This is evident from eq. (10a–b), namely, the relating coefficients $j$ and $J$ are functions of the constants $k'$, $k''$, respectively, which in their turn stand in definite relationship to the critical coefficient $K_{cr}$ of each particular substance. In general we can say that the dispersion is greater where $K_{cr}$ is small (as in permanent gases), and that the curves run closer to each other where the $K_{cr}$ lies between 3.7–3.9 (normal organic liquids).

We express our appreciation to Dr. Henry Fleishmann and the Educational Alliance, New York, for the extension of the financial assistance to one of us (C. S. S.) until completion of this work.

## Conclusions

1. The reduced vapor pressures of chemically different substances are found to be expressible in terms of reduced temperature within the limits of experimental error and in agreement with the accurate test formulas used by observers to check their data.

2. The form of the vapor pressure function is entirely analogous to that of the volume ratio, namely

$$\ln P_{cr}/P_s = k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}} = z \qquad (11a)$$

$$P_s = P_{cr}\, e^{-z} \qquad (11b)$$

3. The parameters $k'$, $m'$, $n'$ vary with the chemical nature of substances. Their values increase parallel to the ascending order of curves and to the increase of the critical coefficient $K_{cr}$, exceptions being very few. The ratio $K_{cr}/k'$ varies from 1.3 for permanent gases to 1.15 for organic liquids, while for helium and nitrogen tetroxide it is, respectively, 1.6 and 0.84.

4. The fact that the reduced vapor pressures are given accurately by the proposed equation leads to the possibility of defining the behavior of all substances when compared at equal reduced temperatures. At equal $\tau$ the reduced vapor pressures of two substances are related definitely to each other. The relating coefficients are in general different from unity and are exponential functions of temperature and of the parameters $k$, $m$, $n$

$$\pi_A/\pi_a = e^{z_a - z_A} = j \qquad (12)$$

5. The coefficients become unity only at the critical point, this being the only temperature at which the properties of substances are identical. At other temperatures the coefficients increase with decrease of $\tau$.

6. Accordingly, the dispersion of curves ln $\pi$–$\tau$ is a normal phenomenon for all substances. Since the coefficients $j$ are functions of the $k'$ and the latter are related to the $K_{cr}$, it follows that the degree of dispersion is somehow influenced by the critical coefficient, the true mechanism of this influence being at present obscure.

NEW YORK, N. Y. RECEIVED DECEMBER 23, 1937

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[CONTRIBUTION FROM THE GATES AND CRELLIN CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 632]

# The Structure of the Hydrides of Boron. V. Tetraborane $B_4H_{10}$ and the Pentaborane $B_5H_{11}$

BY S. H. BAUER*

The hydrides of boron have been classified into two groups on the basis of their constitution, $B_nH_{n+4}$ and $B_nH_{n+6}$.[1] It has been suggested that corresponding differences in physical and chemical properties exist; these differences are, however, not distinct, and, indeed, the first member of the $B_nH_{n+4}$ series, diborane, behaves as though it belonged with the $B_nH_{n+6}$ group.[2] Of the numerous theories which have been proposed during the last decade and a half, only that of Wiberg is sufficiently complete to

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[1] Except when otherwise specified, the chemical information quoted in this paper has been obtained from: A. Stock, "The Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1931; E. Wiberg, *Ber.*, **69**, 2816 (1936).

[2] Unlike $B_5H_9$ and $B_{10}H_{14}$, but like $B_4H_{10}$, $B_5H_{11}$, and $B_6H_{10}$, diborane melts at a temperature at which its vapor tension is not observable on an ordinary mercury manometer. Diborane, tetraborane and the unstable pentaborane also react far more readily with water and ammonia than does the stable pentaborane or decaborane. In further contrast to the latter two compounds, $B_2H_6$ reacts with hydrochloric acid to give a chloro derivative and hydrogen, a behavior shown also by $B_4H_{10}$ and $B_5H_{11}$ (except that the derivatives of these cannot be isolated). It is significant that di-, tetra- and the unstable pentaboranes are converted easily one into the other by the proper choice of experimental conditions, while $B_5H_9$, $B_6H_{10}$, and $B_{10}H_{14}$ are formed slowly and irreversibly from that equilibrium mixture. Hence the classification of the boranes into the series $B_nH_{n+4}$ and $B_nH_{n+6}$ is purely formal, and has no chemical basis.

show structural differences between the two homologous sets. Most of the others, besides being highly artificial, have proved quite sterile even in regard to providing an explanation for the existence of the known compounds. This inadequacy in theory was a consequence of the corresponding lack of experimental data bearing directly on the arrangement of the nuclei in molecules of the hydrides of boron. Electron diffraction methods have now provided some of the information needed. In this way it has already been shown[3] that the configurations of $B_2H_6$ and $B_5H_9$ are very different from those proposed by Wiberg; in this report investigations are described which lead to new structure assignments for the first two members of the $B_nH_{n+6}$ group, and which show that diborane is structurally similar to the latter compounds.

