[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 566]

The Structure of the Pentaborane B_5H_9

BY S. H. BAUER AND LINUS PAULING

The hydrides of boron are especially interesting to the chemist because of the failure of the usual valence theory to account for their observed formulas and properties. Despite the large amount of experimental[1] and theoretical[2] work which has been done in this field in recent years, little progress has been made in assigning structural formulas to these substances, and it seems probable that in order for this to be done with confidence it will be necessary to obtain information about the structure of the molecules by the application of physical methods. Electron diffraction and x-ray methods have been applied in a few cases: the boron–boron distance in B_2H_6 has been evaluated as 1.8–1.9 Å. from x-ray powder photographs,[3] the structure of $B_3N_3H_6$ has been shown to be similar to that of benzene by an electron-diffraction study,[4] and the unit of structure and space-group symmetry of $B_{10}H_{14}$ have been determined.[5] We have now investigated the pentaborane B_5H_9 by the electron diffraction method, and have found a model which accounts satisfactorily for our photographs and which can be accepted with considerable confidence as representing correctly the atomic arrangement in molecules of this substance.

Preparation of the Photographs.—We were provided with 18 cc. (S. T. P.) of B_5H_9 gas through the generosity of Dr. Anton B. Burg of the University of Chicago. The substance (with melting point −46.9° and vapor pressure 65 mm. at 0°) had been prepared from diborane by the method of Schlesinger and Burg[6] and purified by repeated fractional condensation. The amount of boron trichloride and foreign boron hydrides present is believed to have been very small.

Eleven useful photographs, of varying density, were prepared with the electron diffraction apparatus designed and recently described[7] by Brockway, using the standard technique of handling the borane.[8] The gas was kept at liquid-air temperature in a bulb connected with the nozzle of the apparatus through a stopcock and was warmed to room temperature only long enough for each exposure to be made, in order to minimize the chance of decomposition and reaction with stopcock grease. The film distance was 10.43 cm. and the electronic wave lengths used about 0.06 Å.

Description and Interpretation of the Photographs.—The photographs show five rings, with the qualitative character sketched in Fig. 1. The first ring appears as a small maximum followed by a barely perceptible minimum, the second ring looking like a shelf. The third ring is sharp and strong, with well-pronounced minima on each side. The fourth ring appears broad, and the fifth sharp. Values of s ($= (4\pi \sin \theta/2)/\lambda$) for the apparent maxima and minima are given in Table I; these are averages of closely-agreeing measurements made on eleven photographs by two experienced observers (Brockway and Pauling). Estimated apparent intensities (I) of the rings are also given in the table.

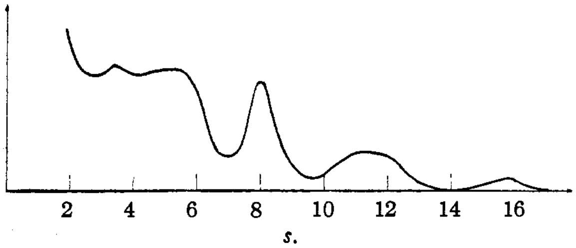

Fig. 1.—Curve representing the visual appearance of electron diffraction photographs of B_5H_9.

TABLE I

Max.	Min.	I	s, obsd.	s, calcd. for model R	B–B, Å.
1		1	3.36	4.18	(2.21)
2		3	5.34	5.59	(1.86)
	3		6.80	6.75	1.767
3		5	8.00	7.94	1.766
	4		9.67	9.40	1.730
4		3	11.49	11.40	1.766
5		1	15.61	15.54	1.771
				Average	1.760

The five-term radial distribution function[9] cal-

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[1] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1932; Stock and collaborators, *Z. anorg. allgem. Chem.*, **225**, 221–270 (1935); H. I. Schlesinger and collaborators, THIS JOURNAL, **58**, 407 (1936), and earlier papers.

[2] See R. S. Mulliken, *J. Chem. Phys.*, **3**, 635 (1935), and references quoted by him.

