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**Unit cell, space group and composition of a lower boron phosphide.** By V. I. MATKOVICH, *Research Laboratories, Allis-Chalmers Manufacturing Company, Milwaukee, Wisconsin, U.S.A.*

(Received 18 March 1960)

Although preparations of a boron phosphide were reported very early (Moissan, 1891; Besson, 1891) there was very little interest in the compound. Interest increased recently when it was shown (Welker, 1952) that the compound has interesting semiconducting properties. A few methods of preparation were since discovered and crystallographic structure was established (Peri, LaPlaca & Post, 1958).

Decomposition of BP into a lower phosphide at high temperatures was first reported by Williams (1959). On basis of weight loss and chemical analysis the decomposition product was believed to have the approximate formula of  $B_6P$ .

The study of boron-phosphorus system has been conducted in this Laboratory for some time. The lower boron phosphide was prepared by the decomposition of BP in graphite crucibles in a neutral gas atmosphere at temperatures of 1400–1700 °C. It was also prepared directly under similar conditions by reacting aluminum phosphide and amorphous boron powder. The remaining aluminum phosphide and aluminum can be easily removed by dilute hydrochloric acid. Some alumina impurities from the AlP should be expected.

The resulting lower phosphide is invariably a very fine

powder and only a few very small crystals were obtained. The unit cell data was obtained from single crystal rotation photographs and powder photographs (Table 1).

The unit cell was found to be rhombohedral with the following hexagonal dimensions.

$$a = 5.984, c = 11.850 \text{ \AA}.$$

Systematic absences place it within the following space groups:  $R\bar{3}m$ ,  $R\bar{3}$ ,  $R3m$ ,  $R3$ ,  $R32$ . However, since the compound appears to be isomorphous with  $B_4C$  and  $B_4Si$  (Matkovich, 1960), the  $R\bar{3}m$  space group is assigned.

The density of crystals measured by heavy liquids method was found to be  $2.74 \pm 0.02$  g.cm.<sup>-3</sup>. On basis of unit-cell sizes and density the molecular weight (per unit cell) is  $202 \pm 1$  which is in excellent agreement with the theoretical molecular weight of  $B_{13}B_2$ . The rhombohedral unit cell contains, therefore, one molecule. Comparing  $B_{13}P_2$  with  $B_4Si$  ( $B_{12}Si_3$ ), the three silicon atoms contained in the unit cell appear to be replaced by two phosphorus and one boron atom. The  $B_6P$  formula appears, therefore, incompatible with the above data. The boron to phosphorus ratio determined by the weight loss during the decomposition of BP at 1600 °C. was found to be about 6.3 and chemical analyses of samples resulted invariably in ratios of 6.4–6.5. Following is a chemical analysis of a  $B_{13}P_2$  sample.

Table 1. *X-ray diffraction powder data for  $B_{13}P_2$*

(Cr $K\alpha$ radiation)					
<i>hkl</i>	<i>d</i>	<i>I/I</i> <sub>1</sub>	<i>hkl</i>	<i>d</i>	<i>I/I</i> <sub>1</sub>
101	4.74 Å	1	220	1.495	50
012	3.88	60	018	1.426	50
110	2.978	60	131		
104	2.569	80	027	1.4173	30
021	2.522	100	223	1.3970	50
015	2.149	40	312		
006	1.971	5	306	1.2999	60
024	1.946	5	134	1.2930	20
211	1.927	50	401	1.2867	30
122	1.854	1	208		
300	1.722	5	042	1.2650	1
116	1.645	70	315	1.2288	60
214	1.632	20	119	1.2054	20
107	1.607	10	226	1.1926	20
303	1.582	10	232	1.1656	10
125	1.509	90	1,0,10	1.1552	20

P	29.2%	Al	1.0%
B	65.5	Fe	0.1
C	1.0	Si	0.2
N	0.6	Cu	0.1
Mg	0.1		

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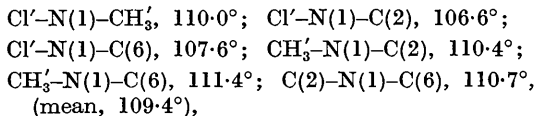
**The crystal and molecular structure of *dl*-alaphrodine hydrochloride. Addendum.** By G. KARTHA, F. R. AHMED and W. H. BARNES, *Pure Physics Division, National Research Council, Ottawa, Canada*

