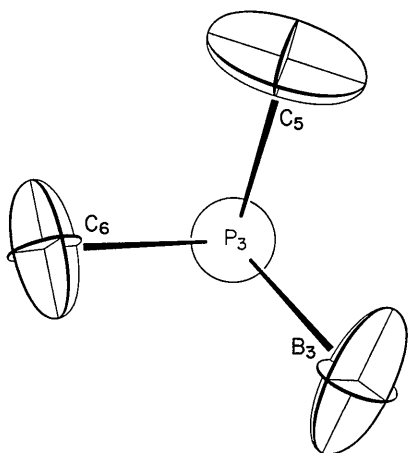


Fig. 3. The vibration ellipsoids for *trans*- $P_2(CH_3)_4 \cdot 2BH_3$. The ellipsoids are shown at twice the scale of the molecule with the principal axes taken equal to the r.m.s. amplitudes.

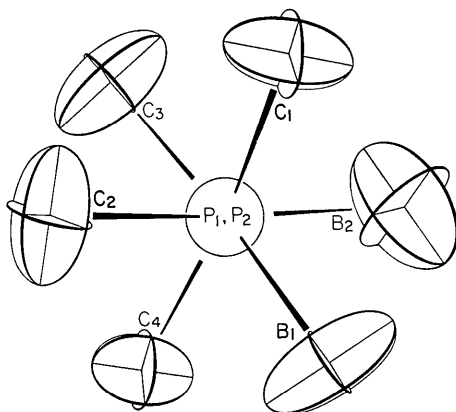


Fig. 4. The vibration ellipsoids for *gauche*- $P_2(CH_3)_4 \cdot 2BH_3$. The ellipsoids are shown at twice the scale of the molecule with the principal axes taken equal to the r.m.s. amplitudes.

The P-C bond

Within experimental error, the six unique P-C bond lengths are equal. The average P-C bond length is 1.827 ± 0.010 Å, the values ranging from 1.813 to 1.836 Å. No attempt was made to correct the bond distances for thermal motion. The average P-C bond length found for $P_2(CH_3)_4 \cdot 2BH_3$ is somewhat, but not significantly, shorter than the value of 1.84 Å obtained by summing the covalent radii of P and C and applying the electronegativity correction of Shoemaker & Stevenson (1941). The value obtained here may be compared with some previously reported results presented in Table 8.

The P-B bond

The average P-B bond length in $P_2(CH_3)_4 \cdot 2BH_3$ is 1.951 ± 0.021 Å. This distance is slightly, but not significantly, longer than the P-B distances of 1.935 ± 0.013 Å found in $[(CH_3)_2PBH_2]_3$ by Hamilton (1955), and of 1.932 ± 0.024 Å found in $[(CH_3)_2PBH_2]_4$ by Goldstein (1964). It is also 0.064 Å longer than the value 1.887 ± 0.013 Å reported for $(NH_2)_3PBH_3$ by Nordman (1960). This difference, however, is within the experimental errors reported ($d/\sigma = 2.6$), so that it cannot be said to be significant.

The large difference of 0.124 Å between the average P-C and P-B bond lengths in the molecule (smallest difference between individual bond lengths, 0.085 Å) is ample confirmation that the carbon and boron atoms have been correctly identified, and excludes the possibility that there is disorder among the three conformations.

Valence angles

The C-P-C valence angles found in both conformations of $P_2(CH_3)_4 \cdot 2BH_3$ are equal within experimental error, the average being $106.0 \pm 0.6^\circ$. This value is some-

Table 7. Selected P-P bond lengths

Distance	Compound	Reference
2.223 ± 0.017 Å	$(PCF_3)_5$	Spencer & Lipscomb (1961)
2.22 ± 0.01	$P_2S_2(C_2H_5)_4$	Dutta & Woolfson (1961)
2.213 ± 0.005	$(PCF_3)_4$	Palenik & Donohue (1962)
2.21 ± 0.01	$(CH_3)_2(C_6H_5)_2P_2S_2$	Wheatley (1960)
2.20 ± 0.01	P_4S_5	Houten & Wiebenga (1957)
2.205 ± 0.004	$P_2(CH_3)_4 \cdot 2BH_3$	This work