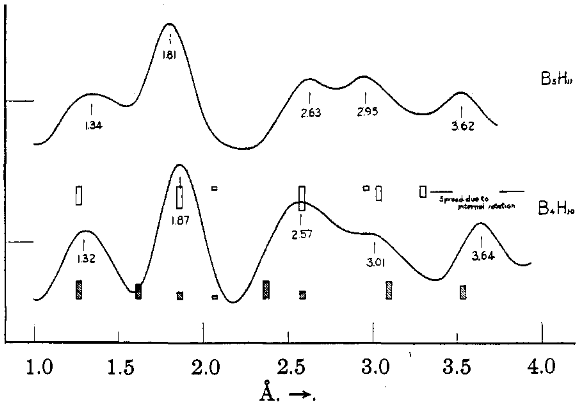

Fig. 1.—Modified radial distribution curves for $B_4H_{10}$ and $B_5H_{11}$. For the former, the important peaks to be expected on the basis of the butane-like model (open rectangles) and Wiberg's model (cross-stroked rectangles) are indicated. A similar situation exists for $B_5H_{11}$.

## Experimental Details

The samples of tetraborane and pentaborane (equivalent approximately to 15 cc. of gas, S. T. P.) were prepared by Dr. A. B. Burg of Chicago,[4] packed in dry-ice, and shipped to this Laboratory. The compounds were then purified by fractional condensations ($B_4H_{10}$ was passed through a trap at $-85°$ and collected at $-110°$; $B_5H_{11}$ was passed through a trap at 0° and caught at $-80°$) and immediately used in the diffraction experiments. They were performed with the boranes at $-12$ and 35°, respectively. In both cases the wave length of the electrons scattered was 0.0613 Å. and the camera distance 10.84 cm. Over ten good photographs of varying densities were obtained for each hydride; their visual appearances plotted on an $s$ scale are indicated in Figs. 2 and 3, together with the intensity distributions calculated for the various models. The similarity of the two patterns is apparent.

## Analysis of the Data

Modified radial distribution calculations[5] using corrected values for the intensities (Tables I and II) are plotted in Fig. 1. Within 3%, the same prominent distances are indicated for both molecules, and these in turn are very near the interatomic separations finally chosen.

(a) 1.32–1.34 corresponds to $\mathrm{B}\longleftrightarrow\mathrm{H}$
(b) 1.81–1.87 corresponds to $\mathrm{B}\longleftrightarrow\mathrm{B}$
(c) 2.57–2.63 corresponds to $\underset{\diagdown\,\mathrm{B}\,\diagup}{\mathrm{B}\longleftarrow - - \longrightarrow\mathrm{H}}$
(d) 2.95–3.01 corresponds to $\underset{\diagdown\,\mathrm{B}\,\diagup}{\mathrm{B}\longleftarrow - - \longrightarrow\mathrm{B}}$
(e) 3.62–3.64 numerous variable distances due to internal rotation

From the curves the following important conclusions may be deduced:

(1) The B–H and B–B distances are larger than would be expected from the sum of the radii (1.21 and 1.78, respectively).[6] The values of (c) and (d) confirm those of (a) and (b) if bonding angles close to tetrahedral are assumed. In diborane a parallel situation exists.[3]

(2) The (B–B/B–H) ratio $(1.84/1.33 = 1.384)$ is smaller than the corresponding value for diborane (1.465).

(3) The observed distribution curve is in harmony with that expected on the basis of the chain-like models involving one B–B separation (case of $B_4H_{10}$—open rectangles, Fig. 1) while it is in definite disagreement with the curve predicted from Wiberg's models (cross-stroked rectangles) which have two types of B–B bonds thus requiring a broad or split peak in the region 1.67–1.87 Å. The peak at 1.81 or 1.87 is narrow.

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(3) See papers I and II of this series, This Journal, **58**, 2403 (1936), and **59**, 1906 (1937).

(4) According to a private communication from Dr. Burg, these samples were separated from a quantity of diboranes which had been standing at room temperature for about three months. The pentaborane was purified in the manner described by Burg and Schlesinger, *ibid.*, **55**, 4009 (1933). The tetraborane, which at first contained a trace of boron trichloride, was freed from that impurity by treatment with methyl ether; the stable non-volatile compound $(CH_3)_2OBCl_3$ was formed, as reported by E. Wiberg and W. Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 22 (1931). The excess of methyl ether was removed easily by fractional condensation.

(5) Modifications of the usual procedure have been suggested by V. F. H. Schomaker, who soon will publish an account of his investigations in This Journal.

(6) For a discussion on the applicability of the "radii," see note **16**.

The following types of models were investigated in detail.

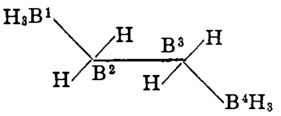
**Tetraborane, $B_4H_{10}$.**—

MODEL 1. Forked chain (isobutane-like); Fig. 2A, B–B = 1.86. B–H = 1.27. All valence angles were assumed to be tetrahedral. Rotation of the $BH_3$ groups was taken into consideration by giving equal weight to all configurations produced by 60° rotations.