(Received 17 August 1960)

Dr R. E. Marsh (1960) has kindly drawn our attention to an oversight, and its implications, in our paper on *dl*-alaphrodine hydrochloride (Kartha, Ahmed & Barnes, 1960, p. 530) in which it is stated that the chlorine ion is 4.02 Å from the nearest nitrogen atom. This distance is

from Cl to N(1) with both atoms in the positions represented by the fractional co-ordinates  $x, y, z$  given in our Table 2. In point of fact, however, the chlorine atom (Cl') at  $x, \frac{1}{2} - y, z - \frac{1}{2}$  is appreciably closer to the nitrogen atom, i.e.,  $N(1) - Cl' = 3.02_6$  Å. Taking 1.48 Å for the radius

of the  $\text{NH}_4^+$  ion and 1.81 Å for the radius of the  $\text{Cl}^-$  ion, an N-Cl distance of at least 3.29 Å might have been expected. The much shorter observed distance, therefore, strongly suggests that Cl' is hydrogen-bonded to N(1), (N-H...Cl). This conclusion receives support from the values of the pertinent bond angles:



all of which are very close to the tetrahedral value of  $109^\circ 28'$ . As Dr Marsh also has pointed out, the direction of this hydrogen bond is almost parallel to the  $z$  axis and, thus, might be responsible for the large apparent temperature-factor anisotropy of the chlorine ion.

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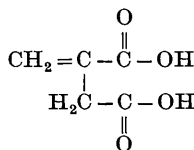
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**Unit cell and space group of itaconic acid.** By AMNON GOLDSTEIN, GERALD MANDEL and DANIEL PINDZOLA,\* *Polytechnic Institute of Brooklyn, Brooklyn 1, N. Y., U.S.A.*

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Itaconic acid (methylene succinic acid):



is of importance as an intermediate in the synthesis of polymers, dyestuffs, and pharmaceuticals.

Material prepared by Chas. Pfizer & Co. was recrystallized twice from water. Large single crystals in the form of octahedra up to 2 cm. in diameter were readily grown by slow evaporation of an aqueous solution of the acid. Analysis of these crystals by the method of neutralization equivalents indicated that they contained 99.5% of the expected acid equivalents. No hydration of the crystals was detected. The crystals showed pronounced cleavage perpendicular to  $a$ .

The crystals were investigated with precession and Weissenberg cameras. The unit cell is orthorhombic. Systematic absences are consistent with either of two possible space groups:  $C_{2v}^5\text{-Pca}2_1$  or  $D_{2h}^1\text{-Pcam}$ .

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Unit-cell dimensions were computed from powder data obtained using a recording diffractometer. The dimensions are:

$$a = 5.45 \pm 0.01, b = 18.45 \pm 0.03, c = 11.45 \pm 0.02 \text{ \AA}.$$

The density calculated on the assumption that there are eight molecules per unit cell is  $1.50 \text{ g.cm.}^{-3}$ . The density measured by floatation in a mixture of  $\text{CCl}_4$  and  $\text{CHCl}_3$  is  $1.49 \pm 0.01 \text{ g.cm.}^{-3}$ . It should be noted that the density generally quoted in the literature,† namely  $1.63 \text{ g.cm.}^{-3}$ , is incorrect.

Efforts were made to resolve the space group ambiguity by means of piezoelectric tests. A positive piezoelectric test would have indicated that the unit cell is non-centrosymmetric. This would have ruled out  $\text{Pcam}$  unambiguously. However, no piezoelectric effect was detected in a series of experiments using several single crystals of itaconic acid of varying sizes.‡ Therefore, we are left with a twofold ambiguity with regard to the space group.

† Beilstein's Handbuch der organischen Chemie. J. Springer, Berlin 1918.

‡ Piezoelectric tests were made by Dr F. Holtzberg of the IBM Watson Scientific Labs., New York City.