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The Structures of the Hydrides of Boron. VIII. Decaborane

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In this paper we shall present an analysis of old and new electron diffraction data obtained on several hydrides of boron. The visual procedure will be used. Since the validity of the method has been questioned in the particular case of the hydrides of boron, we wish to state at the outset that although the various subjective factors have been discussed by several investigators,[1] differences of opinion regarding the "interpretations" of detailed features still remain. In any special case, judgment of these details ultimately lies with the individual. However, it is generally agreed that no spurious peaks or shoulders appear visually unless there are definite inflections in the computed curve.

Since it is so often overlooked, one other point needs emphasis. In equation (1) for the diffraction pattern produced by an assembly of atoms, atom form factors (which are a measure of their relative scattering power) and the distances between atomic centers appear. Were the data of high precision, sufficient to resolve these parameters perfectly, the deduced values would be uniquely interpretable, in most cases, in terms of a molecular structure. Unfortunately, that is far from being the case. Hence a statement to the effect that a model is excluded by the data means that within the limits of error imposed by the visual procedure, that particular location of atoms and closely similar configurations are excluded. To eliminate a given structure (wherein only the connexity between atoms is specified) one must eliminate individually models covering the entire range of interatomic distances and bond angles which seem at all plausible.

Decaborane

Decaborane, $B_{10}H_{14}$, is one of the most stable of the hydrides of boron. It is a colorless, well-crystallized solid at room temperature, and is formed as a product of decomposition of various boranes standing at room or elevated temperatures. It can be heated for considerable periods at 150° without observable change, but decomposition becomes noticeable at 170°.

A variety of structures have been proposed for decaborane. Möller[2] (1931) concluded from X-ray diffraction studies of single crystals that the space group is V_h^{21} with 8 molecules of $B_{10}H_{14}$ in the unit of dimensions

$$a = 14.46 \text{ Å.}; \quad b = 20.85 \text{ Å.}; \quad c = 5.69 \text{ Å.}$$

Assuming that in the solid the molecules are

undissociated and similar in structure, he concludes that each molecule must have a minimum symmetry at C_2 or C_s. Möller states that C_i is also possible. However, if C_i is a minimum symmetry, the molecule must actually possess C_{2v} which is much higher than the minimum requirement of the space group. Much less reliable appear his conclusions that sub-units containing two molecules, with the dimensions $10.43 \times 7.23 \times 5.69$ Å. and possessing the symmetry V, C_{2h} or C_{2v}, are present in the crystal. Formally, it is possible to arrange the eight $B_{10}H_{14}$ units in four groups of two, each pair being disposed about a point in the lattice in such a manner that this pair exhibits the symmetry V, C_{2h} or C_{2v}. However, Möller's conclusion that these pairs are contiguous and that the envelope circumscribing each pair is a rhombohedron with the dimensions 7.23, 10.43 and 5.69 Å. is unwarranted. If the latter is accepted, $B_{10}H_{14}$ must have a naphthalene-like or similar type of structure.

On the basis of the analogy in chemical stability of decaborane with the pentaborane B_5H_9 Pauling and Bauer[3] (1936) suggested the configuration for the former
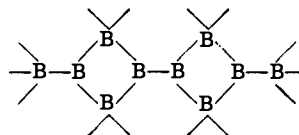
In extending his theory of the "protonated double bond" to the various higher hydrides of boron, Pitzer[4] (1945) suggested the structure
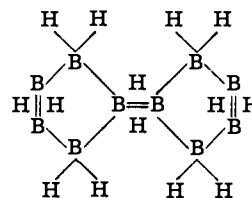
In this Laboratory we diffracted electrons on the vapor of decaborane in the hope of eliminating some of the possibilities which have been suggested. In this we were only partly successful.