MODEL 2. Structure of Wiberg; Fig. 2B. It is difficult to write an unambiguous spatial arrangement to correspond to

$$H_2H^+B^-{=}B^-H^+H{-}HH^+B^-{=}B^-H^+H_2$$

The configuration for which the theoretical intensity curve was calculated is represented by the planar arrangement



$B^1B^2 = B^3B^4 = 1.62$ (double bond factor 87%).[7] $B^2B^3 = 1.86$. BH = 1.27. All valence angles were assumed to be tetrahedral except $\angle B^1B^2B^3 = \angle B^2B^3B^4 = 125°16'$.

MODEL 3. Straight chain (butane-like). B–B = 1.86. B–H = 1.27. Ratio (B–B/B–H) = 1.465. All valence angles were assumed to be tetrahedral. Rotation of the $BH_3$ groups was taken into account. The calculation was divided into two parts; the first involving only the distances which are not affected by internal rotation (Model $3_0$; Fig. 2C′), and the second, a set of three calculations in which the variable distances belonging to the three configurations differing from each other by a 90° rotation about a B–B bond (3a, planar zigzag chain; 3b, planar c form; 3c, one $BH_3$ group out of the plane formed by the other three boron atoms) have been added to the values of $3_0$. The mean of the curves weighted by the factors 2, 1, 4, respectively, was taken as representing the intensity distribution which would be observed (Fig. 2C). As will be noticed from the curves and from Table I, the differences between the values of *s* for the maxima and minima of model $3_0$ and model 3a, b, c (mean) are negligible and the former may be taken as a sufficiently good approximation for the latter. However, the individual curves of the group (3a, b, c) do not represent approximations reliable enough for quantitative considerations.

MODEL $4_0$. As model $3_0$ but ratio (B–B/B–H) = 1.409; Fig. 2D.

MODEL $5_0$. As model $3_0$ but ratio (B–B/B–H) = 1.525.

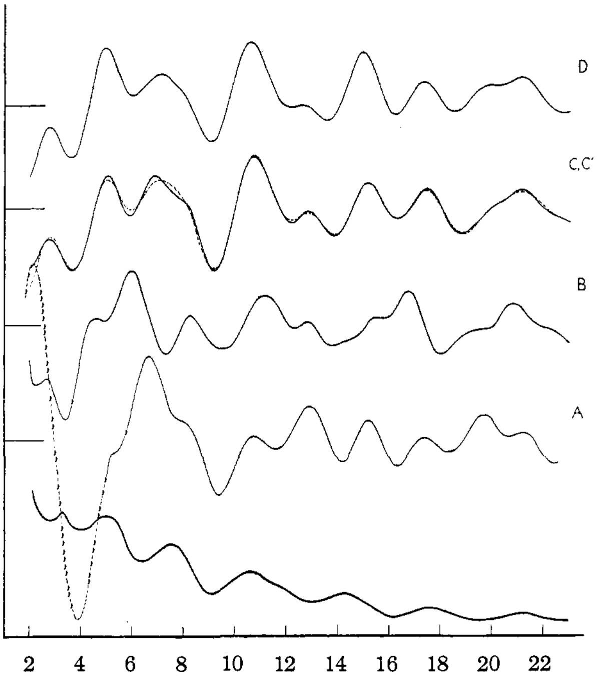


Fig. 2.—$B_4H_{10}$: The observed intensity and that calculated for various models. C is the full curve; C′ is dashed. Terms involving an $l_{ij} > 4$ have been neglected in the region of $s > 20$.

Comparison of the observed intensity distribution with that predicted on the basis of models 1 and 2[8] clearly indicates that they cannot be correct. The wide discrepancy between the general form of curves A and B of Fig. 2 and that of the experimentally determined one further leads to the conclusion that all reasonable variations of the parameters used in the calculations would not result in satisfactory structures. This is substantiated by the fact that changing the (B–B/B–H) ratio in model 3 affects only the relative intensities of the peaks but does not change the general shape of the curve. On the other hand, the distributions of scattered electrons calculated using models 3, 4 and 5 reproduce well

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[7] L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

[8] The factor which superposes the theoretical curves upon a continuously decreasing background has been omitted from the calculations, as is customary.

the form of the observed pattern. As has been indicated above, the $3_0$, $4_0$ and $5_0$ approximations appear to be good enough; a careful study of the curves, considering the relative intensities of peaks 2 and 3, the prominence of the shoulder on 4, and the relative intensities of maxima 5 and 6, suggests that the best value for the (B–B/B–H) ratio is between 1.409 (Fig. 2D) and 1.465 (Fig. 2C′).

