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The Crystal and Molecular Structure of Pentaborane

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Pentaborane crystals are pyroelectric and belong to the space group C_{4v}^9–*I4mm*, with two molecules in a unit cell of dimensions $a = 7{\cdot}16$, $c = 5{\cdot}38$ Å. A molecular symmetry of C_{4v} is demanded, and the boron atoms form a tetragonal pyramid, with slant B–B = 1·66 Å and base B–B = 1·77 Å. The fourfold axes of the molecules lie along the fourfold axes of the unit cell. The diagonal of the base of the pyramid lies in the *a* direction. Five of the hydrogens are 'regular', with an average B—H = 1·20 Å, and one is bonded to each boron; while the other four are 'bridge hydrogens', with B–H = 1·35 Å, and are bonded to the four pairs of base boron atoms.

Introduction

The interatomic bonding and structures of the 'electron deficient' boron hydrides have long been of great interest. The structures of decaborane (Kasper, Lucht & Harker, 1950) and of diborane have now been established unambiguously and are strikingly different from those originally accepted. At this time, however, if one compares the icosahedron of boron atoms in boron carbide (Zhdanov & Sevast'yanov, 1941; also Clark & Hoard, 1943) with the decaborane molecule, one might expect the pentaborane molecule to be related in structure to the boron octahedron in calcium boride (Pauling & Weinbaum, 1934). This point of view leads, of course, to the C_{4v} tetragonal pyramidal model. Apparently a molecule of this structure was overlooked in the experimental part of the first electron-diffraction study (Bauer & Pauling, 1936), because a recent investigation (Hedberg, Jones & Schomaker, 1951) shows that the electron-diffraction pattern is consistent with such a model. On the other hand this latter study is not inconsistent with some quite different, but chemically less reasonable, models. Until this recent electron-diffraction study the proposed structures for this molecule were based on puckered or planar five-membered rings of boron atoms such as that proposed by Pitzer (1945), while the earliest investigation indicated a methyl cyclobutane type of structure. These possibilities are now definitely eliminated in view of the C_{4v} molecular symmetry.

Experimental

Pure pentaborane was distilled into the tips of thin-walled pyrex capillary tubes of approximately 0·5 mm. diameter, frozen by liquid nitrogen and sealed off under vacuum. The crystalline pentaborane was found to be pyro-electric and its melting point was about −48° C., as measured by a thermocouple touching a capillary located in a stream of cold nitrogen gas. Buerger precession photographs of single crystals maintained roughly at −115° C. were taken with Mo $K\alpha$ radiation using techniques which have already been described (Abrahams, Collin, Lipscomb & Reed, 1950; Reed & Lipscomb, to be published). In this laboratory we have found zero-level precession photographs to be of much better quality than those of *n* levels and for this reason have obtained *hkl* data out to $\sin\theta/\lambda = 0{\cdot}50$ by photographing zero levels only. From one to three photographs were taken of reciprocal-lattice planes normal to the [001], [010], [$1\bar{1}0$], [102], [201], [210] and the [111] axes. Except for three photographs, where the precession angle ($\bar{\mu}$) was 25°, all photographs were taken with $\bar{\mu} = 28°$. The revised expression (Waser, 1951) for the Lorentz factor was used in applying the Lorentz and polarization corrections to the visually estimated intensities. All reflections common to two or more zones were used in correlating the intensities of reflections in the different zones.

Crystal data

Pentaborane, which has a molecular weight of 63·17, melts at −46·6° C. The symmetries of the zero-level photographs were C_{4l} about [001], C_2 about [111], and C_{2l} about the other axes. It follows that the reciprocal lattice belongs to the centrosymmetrical point group D_{4h}. The only systematic extinctions observed were those leading to body centering and, since the crystals were found to be pyroelectric, we assumed that the space group C_{4v}^9–*I4mm* is correct. The tetragonal cell, which contains two molecules, has the dimensions

$$a = 7{\cdot}16 \pm 0{\cdot}02, \quad c = 5{\cdot}38 \pm 0{\cdot}02 \text{ Å} .$$

The volume of the unit cell is thus 276 Å^3 and the calculated density is 0·761 g.cm.$^{-3}$.

Determination of the structure

With two molecules of pentaborane in the unit cell the molecular symmetry demanded by the space group C_{4v}^9–*I4mm* is C_{4v}–*4mm*.