This electron diffraction study was performed on the equivalent of 8 cc. (STP) of the material, kindly furnished to us by Professor A. B. Burg, to whom we wish to express our sincerest appreciation. The sample, contaminated with mercury, was distilled under vacuum (all joints of the magnetic breaker kind) into a high temperature nozzle. Some fluffy brown material was left in the tube after distillation. The photographs were ob-

(1) (a) L. Pauling and L. O. Brockway, J. Chem. Phys., **2**, 867 (1934); (b) L. R. Maxwell, S. B. Hendricks and V. M. Mosley, J. Chem. Phys., **3**, 699 (1935); (c) V. Schomaker, private communication.

(2) H. Moller, Z. Krist., **76**, 500 (1931).

(3) S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936).

(4) K. S. Pitzer, ibid., **76**, 1136 (1945).

tained with the sample tube at 104–115° and the nozzle at 110–120°; these were recorded on Eastman Commercial plates. The intensity and s values estimated by the usual visual procedures are shown in Table I. Although not shown in the table, slight shoulders were observed to the right of the fourth maximum, and to the left of the sixth maximum.

Figure 1 shows the radial distribution curve calculated after Walter and Beach.[5] The maxima at 1.28 and 1.78 Å. are very likely due to the B–H and B–B bonded distance, respectively, while the one at 2.88 Å. can be attributed to the distance between boron atoms separated by another boron atom as in a chain or ring; the ratio (2.88/1.78) corresponds to a B–B–B bond angle of 108°. Due to the sharpness and intensity of the peak at

TABLE I

| Max.	Min.	I	s_0	Model J $s_{calcd.}/s_{obs.}$
2		10	2.69$_3$	(1.040)
	2	– 8	3.75$_2$	(0.973)
3		25	4.87$_9$	1.025
	3	–15	6.25$_4$	0.999
4		10	7.20$_0$	1.035
	4	– 5	9.61$_2$	1.028
5		3	11.23$_4$	1.006
	5	– 2	12.84$_6$	1.012
6		1	15.31$_4$	1.010

Final B–B$_{av}$, 1.80 ± 0.03 Å.   Average 1.016
  B–H$_{av}$, 1.29 ± 0.04 Å. Average deviation 0.011

2.88 Å., we are able to eliminate models which do not have tetrahedrally bonded $B\diagup^{B}\diagdown_B$ atoms or those which do not contain a pentagon structure with angles of 108°. Therefore the configuration including two-four membered rings of boron suggested by Bauer and Pauling[3] is eliminated. For the same reason we were able to eliminate the planar hexagon configurations proposed by Nekrasov[6] and later by Pitzer[4] as an alternate possibility. All other models considered involved enough angles near 108° to necessitate the computation of diffracted intensity curves. The following structures were considered
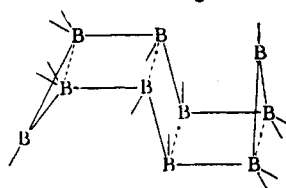
A. Branched chain
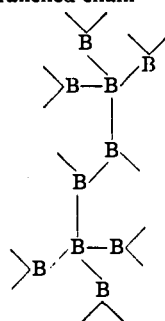
BH = 1.28 Å.
BB = 1.78 A.
All ∠'s 109°30′

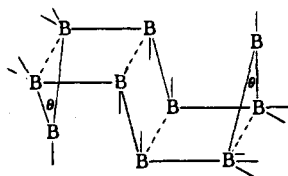B. Branched chain
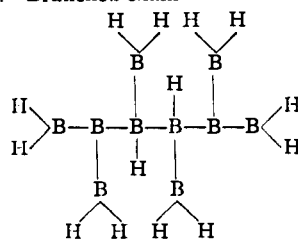
BH = 1.28 A.
BB = 1.78 Å.
All ∠'s 109°30′

C. Ten membered ring

BH = 1.28 Å.
BB = 1.78 Å.
All ∠'s 109°30′

Fig. 1.—Radial distribution curves for B_5H_9 and $B_{10}H_{14}$. R. D. B_5H_9 and R. D. $B_{10}H_{14}$ were computed from diffraction data; A, B, C_1 and C_2 are "synthetic" for B_5H_9.