Variations as much as 10% in the individual B–B separations within the molecule are completely eliminated by curve 2B; smaller differences appear improbable due to the fact that the peak corresponding to the B–B separation in the radial distribution curve is sharp and intense. Three or four membered ring models were not considered, not only because such configurations would necessitate that some boron atoms have a valence greater than four, but also because curves predicted from them undoubtedly would be unsatisfactory.[9]

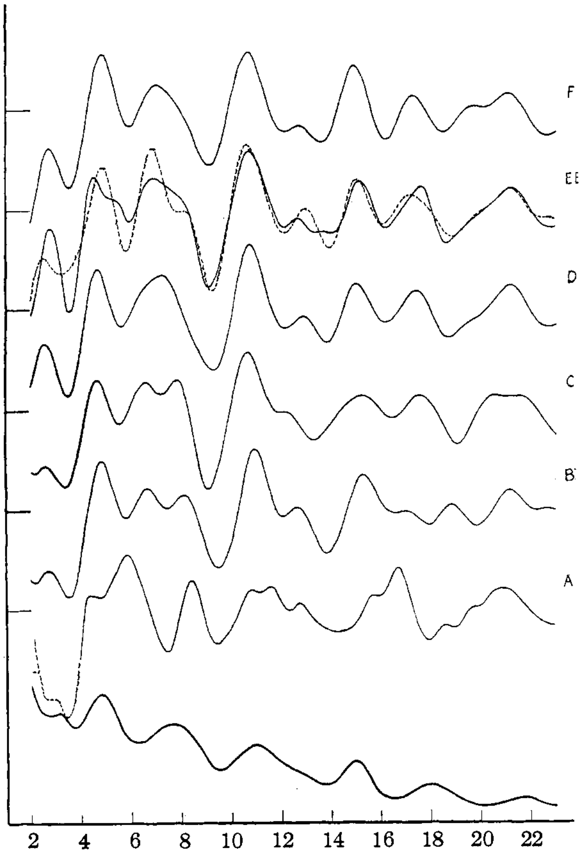

Fig. 3.—$B_5H_{11}$: Intensity observed and that calculated for various models. E is the continuous curve; E′ dashed. Terms involving an $l_{ij} > 4$ have been neglected in the region of $s > 20$.

In Table I a comparison is made between the $s_{\text{obsd.}}$ and $s_{\text{calcd.}}$ for models $3_0$, 3a, b, c (mean) and $4_0$. The individual values scattered more than is usual, particular discrepancies showing for peaks possessing structure. As would be expected, the diameters of the corresponding rings obtained from photographs of low density differed from those measured on heavily exposed photographs, thus introducing an uncertainty in the corresponding $s$ values. Two methods of averaging are therefore indicated; the results differ by less than the experimental error. In summary, tetraborane has a chain-like structure corresponding to butane, with the following interatomic distances

B–B = 1.84 ± 0.04 Å.; B–H = 1.28 ± 0.03 Å.

leading to 1.436 for the (B–B/B–H) ratio. The valence angles are close to tetrahedral and rotation about the various B–B bonds must be assumed.

TABLE I

$B_4H_{10}$

| | | $s_{\text{obsd.}}$ | $I$ | $I_{\text{corr.}}$ | $s_{\text{calcd.}}/s_{\text{obsd.}}$ Model $3_0$ | Model 3 | Model $4_0$ |
|---|---|---|---|---|---|---|---|
| 1 | | 3.27 | 22 | 20 | (0.853) | (0.844) | (0.850) |
| | 2 | 4.04 | | | .913 | .908 | .893 |
| 2 | | 4.99 | 20 | 46 | 1.004 | 1.012 | 1.000 |
| | 3 | 6.33 | | | 0.942 | 0.931 | 0.946 |
| 3 | | 7.58 | 15 | 74 | .943 | .950 | .936 |
| | 4 | 9.07 | | | 1.012 | 1.016 | 1.003 |
| 4 | | 10.80 | 9 | 78 | 0.993 | 0.992 | 0.981 |
| | 5 | 12.86 | | | 1.079 | 1.075 | 1.056 |
| 5 | | 14.27 | 4 | 43 | 1.062 | 1.062 | 1.048 |
| | 6 | 16.06 | | | 1.014 | 1.014 | 1.009 |
| 6 | | 17.61 | 2 | 23 | 0.988 | 0.990 | 0.982 |
| 7 | | 21.2 | 1 | 11 | .997 | .997 | .995 |
| Mean (omitting 5th max. and min.) | | | | | 0.978 | 0.979 | 0.972 |
| Average deviation | | | | | .031 | .033 | .031 |
| B–B distance | | | | | 1.82 | 1.82 | 1.81 |
| B–H distance | | | | | 1.24 | 1.24 | 1.28 |
| Mean (total) | | | | | 0.995 | | 0.986 |
| Average deviation | | | | | .036 | | .035 |
| B–B distance | | | | | 1.85 | | 1.83 |
| B–H distance | | | | | 1.26 | | 1.30 |

Final values B–B 1.84 ± 0.04 Å.
B–H 1.28 ± 0.03 Å.