One boron atom from each molecule must be located on a fourfold axis. Then, if we consider that the other four borons form the base of a tetragonal pyramid, the relative intensities of the (110) and (130) reflections establish that the diagonal of the square base lies along a so that the basal borons belong to the eightfold set, $x, 0, z$, $\bar{x}, 0, z$, $0, x, z$, $0, \bar{x}, z$, plus the body-centered positions. Similarly, two of the hydrogens must lie in twofold locations. Sixteen hydrogen atoms then remain to be placed. Now, since there are only two values of the z coordinate in the sixteenfold positions, it does not appear possible to achieve satisfactory packing of molecules in both the a and c directions. Moreover, these sixteenfold positions lead to unreasonably short hydrogen–hydrogen distances within the molecule. Thus we are led to place the sixteen remaining hydrogen atoms in two sets of eightfold positions. Molecular packing along a, together with anticipated boron–hydrogen distances, would require eight hydrogens to be in $x, 0, z$, $\bar{x}, 0, z$, $0, x, z$, $0, \bar{x}, z$, plus the body-centered permutation. If we then require reasonable hydrogen–hydrogen approaches, both within the molecule and between different molecules, the only reasonable positions for the remaining eight hydrogen atoms are x, x, z, $x, \bar{x}, z$, $\bar{x}, x, z$, $\bar{x}, \bar{x}, z$, plus the body centered permutation. These hydrogen atoms, necessarily of the 'bridge' type, must be at least 0·6 Å below the plane of the basal boron atoms and also must be reasonably close to the fourfold axes in order to pack with the apex hydrogen atoms of the neighboring molecules. It must be said, however, that two years before the time of this analysis M. V. King and W. N. Lipscomb had discussed the possibility of this structure, and also Hedberg, Jones & Schomaker (private communication)* had independently arrived at the same model (see Fig. 1).

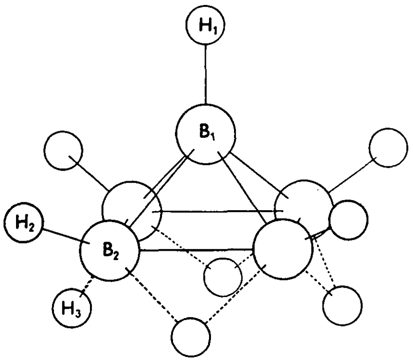

Fig. 1. The pentaborane molecule.

With the use of reasonable x and y parameters for the boron and hydrogen atoms, calculated and observed $hk0$ structure factors showed good agreement. A Fourier synthesis of this centrosymmetric zone was made to give the c-axis projection of the electron density on the lines x, x and $x, 0$. These projections showed excellent convergence and indicated only slight shifts in the trial coordinates. A recalculation of the structure factors showed no sign changes. The parameters given by this synthesis are listed in Table 1.

Table 1. *Preliminary parameters*

Atom	x	y
B_1	0·000	0·000
B_2	0·176	0·000
H_1	0·000	0·000
H_2	0·329	0·000
H_3	0·136	0·136

The z parameters and better values of the x and y parameters were obtained by refinement of the Fourier sections, $\varrho(x, 0, z)$ and $\varrho(x, x, z)$. The first $\varrho(x, 0, z)$ section indicated that the height of the molecule was appreciably less than we had expected from the results of Hedberg, Jones & Schomaker. For this reason the final Fourier series were evaluated using calculated structure factors for comparison with those obtained from the observed data. In this way we were able to correct the apparent coordinate changes for the 'back shift' correction (Shoemaker, Donohue, Schomaker & Corey, 1950). For this purpose it was desirable to have the observed data on an absolute scale and necessary to have the calculated structure factors corrected by an appropriate temperature factor. It was observed that this factor was very nearly isotropic and the temperature factor constant, B, was obtained from the slope of a plot of the expression:

$$\log F_c/F_o = \log \lambda + (B/2{\cdot}303)\,(\sin\theta/\lambda)^2\,.$$

The value of B so obtained was 10·2 Å^{-2}, which was rounded off to 10·0 Å^{-2}. The intercept of the $\log F_c/F_o$ axis showed that the scale factor (λ) was about 0·73, whereas the value finally chosen was $\lambda = 0{\cdot}755$. This latter value was obtained by averaging F_c/F_o for all but two or three of the weakest reflections.