(5) J. Walter and J. Y. Beach, J. Chem. Phys., 8, 601 (1940).
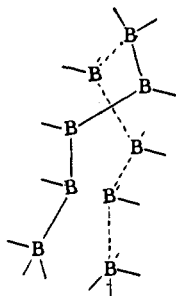
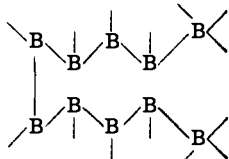(6) B. V. Nekrasov, J. Gen. Chem. (U. S. S. R.), 10, 1021 (1940); 10, 1156 (1940).

D. Ten membered ring

BH = 1.28 Å.
BB = 1.78 Å.
θ = 120°
All other $\angle$'s = 109°30'

E. Folded chain

Top view
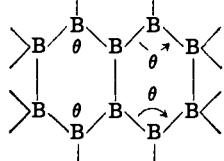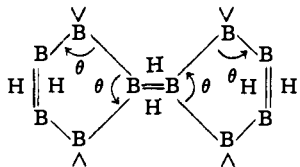
BH = 1.28 Å.
BB = 1.78 Å.
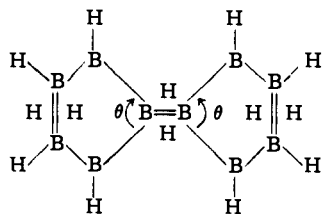All $\angle$'s 109°30'

side view

F. Puckered hexagons

BH = 1.28 Å.
BB = 1.78 Å.
θ = 120°
All other $\angle$'s 109°30'

G_1.
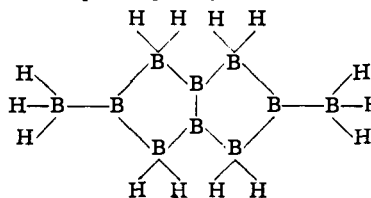G_2. } Bridge pentagons

G_1 BH = 1.39 Å.
    bridge
BH   = 1.18 Å.
B=B   = 1.76 Å.
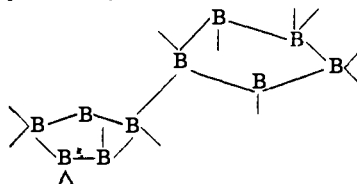B—B   = 1.82 Å.
θ = 107°

G_2 BH = 1.39 Å.
    bridge
BH   = 1.25 Å.
B=B   = 1.76 Å.
BB   = 1.82 Å.
θ = 110°

H. Coplanar pentagons

BH = 1.28 Å.
BB = 1.78 Å.
$\angle$'s in ring 108°
all others
    tetrahedral

J. Pentagons in parallel planes

BH = 1.28 Å.
BB = 1.78 Å.
regular pentagons
all other $\angle$'s 109°30'

In selecting the above models, we considered as many diverse types as we could picture; we assumed interatomic distances and disposed the hydrogen atoms in such a manner as to get "synthetic" R.D. curves which agree best with the
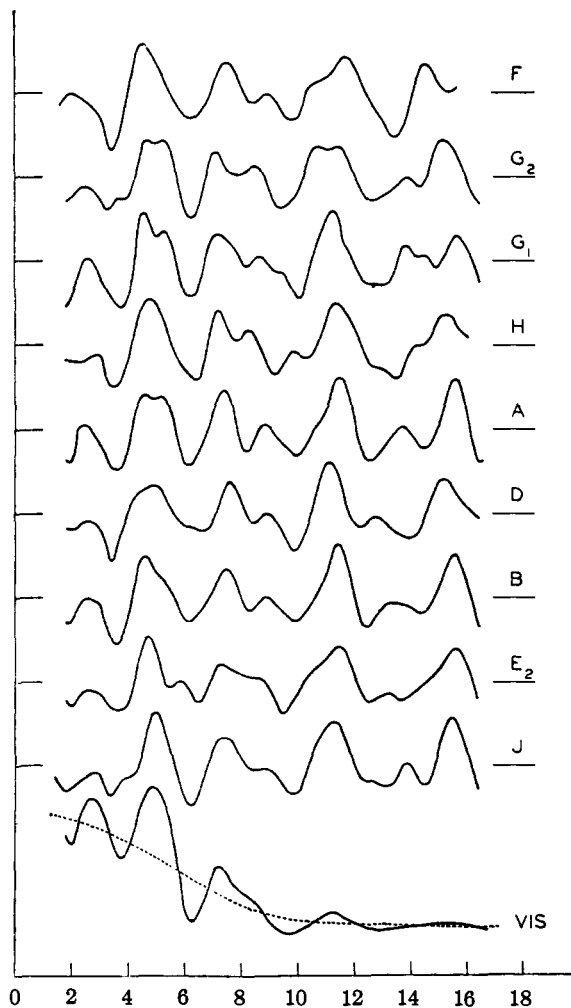