[3] H. Mark and E. Pohland, *Z. Krist.*, **62**, 103 (1925).

[4] A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).

[5] H. Möller, *Z. Krist.*, **76**, 500 (1931).

[6] I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931).

[7] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[8] See A. B. Burg, THIS JOURNAL, **56**, 499 (1934), and references quoted therein.

[9] L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

culated for these s and I values is shown in Fig. 2. The peaks at 1.17 and 1.73 Å. can be accepted as representing bonded B–H and B–B interactions, respectively, and that at 2.52 Å. as representing in the main the interaction of boron atoms separated by another boron atom in a chain or ring, the ratio 2.52/1.73 corresponding to a B–B–B bond angle of 93°. The outer peaks are not reliable, and the curve provides no further evidence for choice among various ring and chain models.

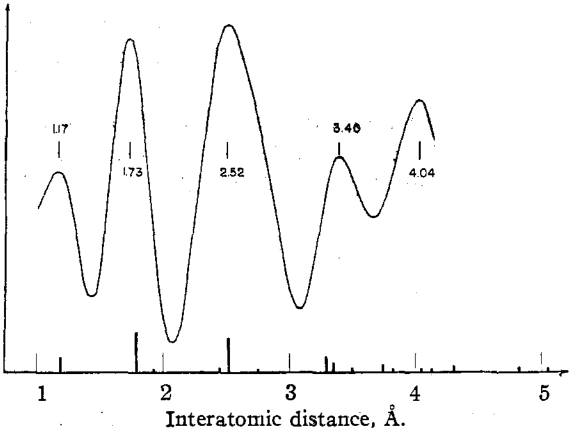
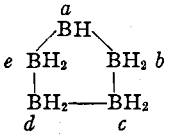


Fig. 2.—Radial distribution curve for B_5H_9. The small rectangles below represent interatomic distances for the final model R.

Intensity curves were calculated for eighteen models, described below. In all of these models except B the B–H distances were taken as 1.18 Å., the sum of the single-bonded radii,[10] this value being supported by the radial distribution value 1.17 Å. Bonded B–B distances were assumed in the neighborhood of 1.78 Å. (the sum of single-bond radii), 1.73 Å. (as given by the radial distribution curve), or 1.60 Å. (sum of double-bond radii). The hydrogen atoms were located at tetrahedron corners for boron atoms forming four bonds and at coplanar triangular corners for boron atoms forming three bonds. The B–B–B bond angles were taken as 109°28′ for boron atoms forming four bonds and 120° for those forming three bonds except where otherwise noted.

A–D, Models of type



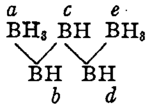
A. All angles 108°; all B–B bond distances 1.78 Å.

B. Same as A, except all B–H distances 1.25 Å.

C. Angles c and d 107°, b and e 105°, a 116°; B–B distances ab and ae 1.66 Å., others 1.78 Å.

D. Angles c and d 106°, b and e 104°, a 120°; B–B distances ab and ae 1.60 Å., others 1.78 Å.

E–G, Models of type

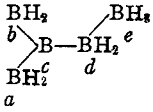


E. All B–B–B angles tetrahedral; B–B distances 1.78 Å.

F. Angles at c 120°, others tetrahedral; B–B distances bc and cd 1.66 Å., others 1.78 Å.

G. Same as F, but with bc and cd 1.60 Å.

H–J, Models of type

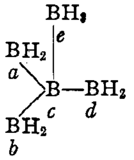


H. B–B–B angles at c 120°, others tetrahedral; B–B distances ca, cb, and cd 1.60 Å., de 1.78 Å.

I. All B–B–B angles tetrahedral; all B–B distances 1.78 Å.; boron atom e oriented to minimize distances ae and be.

J. Same as I, but with maximum values of ae and be.

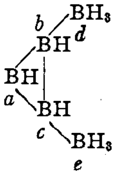
K.



Boron atoms $abcd$ coplanar, with 120° angles at c, and bond ce perpendicular to plane; B–B distances ac, be and cd 1.60 Å., ce 1.78 Å.