**The Pentaborane, $B_5H_{11}$.**—

MODEL 1. Corresponding to the structure of Wiberg

$$\mathrm{H_2H^+B^-{=}B^-H^+H{-}HH^+B^-{=}B^-H^+{=}B^-H^+H_2}$$

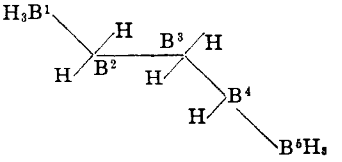

Fig. 3A.

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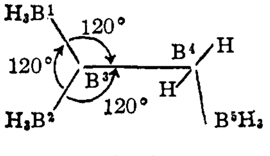
(9) Refer to the intensity distribution obtained for such models in the case of $B_5H_9$ (I).

Boron atoms are coplanar. All B–B distances equal to 1.62 (double bond factor 87%) except $B^2B^3 = 1.86$. B–H = 1.27. $B^3$, $B^4$, $B^5$ are collinear. All angles were assumed to be tetrahedral except $\angle B^1B^2B^3 = \angle B^2B^3B^4 = 125°16'$.

MODEL 2. Forked chain; Fig. 3B.



Valence bonds of the central atom ($B^3$) coplanar. All B–B distances equal to 1.76 except $B^4B^5 = 1.86$, B–H = 1.27. All valence angles were assumed to be tetrahedral except where indicated. In the calculation, the rotation of $B^5H_3$ about the bond $B^3B^4$ was taken into account but all BH distances which are variable due to the rotation of hydrogen atoms (of a $BH_3$ group) in their plane, have been neglected.[10]

MODEL 3. Forked chain; Fig. 3C. As model 2 except that all B–B separations were taken equal to 1.86.

MODEL 4. Forked chain, isopentane-like; Fig. 3D. All valence angles were assumed to be tetrahedral. B–B = 1.86. B–H = 1.27. Approximations used in this calculation are the same as those used for model 2.

MODEL 5. Straight chain, pentane-like: B–B = 1.86. B–H = 1.27. Ratio (B–B/B–H) = 1.465. All valence angles were assumed to be tetrahedral. The electron diffraction method is not sufficiently sensitive to distinguish between configurations differing only as to whether the boron atom to which one hydrogen is attached is in the 2- or 3-position. To simplify the calculations, the structure of the greatest symmetry was used. The procedure followed was similar to the one employed in calculating the theoretical intensity curves for model 3 of tetraborane. Curve $5_0$ involving the non-variable distances was calculated first and then the specific curves 5a, b, c, d, e, f were obtained for the various configurations resulting from 90° rotations about B–B bonds. Curves for the two extreme forms are given (5a, planar zig-zag chain, Fig. 3E; 5f, planar pentagon, Fig. 3E′); the others have forms intermediate between them. Since the exact locations of the extreme values would depend upon an arbitrary weighting of the component curves, a mean was not calculated.

MODEL $6_0$. As model $5_0$ but the ratio (B–B/B–H) = 1.409; Fig. 3F.

MODEL $7_0$. As model $5_0$ but the ratio (B–B/B–H) = 1.525. That models $6_0$ and $7_0$ may be used as sufficiently good approximations to determine the best value for the ratio (B–B/B–H) is justified by reasons identical with those given in the case of tetraborane.

From the curves of Fig. 3 it is clear that models 1, 2, and 3 are not correct; a detailed comparison of 2 and 3 (involving a radius change of the tricoördinated boron) further suggests that reasonable variations of the parameters would not remove the discrepancy. The curve for model 4 reproduces all the features of the observed pattern and could be brought into complete agreement with the experimentally observed peak heights by choosing a smaller value for the (B–B/B–H) ratio. Models $5_0$, $6_0$, and $7_0$ also lead to curves having the proper form. Of these, Fig. 3F apparently has the added virtue that the relative intensities of peaks 2 and 3, 5 and 6, and the prominence of the shoulder to the right of 4 correspond closely to those observed.

From Fig. 3E′, it is evident that a five-membered ring would not be satisfactory. It is only when the contribution of this particular arrangement to the straight chain pattern is made relatively small that its disturbing form introduces no difficulties. Three and four membered ring structures have not been investigated. That the intensity of scattering which would be predicted from them would not be acceptable can be deduced from the curves calculated for similar arrangements of $B_5H_9$(I). A chain-like model with the valences of the middle boron atom like those of the central atom in model 2 ($sp^2$ bonds) may be also eliminated on basis of the corresponding curve calculated for the stable pentaborane, and from the comparison of curves Fig. 3B, C, and D. We may therefore conclude that the unstable pentaborane has a structure analogous to pentane or isopentane, with a (B–B/B–H) ratio close to 1.409. The difficulty of distinguishing between the forked and straight chain models is to be expected for the

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[10] For justifications of this approximation refer to L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937), who considered the case of neopentane and paper III of this series where borine trimethylammine is discussed. I also proved this to be justifiable for model 5a of $B_5H_{11}$.

longer boranes, since the amplitudes of the higher frequency sin $x/x$ terms become almost identical for the two cases.