Fig. 2.—Intensity curves for $B_{10}H_{14}$.

R.D. computed from the data. After comparing the visually estimated diffraction pattern with those computed from the models (Fig. 2) using the equation

$$I\ (s)\ =\ \sum_i{}'\sum_j{}'(Z-F)_i(Z-F)_j\frac{\sin l_{ij}s}{l_{ij}s}{}^7 \qquad (1)$$

we divided the group into three classes,

DEFINITELY ELIMINATED: A, F, G_1, G_2 and H
POSSIBLE: J, B, C, D and E
MOST PROBABLE: J

It is clear that G_1 and G_2 are eliminated because of the assymmetry introduced in the pentagons by the protonated double bonds. Of the structures considered "possible," we have been able to group only J, C, and D in pairs about a point so that each pair exhibits a symmetry V, C_{2h} or C_{2v} (Fig. 3). Apparently the bent chains, B and E, do not permit such symmetrical arrangements. The planar pentagon configurations (G_1, G_2, H) which were eliminated on the basis of the electron diffraction data could also be arranged to form a unit with V, C_{2h} or C_{2v} symmetry. Finally, although a coplanar pentagon configuration similar to J was not considered, it would fit the X-ray data and probably the E.D. data as well as does model J.
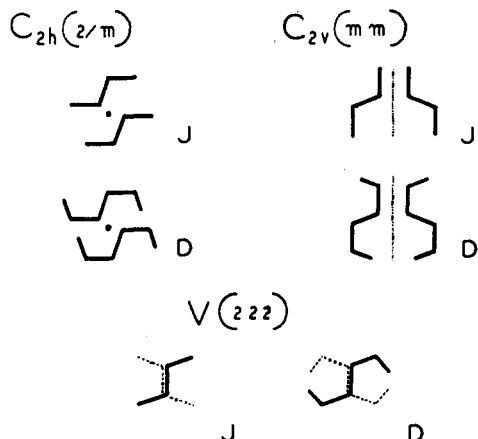

Fig. 3.—Arrangement of two molecules of the J and D configurations for decaborane so as to satisfy the symmetries suggested by Möller: C_{2h} (2/m)-plane of symmetry in plane of page; C_{2v} (m m)-planes of symmetry in plane of page and perpendicular to page at the dotted lines; V(222)-dotted line in plane parallel to that of page.

A careful study of the X-ray data and computations leading to a Fourier projection should permit the elimination of those structures at present considered possible. Were larger amounts of

(7) This equation, rather than $\sum Z_i Z_j \frac{\sin l_{ij}s}{l_{ij}s}$ was used because in taking the photographs a stop was inserted to remove the main beam about 1 cm. from the nozzle. This served not only to clear up the inner region of the photographs, but also acted as a selective mask for small angles, so that the pattern was in effect multiplied by some low power of s. Equation (1) satisfactorily accounts for this change.

decaborane available for this investigation so that more fully developed electron diffraction photographs could be obtained, a definite structure assignment might have resulted.