No back shift was indicated for the x parameters of boron, or for the z parameter of the base boron atoms. However, comparison of $\varrho_c(0, 0, z)$ with the trial parameters led to a back-shift correction for the apex boron atom of $-0{\cdot}005$, which when applied to $\varrho_o(0, 0, z)$ led to a change of this z parameter of $-0{\cdot}003$ from the trial value (cf. Tables 2 and 3). In order to locate the apex hydrogen the electron density of the boron atom was subtracted from $\varrho_c(0, 0, z)$ and $\varrho_o(0, 0, z)$ in the region of the hydrogen atom. Thus the back shift of the hydrogen atom was found to be $-0{\cdot}008$ and the observed curve then indicated that this z parameter should be smaller by about 0·010. Similarly, a comparison of the $\varrho(x, 0, z)$ syntheses (for $\varrho_o(x, 0, z)$ see Fig. 2) in the region of the 'regular' base hydrogen atoms suggested the changes $\Delta x = -0{\cdot}003$ and $\Delta z = -0{\cdot}004$. For the

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* A preliminary Report on this determination was made at the Chicago meeting of the American Chemical Society, September, 1950. We are indebted to these authors for making available to us their results.

$\varrho(x, x, z)$ syntheses (see Fig. 4 for $\varrho_o(x, x, z)$) within a radius of 0·5 Å about the bridge hydrogen atom the calculated and observed Fouriers gave electron densities which were in agreement to within 0·1 e.Å^{-3}. At the chosen location for these atoms the electron densities had the same value and no change was indicated for the bridge-hydrogen atom parameters.

Fouriers obtained from observed data give atomic positions which are in part determined by the phases calculated from the trial structure, so that in principle such syntheses should be refined until observed and calculated data give the same coordinates. Our results satisfy this requirement to within ±0·01 Å for the short B–B distance and within considerably less for the base B–B distance. From our earlier refinements it may be asserted that the hydrogen positions are not appreciably affected by this small difference, and that the final hydrogen positions are well within our estimates of the probable errors stated below. The final syntheses, from observed structure factors, and their interpretations are shown in Figs. 2–5. It will be noticed that there is no background as great as ±0·5 e.Å^{-3}.

Results and discussion

Table 2 lists observed and calculated structure factors for which the usual index of reliability, $\Sigma||F_c|-|F_o|| \div \Sigma|F_o|$, is 0·13 with non-observed reflections excluded, and 0·16 with their inclusion.

Table 3 lists the final values of the parameters along with a conservative estimate of their errors.

On the basis of these final parameters the intra-

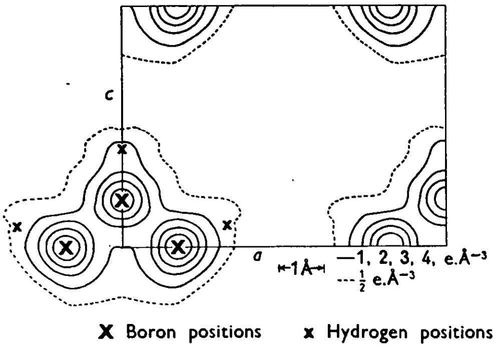

Fig. 2. Section $\varrho_o(x, 0, z)$.

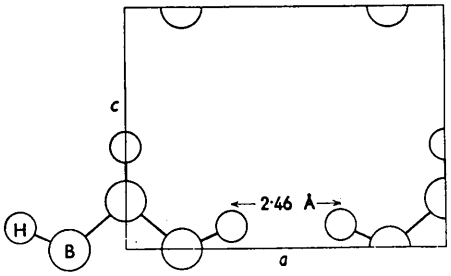

Fig. 3. Interpretation of Fig. 2.

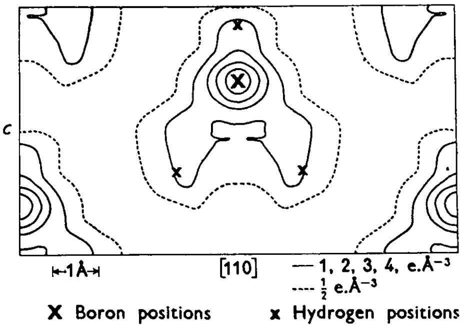

Fig. 4. Section $\varrho_o(x, x, z)$.

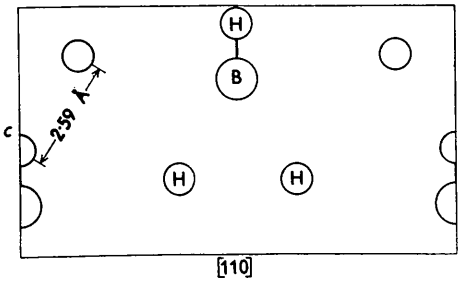

Fig. 5. Interpretation of Fig. 4.