The fact that the appearance of the 6th and 7th maxima is so profoundly altered in going from Fig. 3B to C indicates that a 5% variation in the B–B distances within the molecule would be sufficient to destroy the observed agreement. Smaller variations have not been considered; the tricoördinated boron atom would probably have a radius less than the observed mean.[16] Ratios of $s_{\text{obsd.}}$ to those calculated for models 4, 5a, f, and $6_0$ are tabulated in Table II. The fluctuations between the values obtained from the various rings is that usually found. As will be noticed, the final interatomic separations derived from 5a and 5f are identical and within the experimental error equal to those deduced from the other models tabulated. The presence of all the possible arrangements 5a–5f explains the fuzziness of the peaks 2, 3, and the shoulder of 4, with the consequent lack of detailed structure.

TABLE II

$B_5H_{11}$

| | | | | | $s_{\text{calcd.}}/s_{\text{obsd.}}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | | $s_{\text{obsd.}}$ | $I$ | $I_{\text{corr.}}$ | Model 4 | Model 5a | Model 5f | Model $6_0$ |
| 1 | | 3.10 | | | (0.832) | (0.900) | (0.813) | (0.894) |
| | 2 | 3.81 | | | .916 | .932 | .848 | .940 |
| 2 | | 4.84 | 10 | 22 | .967 | .938 | 1.008 | 1.006 |
| | 3 | 6.24 | | | .901 | .950 | 0.934 | 0.951 |
| 3 | | 7.67 | 5 | 25 | .945 | .945 | .955 | .932 |
| | 4 | 9.50 | | | .979 | .957 | .972 | .960 |
| 4 | | 10.99 | 3 | 24 | .978 | .975 | .966 | .970 |
| | 5 | 13.72 | | | 1.009 | .995 | 1.013 | .991 |
| 5 | | 14.56 | 2 | 20 | 1.032 | 1.038 | 1.032 | 1.025 |
| | 5 | 16.44 | | | 0.986 | 0.986 | 0.977 | 0.985 |
| 6 | | 17.95 | 1 | 12 | .970 | .980 | .958 | .964 |
| 7 | | 21.69 | $^1/_2$ | 6 | .979 | .978 | .975 | .974 |
| Mean | | | | | .969 | .970 | .967 | .973 |
| Average deviation | | | | | .026 | .021 | .030 | .022 |
| B–B distance | | | | | 1.80 | 1.80 | 1.80 | 1.81 |
| B–H distance | | | | | 1.23 | 1.23 | 1.23 | 1.28 |

Final values B–B 1.81 ± 0.03 Å.
B–H 1.26 ± 0.03 Å.

The configuration of $B_5H_{11}$ therefore corresponds either to that of pentane or isopentane.[11] The best values of the interatomic distances appear to be: mean B–B = 1.81 ± 0.03 Å.; B–H = 1.26 ± 0.03 Å. The observed angles are close to tetrahedral and internal rotation must be assumed.

## Discussion

A summary of the various boron–boron and boron–hydrogen internuclear separations already determined is given in Table III. It is seen that diborane is structurally related to the members of the $B_nH_{n+6}$ series, as was stated in the introductory section of this paper. A reaction analogous to a Wurtz synthesis has been definitely established

$$2B_2H_5I + 2Na \longrightarrow B_4H_{10} + 2NaI$$

The B–H separations in the first three compounds listed in Table III seem to be uniformly large while the B–B distances appear (in spite of the large experimental error) to decrease progressively from a high value to one almost equal to twice the boron radius. This is readily explicable in terms of the varying contributions to each bond of one-electron-bond and no-bond structures introduced by the "electron deficiency" of the molecule as a whole. The problem was discussed at length in paper II, for the case of diborane; to make the extension to $B_4H_{11}$ and $B_5H_{11}$ one must specify further that structures involving a one-electron-bond or a no-bond between two boron atoms have a higher energy content than configurations with such bonds between a boron and hydrogen atom,[12] and thus contribute to a lesser extent to the ground state. As the number of atoms in the molecule increases, the B–B links tend to be more fully covalent at the expense of the B–H bonds resulting in a boron–boron separation closer to that expected for a pure covalent bond. In terms of molecular orbitals the above could be expressed by the statement that apparently structures having a completely filled orbital of the type analogous to $[\sigma + \sigma, a_{1g}]^2$ of diborane are of a lower energy than those having the correspondingly completed $[\pi e]^4$ orbital. It is interesting to note that the tricoördinated boron atom in $B_5H_{11}$ appears to be like the other boron atoms with regard to its valence angles in spite of its supposed $sp^2$ bonds. Pentaborane ($B_5H_9$) does not show the effect of its "electron deficiency" presumably because of the triply bonded boron. However, it is difficult to see why a boron atom surrounded by a sextet with its valence angles greatly distorted to form the ring should contribute particularly to the stability

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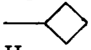
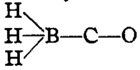
(11) If the sample used were a mixture of the isomers one would have to conclude that their physical constants are unusually alike. When the vapor pressure curve was originally determined by Burg and Schlesinger,[4] they found that after repeated fractionations the vapor pressure of successive samples was exactly constant (= 53.0 mm. at 0°). For comparison, the boiling points of pentane and isopentane are 37 and 30°, respectively.