Pentaborane, B_5H_9

Since hydrogen bridge structures[4,8] were not considered in the original electron diffraction study of B_5H_9,[8] we reconsidered these data with the view of testing the acceptability of a bridge type configuration. The radial distribution curve, recalculated after the method of Walter and Beach[5] (Fig. 1), shows a slightly different ratio of BH/BB distances than was presented in the original report. The slight shift in maxima suggests an increase in the length of the BH distance and permits an even better match between the Bauer–Pauling structure (B, Fig. 1) and the observed data.

BB = 1.76 Å.
BH = 1.17 Å.
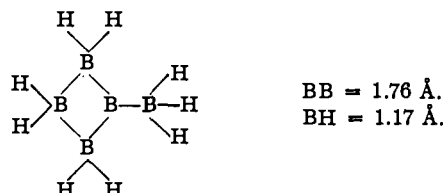
Maxima appeared at 1.21, 1.73 and 2.47 Å. These we interpreted as being due to the BH, BB and the $\underset{B\xleftrightarrow{\ }B}{\overset{B}{\diagup\diagdown}}$ interactions in the ring, respectively. Because of the intensity of the peak at 2.47 Å. it cannot be assigned to BH interactions only. Since the combination 1.73 and 2.47 Å. leads to a BBB angle of approximately 90°, no model without this 90° angle can be made to agree with the observed pattern. The two suggested models, involving hydrogen bridges contain no BBB angles of 90°. The synthetic R.D. patterns C_1 and C_2 (Fig. 1) were calculated following the suggestion of Longuet-Higgins and Bell.
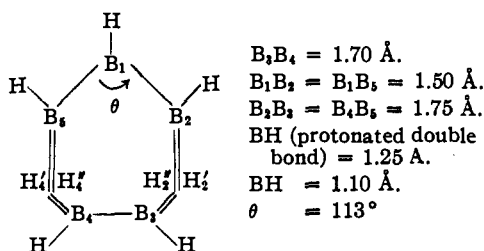
C_1.

B_1B_2 = B_1B_3 = 1.70 Å.
BH = 1.18
BH' = 1.24
B_3B_4 = 1.76
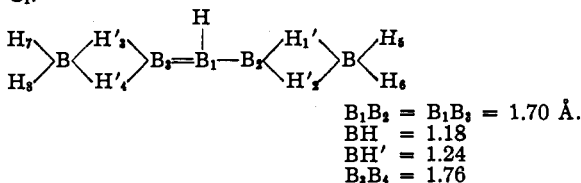
Due to resonance, B_1B_2 equals B_1B_3; H'_1, H'_2, H'_3 and H'_4 determine a plane perpendicular to the plane of H_5, H_6, H_7 and H_8; C_2 is identical with C_1 except that $\angle B_2B_1B_3 = \angle HB_1B_2 = \angle HB_1B_3 = 120°$. As can be seen from a comparison of the synthetic and calculated radial distribution curves, there is no way of varying bond distances or angles for C_1 or C_2 to obtain a suitable fit, since there is no way of obtaining a sufficiently high maximum at 2.47 Å. Thus this bridge structure is definitely eliminated.

(8) (a) H. C. Longuet-Higgins and R. P. Bell, J. Chem. Soc., 250 (1943); (b) Proc. Roy. Soc. (London), A183, 357 (1944–1945).

When Pitzer first presented the protonated double bond structures he claimed that the following angles and bond lengths for B_5H_9 fitted the electron diffraction data.

$B_3B_4 = 1.70$ Å.
$B_1B_2 = B_1B_5 = 1.50$ Å.
$B_2B_3 = B_4B_5 = 1.75$ Å.
BH (protonated double bond) = 1.25 A.
BH $= 1.10$ Å.
$\theta = 113°$

H_2' and H_2'' (also H_4' and H_4'') were placed 0.86 Å. above and below the plane of the B atoms and displaced outward from the line B_2B_3 (B_4B_5) by 0.25 Å.

That appeared doubtful, since there are no BBB angles of approximately 90° in this configuration. There are other discrepancies in the R.D. curve (A, Fig. 1) which argue against it. Nevertheless, we calculated intensity curves using the distances and angles proposed (Fig. 4A). This should be compared with the curve computed for the methylene cyclobutane model (Fig. 4B) and with the visually estimated pattern. Since the relative intensities and shapes of the maxima are as important as their positions, the curve computed assuming the protonated double bond structure is definitely eliminated.