Table 8. Selected P-C bond lengths

Distance	Compound	Reference
1.937 ± 0.017 Å	$P(CF_3)_3$	Bowen (1954)
1.906 ± 0.017	$(PCF_3)_5$	Spencer & Lipscomb (1961)
1.867 ± 0.014	$(PCF_3)_4$	Palenik & Donohue (1962)
1.868 ± 0.012	$[(CH_3)_2PBH_2]_4$	Goldstein (1964)
1.841 ± 0.003	$P(CH_3)_3$	Lide & Mann (1958)
1.837 ± 0.012	$[(CH_3)_2PBH_2]_3$	Hamilton (1955)
1.83 ± 0.01	$[P(C_2H_5)_3]_2Ni[-C \equiv C - C_6H_5]_2$	Carfagna & Amma (1966)
1.836 ± 0.010	$[P(CH_3)_3]Ag[-C \equiv C - C_6H_5]$	Corfield & Shearer (1966)
1.827 ± 0.010	$P_2(CH_3)_4 \cdot 2BH_3$	This work

what less than the tetrahedral value, and is expected to be so in light of the previously reported values for this angle, as shown in Table 9.

The average B-P-C valence angle in $P_2(CH_3)_4 \cdot 2BH_3$ is $114.8 \pm 1.4^\circ$, with range of $112.2-116.1^\circ$. This average B-P-C valence angle is somewhat larger than that of $109.1 \pm 1.2^\circ$ found for $[(CH_3)_2PBH_2]_3$ by Hamilton (1955) and a (not significantly different) value of $110.2 \pm 0.7^\circ$ found for $[(CH_3)_4PBH_2]_4$ by Goldstein (1964).

The P-P-C valence angles found for both conformations of $P_2(CH_3)_4 \cdot 2BH_3$ are equal within experimental error, the average being $104.4 \pm 1.0^\circ$. The P-P-B angles for the two conformational isomers show a seemingly significant difference, these values being $109.7 \pm 0.6^\circ$ and $110.5 \pm 0.6^\circ$ for the *gauche* conformation while the value found for the *trans* conformation is $114.4 \pm 0.6^\circ$. We do not understand this difference; the possibility of systematic errors in the data should not be excluded, especially because there seems to be no indication of undue strain in the molecular packing.

The samples of $P_2(CH_3)_4 \cdot 2BH_3$ were given to us by Professor A.B. Burg. The Figures were prepared by

Mrs Maryellin Reinecke. This work was supported by the National Science Foundation.

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Table 9. Selected C-P-C bond angles

C-P-C angle	Range	Compound	Reference
$100.4 \pm 1.9^\circ$	98.6-102.3°	$[(CH_3)_2PBH_2]_3$	Hamilton (1955)
101.9 ± 1.3	100.4-103.0	$[P(CH_3)_3Ag[-C \equiv C-C_6H_5]]$	Corfield & Shearer (1966)
104.2 ± 1.7	101.9-106.0	$[(CH_3)_2PBH_2]_4$	Goldstein (1964)
106.0 ± 0.6	105.4-106.5	$P_2(CH_3)_4 \cdot 2BH_3$	This work