(12) This would be expected on basis of the slightly greater electronegativity of boron.

TABLE III

| Compound | Electron deficiency[13] | Structure | B–B | B–H | $k_{B-B}$[14] | $k_{B-H}$ | Source |
|---|---|---|---|---|---|---|---|
| $B_2H_6$ | 2 | Ethane-like | 1.86 ± 0.04 | 1.27 ± 0.03 | 0.113 ± 0.01 | 0.228 ± 0.02 | II |
| $B_4H_{10}$ | 4 | Butane-like | 1.84 ± .04 | 1.28 ± .03 | .119 | | V |
| $B_5H_{11}$ | 4 | Pentane or iso-pentane-like | 1.81 ± .03 | 1.26 ± .03 | .129 | | V |
| $B_5H_9$ | 4 |  | 1.76 ± .02 | 1.17 ± .04 | .148 | .320 ± .04 | I |
| $H_3BCO$ | 0 |  | | 1.20 ± .03 | | .287 ± .03 | III |
| BH | 0 | Linear | | 1.226 | | .263 | Note 15 |
| Radius sum (extrapolated) | | | 1.78 | 1.21 | | | Note 16 |

of a compound when a corresponding $sp^2$-bonded boron in an open chain does not.

The investigation of $B_4H_{10}$ and $B_5H_{11}$ completes the study of the known stable members of the $B_nH_{n+6}$ group;[17] of the $B_nH_{n+4}$ series there remain yet $B_6H_{10}$ and $B_{10}H_{14}$. It is a matter of great interest to determine whether the structures of the latter have four-membered ring systems upon which their stability may depend, as has been suggested by Prof. Pauling and the author (I). Unfortunately, the present electron diffraction investigations have been terminated at this stage.

We may now list an empirical set of conditions with which the formulas of the hydrides of boron would tend to comply.

**a.** A boron atom cannot have more than four orbitals (Pauli exclusion principle for first row elements).

**b.** The greatest stability is attained when each boron atom makes use of all its orbitals. (In a number of cases full use of the orbitals is possible only when an "electron deficiency" in the molecule is introduced, and simultaneously the possibility of resonance.)

**c.** The "electron deficiency" tends to be even (if odd, the ground state will be at least doublet, and probably with several near-lying excited states, a condition usually associated with high energy or particular reactivity in the case of large molecules).

**d.** The "electron deficiency" of the boron compounds whose structures are known is not greater than four.[18] As a tentative final condition let us consider this to be generally valid.

One may now better understand the constitution of the hydrides.

α.—Members of a series analogous to the hydrocarbons, $B_nH_{2n+2}$ or $B_nH_{2n+1}$ ($n$ even or $n$ odd, respectively—rule **c**) would not be stable (rule d).[19] The formulas $B_2H_6$ and $B_3H_7$ should be grouped with the series $B_nH_{n+4}$ since they comply with rule **d**.

β.—Structures involving double bonds between some atoms in a molecule would not contribute to an appreciable extent to the ground state when at the same time other bonds in this molecule are of the one-electron type. Hence an olefin series, $B_nH_{2n}$ or $B_nH_{2n-1}$ ($n$ even or $n$ odd, respectively) would not be stable.

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(13) The "electron deficiency" is set equal to twice the number of valence bonds minus the total number of valence electrons; hence its value depends upon the structure assigned to the compound.

(14) Force constant for the stretching vibration (in megadynes per cm.) calculated by means of Badger's equation; *J. Chem. Phys.*, **2**, 128 (1934). One therefore would expect that the characteristic B–B frequency would gradually increase in going from the compounds at the top of the list to those at the bottom, whereas the frequency of the B–H vibration would remain fairly uniform for $B_2H_6$, $B_4H_{10}$, and $B_5H_{11}$.

(15) H. Sponer, *Molekülspektren*, Vol. I, Verlag von Julius Springer, Berlin, 1935.

(16) For the extrapolation, see L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934). It may be argued that in the case of boron the concept "radius" may be particularly inapplicable since no one assignment can account for the observed distances. One should realize, however, that *all* the deviations except those for the hydrides of boron lead to a *smaller* value of the radius than the one obtained from the extrapolation, and that in most of those cases an explanation may be presented to account for the discrepancy. See H. A. Lévy and L. O. Brockway, THIS JOURNAL, **59**, 2085 (1937), and paper IV of this series.

(17) The existence of $B_6H_{12}$ has been suspected. An analysis gave $(BH_2)_x$ for the empirical formula but an attempted molecular weight determination led to 65.2 rather than 77. However, the substance is highly unstable and there was unmistakable evidence that decomposition producing hydrogen had taken place during the measurement. Its relatively low melting point would classify it as a member of the $B_nH_{n+6}$ series with $n = 6$, but $B_6H_{10}$ cannot yet be definitely excluded. It is interesting to note that on the basis of the set of rules formulated in the latter part of this paper one would expect $B_6H_{12}$ to be more stable than $B_6H_{10}$ though less stable than $B_5H_{11}$ (rules **b** and d).