It is worthwhile to emphasize that for this compound it is the location of the boron atoms and not of the hydrogen atoms which determine the essential features of the pattern. Thus the intensity curves computed for models of the type wherein BB = 1.76 Å.; B–H = 1.17 Å.; and 90 < θ < 100°, will be generally satisfactory. The characteristic features are not specially sensitive to the location of atom B'; and one

really cannot specify the type of bonding suggested by the – – – links. This is evident from inspection of the curves plotted in Fig. 5, ref. 3.
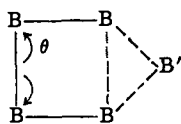
Diborane

A recently reported infrared study of diborane[9] argues very strongly in favor of the bridge structure, whereas the original electron diffraction data[10] were interpreted to favor the ethane type configuration. Since that conclusion depends on whether a faint inner ring is present or absent in the region of $s = 3$, the electron diffraction work is being repeated, employing an apparatus with a rotating sector, with the hope of obtaining objective microphotometer traces of the pattern.

Summary

New electron diffraction data on decaborane are reported. Using the visual procedure we

(9) W. C. Price, J. Chem. Phys., 15, 614 (1947).
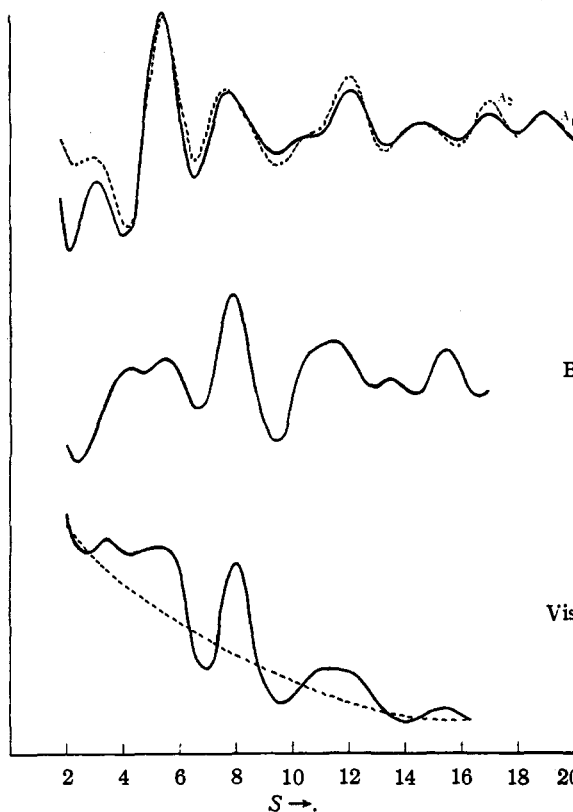(10) S. H. Bauer, THIS JOURNAL, 59, 1096 (1937).

Fig. 4.—Intensity curves for B_5H_9: A_1 was computed using $\Sigma Z_i Z_j \sin (sl_{ij}/sl_{ij})$ for Pitzer's model; A_2 was computed using eq. (1) for the same model; B methylene cyclobutane model, and visual curve from reference 3.

found that

$$B—B_{av.} = 1.80 \pm 0.03 \text{ Å.}$$
$$B—H_{av.} = 1.29 \pm 0.04 \text{ Å.}$$
$$\angle B—B—B \ 109 \pm 3°$$

Although a unique structure assignment is not possible, the data can best be interpreted on the assumption that $B_{10}H_{14}$ consists of two symmetrical pentagons held together by a B–B bond. Furthermore, we consider the data sufficient to eliminate the H-bridge type configurations which were tested.
Previously published electron diffraction data on B_5H_9 were reviewed, and it is demonstrated that Pitzer's model for this compound is definitely not acceptable.

ITHACA, N. Y.   RECEIVED DECEMBER 26, 1947