Table 2. *Observed and calculated structure factors and phase angles*

hkl	F_o	F_c	α (°)
110	200	190	0
130	< 10	0	0
150	24	31	0
170	8	6	0
200	110	105	0
220	52	51	180
240	14	12	180
260	9	9	0
280	< 10	2	0
330	36	30	180
350	6	5	0
370	< 10	1	180
400	24	38	0
440	< 9	0	0
460	7	6	0
550	10	10	0
600	33	31	0
800	< 9	2	0
002	110	110	8
004	31	35	353
006	8	5	13
101	200	200	11
103	22	29	346
105	19	13	5
202	14	18	72
204	10	11	321
206	< 9	1	47
301	37	54	78
303	7	6	198
305	< 8	2	6
402	8	15	47
404	9	8	329
501	36	36	18
503	10	12	348
505	8	4	2
602	12	12	11
604	7	5	349

molecular angles and distances and close intermolecular distances were calculated, and are shown in Table 4.

Table 2 (*cont.*)

hkl	F_o	F_c	α (°)
701	8	7	18
703	<' 8	2	337
121	44	38	125
141	19	18	86
161	17	16	17
112	19	26	341
132	34	31	152
152	17	11	15
123	14	17	219
143	< 14	5	250
163	13	5	344
114	13	20	336
134	16	6	240
154	< 15	6	340
125	< 15	2	12
231	56	60	340
251	< 16	7	72
222	60	61	178
242	24	25	175
262	< 14	2	96
233	38	34	187
253	< 15	3	235
224	12	12	211
244	12	5	219
341	21	22	340
332	42	50	173
352	13	6	161
343	14	16	189
334	11	12	190
451	15	5	4
442	< 11	11	176
444	< 11	2	226

The values from which these structure factors were calculated are $z_{B_1} = 0{\cdot}205$, $x_{B_2} = 0{\cdot}175$, $x_{H_2} = 0{\cdot}331$, $z_{H_1} = 0{\cdot}437$, $z_{H_2} = 0{\cdot}096$, $x_{H_3} = 0{\cdot}136 = y_{H_3}$, and $z_{H_3} = -0{\cdot}165$. The differences between structure factors calculated from these and from our final parameters (Table 3) are well within our uncertainties in the F_o's.

Table 3. *Final parameters*

Atom type	*x*	*y*	*z*
B_1	0·000	0·000	0·202 ± 0·004
B_2	0·175 ± 0·002	0·000	0·000
H_1	0·000	0·000	0·427 ± 0·009
H_2	0·328 ± 0·006	0·000	0·092 ± 0·009
H_3	0·136 ± 0·006	0·136 ± 0·006	−0·165 ± 0·009

Table 4

Intramolecular distances and angles

(*a*) Bonded distances

B_2–B_2 = 1·77 ± 0·02 Å
B_1–B_2 = 1·66 ± 0·02 Å
B_1–H_1 = 1·21 ± 0·05 Å
B_2–H_2 = 1·20 ± 0·07 Å
B_2–H_3 = 1·35 ± 0·04 Å

(*b*) Non-bonded distances

H_3–H_3 = 1·95 ± 0·09 Å
H_2–H_3 = 2·17 ± 0·09 Å

(*c*) Molecular angles

∠ B_1–B_2–H_2 = 115 ± 5°
∠ Plane of boron base to plane of $B_2B_2H_3$ = 119 ± 5°

Close intermolecular distances

H_2–H_2 = 2·46 ± 0·09 and 2·96 ± 0·09 Å
H_1–H_3 = 2·59 ± 0·09 Å
B_2–H_3 = 3·40 ± 0·07 Å

The two shortest intermolecular distances are as expected. The other values, which are the closest approaches between corner and body-centered molecules, are somewhat longer than normal van der Waals distances, which would be 2·40–2·50 Å for hydrogen-hydrogen approaches, and about 2·85 Å for boron-hydrogen contacts. On the other hand, the very large temperature factor does suggest that there would be some relatively long intermolecular distances.

The angle B_1–B_2–H_2 = 115° compares well with similar angles in decaborane where they ranged from 110 to 134°, and with the angle of 120° found by Hedberg, Jones & Schomaker.

Similarly, the angle of 119° between the plane of basal boron atoms and the plane containing the bridge hydrogens is only about 5° smaller than that found in the electron-diffraction study. The short bridge-hydrogen approaches of 1·95 Å compare favorably with the electron diffraction value and with the 1·98 Å distance found for the bridge-hydrogen contacts in decaborane.