(18) The electron deficiency of $B_6H_{12}$ (chain-like structure, analogous to $B_4H_{10}$ and $B_5H_{11}$) would be four, while that of decaborane (double four-membered ring configuration) might be six. It is, of course, impossible to estimate the deficiency of the compound $(BH)_x$ [A. Stock and W. Mathing, *Ber.*, **69**, 1469 (1936)] or of the substance suspected of being $B_5H_x$ [A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4009 (1933)]. Both compounds are solids at room temperature.

(19) The word *stable* needs qualification. Whether a compound exists in the chemical sense depends upon a variety of factors, such as (1) the rates of the reactions involved in its synthesis; (2) the rate of its thermal decomposition; (3) reactivity of the compound toward itself and toward other compounds, etc. Further, its physical state plays an important role in limiting the extent to which 2 and 3 progress. In the statements α-δ, stability with regard to thermal decomposition in the gas phase is considered.

γ.—Of the $B_nH_{n+6}$ series, the compounds with $n = 1$, 2 or 3 could not exist (rule **a**) and those with $n > 5$ would tend to become increasingly unstable as $n$ grew larger (rule **b**).

δ.—If the four-membered ring system is the fundamental nucleus of the $B_nH_{n+4}$ series (for $n \geqslant 4$), the compounds $B_7H_{11}$ and $B_8H_{12}$ would tend to be relatively unstable just as $B_6H_{10}$ is clearly less stable than either $B_5H_9$ or $B_{10}H_{14}$ (rule **b**).

ε.—The non-existence of $BH_3$ has already been accounted for qualitatively by R. S. Mulliken;[20] 44 kcal. has been estimated (paper II) as a minimum value for the heat evolved in the reaction $2BH_3 = B_2H_6$.

Among the consequences of the present set of investigations there are the following outstanding ones.

Definite configurations have been assigned to a number of the hydrides of boron and their derivatives; interatomic distances in these molecules have been determined.

These configurations are in harmony with the known chemical and physical data;[21] furthermore, they lead to a logical set of rules, which although qualitative and incomplete indicate that the constitutions of the hydrides of boron do follow an orderly scheme.

The structural theory of Wiberg was unquestionably eliminated. First, results of the electron diffraction method indicate that for those hydrides of boron which have been studied, the molecular dimensions are much too large to allow double bonds to be present; second, direct evidence is available that all the hydrogen atoms are equivalent in diborane and, indirectly, a case of nonequivalence in tetraborane would have led to differing B–B distances within the molecule, contrary to observation.

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## Summary

An electron diffraction investigation of tetraborane and the pentaborane $B_5H_{11}$ led to the following conclusions. $B_4H_{10}$ has a configuration analogous to butane; the B–B distance is equal to 1.84 ± 0.04 Å. and B–H = 1.28 ± 0.03 Å.[22] The structure of $B_5H_{11}$ is similar to that of either pentane or isopentane (the location of the trivalent boron atom cannot be determined); the mean B–B separation is 1.81 ± 0.03 Å. and B–H = 1.26 ± 0.03 Å. In both cases the valence angles are close to tetrahedral and internal rotation must be assumed. The implications suggested by the observed distances with regard to the electronic configuration of the respective molecules are discussed briefly and it is pointed out that the structural data as well as chemical evidence clearly place diborane with the compounds of the $B_nH_{n+6}$ group. A set of rules, some of qualitative nature, is deduced to help formulate the constitution of the hydrides of boron.

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[20] R. S. Mulliken, *J. Chem. Phys.*, **3**, 635 (1935).

[21] See Wiberg,[1] p. 2834; also II and H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

[22] At the Indianapolis meeting of the A. A. A. S., at which a report of this work was given, the question was raised whether the assignment of a definite value to the B–H separation is justifiable since the scattering power of hydrogen is so low. It is true that to locate an individual H atom is not possible by the X-ray or electron diffraction method; but in a compound containing a large proportion of hydrogen, particularly when the heavier atoms are first row elements, a mean X–H distance may be determined with the accuracy specified. This is evident from the following argument.

Every B–B distance in a borane molecule contributes to the total intensity an amount proportional to $(5 \times 5)(\sin s\, l_{B-B}/s\, l_{B-B})$. Since there are roughly two hydrogen atoms per boron, there is an additional contribution of $(4 \times 5 \times 1.25)\ (\sin s\, l_{B-H})/s\, l_{B-H})$, which directly determines the B–H separation, *plus* the term $(4 \times 5 \times 1.25)\ (\sin s\, l_{\underset{\diagdown B \diagup}{B \longleftrightarrow H}}/s\, l_{\underset{\diagdown B \diagup}{B \longleftrightarrow H}})$, *plus* lower frequency terms involving both the B–B, B–H distances, and the valence angles. The intensity distribution is consequently greatly affected by the positions of the hydrogen atoms.