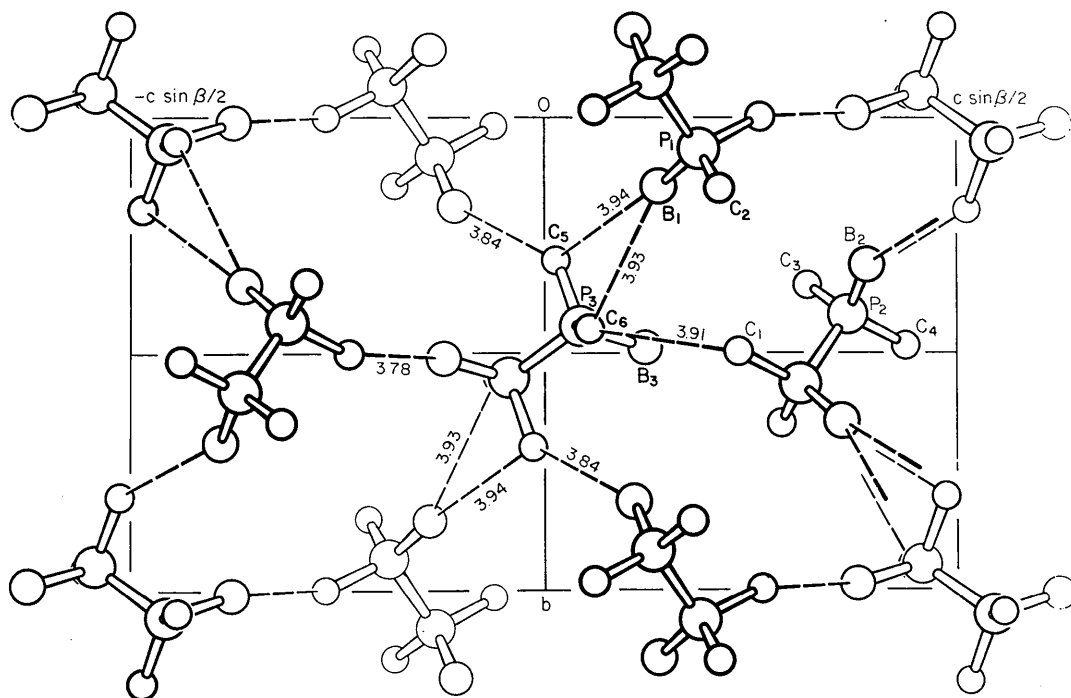


Fig. 5. Projection of the contents of the unit cell down the *a* axis showing the closest intermolecular distances between non-hydrogen atoms.

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The Crystal Structure of Compounds with (N-P)_n Rings IV*. The Stable Modification (*T* Form) of Tetrameric Phosphonitrilic Chloride, N₄P₄Cl₈

BY A. J. WAGNER AND AAFJE VOS

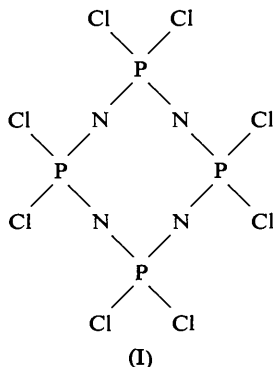
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(Received 17 July 1967)

The *T* form of tetrameric phosphonitrilic chloride, N₄P₄Cl₈, crystallizes in the tetragonal space group *P*4₂/*n* with cell dimensions *a* = 15.324 and *c* = 5.988 Å. There are four molecules in the unit cell on special positions of symmetry $\bar{1}$. The intensities of 1080 reflexions, measured on Weissenberg films, were used in the structure analysis. Anisotropic least-squares refinement reduced the *R* value to 0.07. The molecules have an eight-membered (N-P)₄ ring and are chair-shaped with approximate symmetry 2/*m*. The two independent valence angles PNP are significantly different: 133.6 and 137.6°, s.d. 0.8°. This difference is explained in terms of steric interactions between chlorine atoms. No further significant differences are observed between chemically equivalent bonds or angles. Average values with individual standard deviations are: P-N 1.559 Å, s.d. 0.012 Å; P-Cl 1.992 Å, s.d. 0.004 Å; NPN 120.5°, s.d. 0.7°; ClPCL 103.1°, s.d. 0.2°.

Introduction

Tetrameric phosphonitrilic chloride (I) was first prepared by Stokes (1897).



Two crystal modifications of the compound, generally called the *K* and the *T* form, are known. The crystal structure of the *K* form was determined by Ketelaar & De Vries (1939). This structure has recently been refined in our department as part of a program of structure analyses of compounds having (N-P)_n rings (Hazekamp, Migchelsen & Vos, 1962).

The first evidence for the existence of the *T* form was obtained by Chapman & Wilson (Paddock, 1964,

ref. 141) in 1960 from measurements of the pure ³⁵Cl nuclear quadrupole resonance spectrum. Preliminary X-ray work on this modification has been done by Wilson (Paddock, 1964, ref. 138).

At room temperature the *T* form is the stable modification. Crystallization of N₄P₄Cl₈ from solutions at room temperature, however, yields the metastable *K* form. The *T* form can be obtained by heating crystals of the *K* form to about 70°C and during the transition the crystals remain single. The *T* form can also be obtained directly by crystallizing N₄P₄Cl₈ from solutions above 70°C or from the melt.

In this paper the structure determination of the *T* form by X-ray diffraction is described.

Experimental

Crystals of N₄P₄Cl₈, *K* form, were available in the laboratory [melting point 123.4°C; literature value 122.8°C (Lund, Paddock, Proctor & Searle, 1960)]. They were transformed into crystals of the *T* form by keeping them at 70°C for a few hours. The density of the crystals obtained was measured by flotation [2.17 g.cm⁻³; literature value for the *K* form 2.18 g.cm⁻³ (Lund *et al.*, 1960)]. The crystallographic data of the two modifications are compared in Table 1. The cell dimensions of the *T* form were measured from a powder diffractogram, on which silicon powder lines were superposed for calibration purposes [$\lambda(\text{Cu } K\alpha_1) = 1.54051$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å].

* Part III: Migchelsen, T., Olthof, R. Vos, A. *Acta Cryst.* (1965). **19**, 603.