L. Same as K but with all angles at c tetrahedral and all B–B distances 1.78 Å.

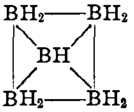
M.



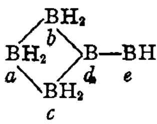
Angles tetrahedral except for distortion to 60° in triangle; B–B distances 1.78 Å.: atoms d and e both above plane of triangle.

N. Same as M except d above and e below plane of triangle.

O. Square pyramid, with BH above plane of BH_2's.
All B–B distances 1.78 Å.



P–R. Models



Angles in coplanar square 90°; HBH angles tetrahedral; all B–B distances 1.78 Å.

P. Boron atom e above plane of square, with angle ade 90°.

Q. Same as P but with ade 135°.

R. All boron atoms coplanar.

In calculating the intensity curves, shown in Figs. 3, 4 and 5, all terms in the expression[11] $I = \Sigma_{ij}Z_iZ_j(\sin l_{ij}s)/l_{ij}s$ were used except those corresponding to two hydrogen atoms separated by three or more boron atoms. Only one orientation of each BH_3 group was considered, the effect of rotation being negligible.

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[10] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[11] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

All models A to N are eliminated by comparison of their curves (Figs. 3 and 4) with the photographs (Fig. 1), there being not even rough qualitative agreement in any case. The discrepancies are so striking as to show that not only these models but also others obtained from them by small changes in distances and angles or by rearrangement of hydrogen atoms are unsatisfactory.[12]

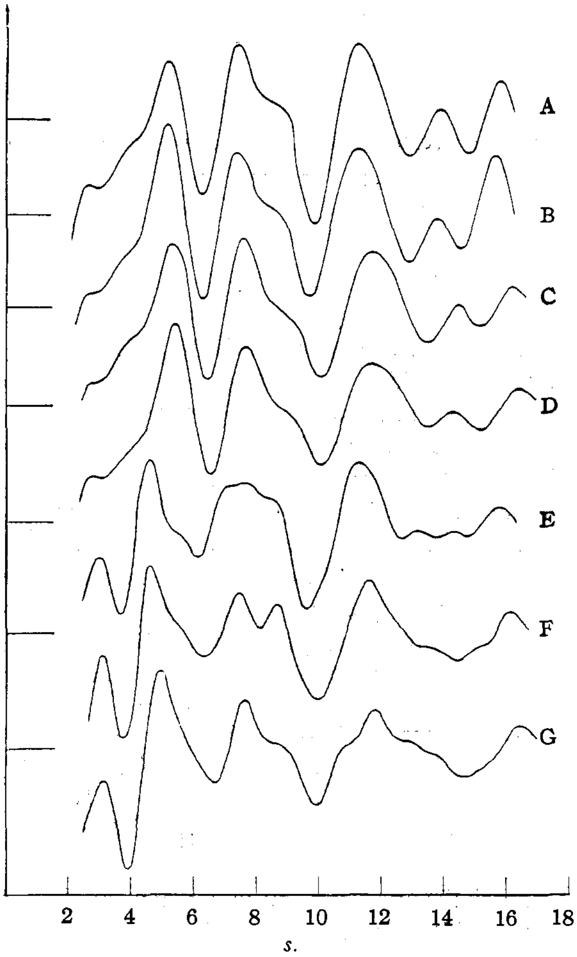

Fig. 3.—Calculated intensity curves for models A to G, with vertical scale twice that in Figs. 4 and 5.

On the other hand, each of the models involving a four-membered square boron ring (Fig. 5) shows rough agreement with the photographs, especially in regard to the strong and sharp third ring. Whereas models O, P and Q are not completely satisfactory, however, the agreement shown by model R is extremely good, the visual appearance of the photographs being well reproduced for all five rings. (The absence on the photographs of a small peak shown at about $s = 14$ on the curve for R may be attributed to the weakness of the photographs in this region, the much larger peak at $s = 16$ appearing only faintly.) We accordingly accept model R as representing the structure of the B_5H_9 molecule. The quantitative comparison of $s_{\text{obsd.}}$ and $s_{\text{calcd.}}$ values shown in Table I leads to the value 1.76 Å. for the B–B distances, with an estimated probable error of ±0.02 Å.