The boron-hydrogen bonded distances agree well with the electron-diffraction study and are intermediate in value between those found for diborane and decaborane. The boron–boron distances are only in fair agreement however, 1·77 and 1·66 Å compared with 1·80 and 1·70 Å, and it may well be that these differences are at least partly real. The 2% average decrease in the boron–boron distances for pentaborane in the solid state compared to the gaseous state is about that found for the C–N distance in hexamethylenetetramine (Schomaker & Shaffer, 1947) the only similar case previously reported. Our bridged B_2–B_2 distance of 1·77 Å may be compared with the boron–boron distance of 1·77 Å in diborane (Hedberg & Schomaker, 1951) and with the two bridged distances of 1·76 and 1·78 Å in decaborane. The shortest boron–boron distance observed in decaborane is 1·73 Å, where, however, all boron atoms have a 'coordination' number of six while in pentaborane the apex boron has a total of only five atoms bonded to it.

A discussion of the bond orders and distances in pentaborane has been presented in a short com-

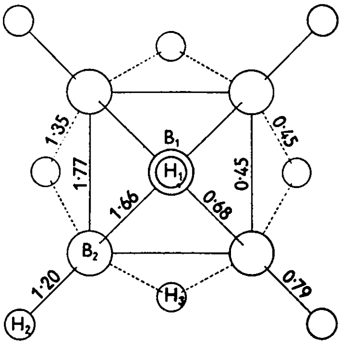

Fig. 6. Topological diagram of the pentaborane molecule with bond lengths shown on the left and bond numbers on the right. The B_1–H_1 bond distance of 1·21 Å and its order of 0·76 are omitted from the diagram.

munication (Dulmage & Lipscomb, 1951). These distances and bond orders are summarized in Fig. 6.

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Overgrowths of Alkali Halides on $CaCO_3$ and $NaNO_3$

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Crystals of ten alkali halides (NaCl, KCl, KBr, CsCl, CsBr, RbI, KI, NaF, LiF, and CsF) were grown from the vapor and from solution on cleavage surfaces of $CaCO_3$ and $NaNO_3$. The orientations observed (Schulz, 1951*a*) with the electron-diffraction techniques employed in previous experiments (Schulz, 1949, 1951*b*) are listed in Table 1 with certain details added in Figs. 1 and 2. From the vapor, growth was by the oriented nucleus mechanism (Schulz, 1951*b*) for all deposits. Usually a deposit of 10 Å average thickness was sufficient to show a well-defined pattern. With thicknesses above about 150 Å there was a transition to random orientation. The size of the crystals grown from the vapor was about 200 Å on an edge; from solution, about 3000 Å or larger.

The experimental results listed in Table 1 may be explained by considering the following general factors:

I. Low-index planes parallel to the substrate. NaCl-type deposits (except for LiF) were oriented with the (100), (110) and (111) planes parallel to the substrate. For CsCl-type materials only the (110) plane was parallel to the substrate, but possibly with a greater range of lattice constants other orientations would also appear.

II. Electrical neutrality at the interface. There was a tendency for a plane of mixed ions (both positive and negative) of the deposit to contact the substrate plane, also a mixed ion plane. For a NaCl-type deposit these are the (100) and (110) planes and for CsCl the (110) plane. Exceptions in growth from solution are RbI and KI on both substrate materials. In growth from the vapor there is the additional exception of CsF on $CaCO_3$.

III. Atomic matching along rows of like ions. In Fig. 2(*A*) are shown the atomic separations in the $CaCO_3$ substrates, 4·99 and 4·03 Å. A deposit grew in such a manner that one of these distances was matched as closely as possible. This result would be expected from the short range of the orienting forces. There was no orientation which exhibited a tendency to get the best overall match for both separations. Even for

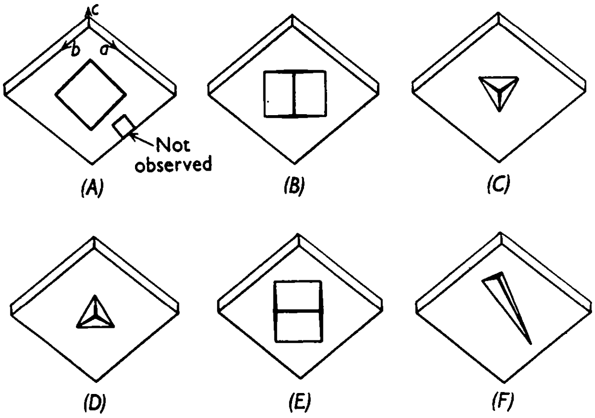

Fig. 1. Schematic representation of orientations. The faces of the substrates are bounded by cleavage surfaces while those of the deposits are (100) planes. The axes of the substrate are defined by the edges of the cleavage rhomb in the manner shown in (*A*).