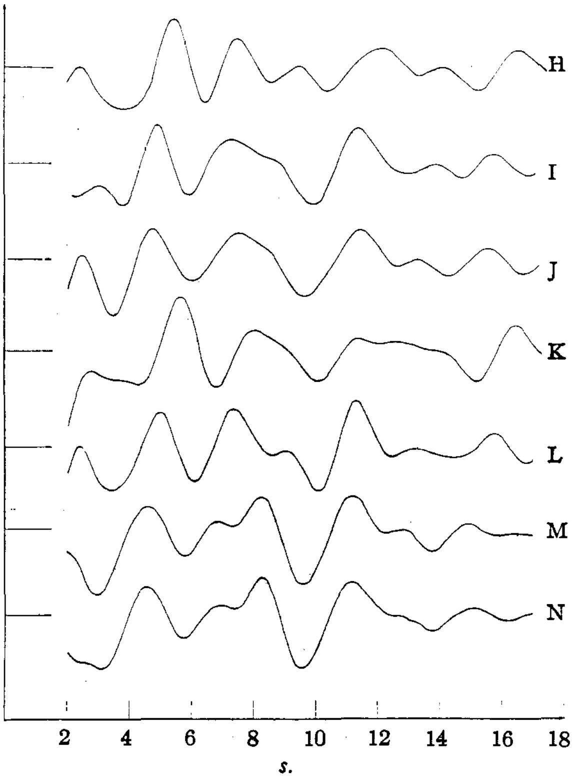

Fig. 4.—Calculated intensity curves for models H to N.

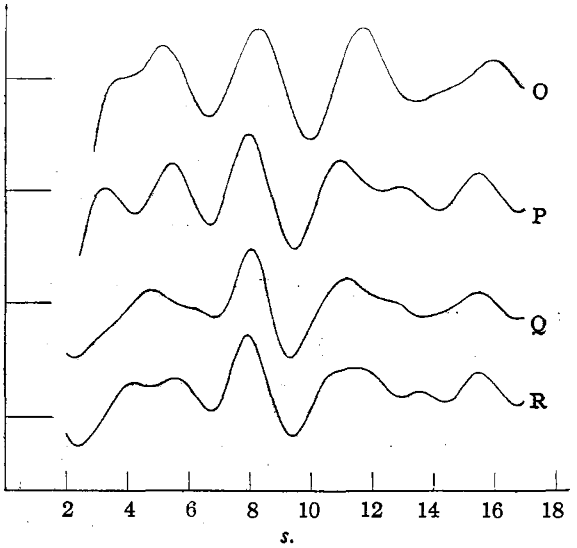

Fig. 5.—Calculated intensity curves for models O to R

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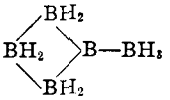
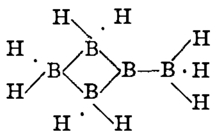
[12] Models A to G were also eliminated by application of the analytic method [S. H. Bauer, *ibid.*, 4, 406 (1936)].

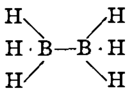
Discussion of the Structure.—We have shown that the various ring and chain models which suggested themselves to us for test are unsatisfactory except for those involving a four-membered ring of boron atoms, and that of these the model in which the fifth boron atom is coplanar with the ring is definitely superior to the others. In this structure



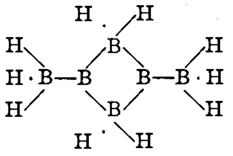
we have not tested the assumed distribution of the hydrogen atoms among the boron atoms; that shown seems to us to be the only reasonable one. The value 1.76 ± 0.02 Å. found for the boron–boron bond distances may be an average of several which differ slightly from one another. For the B–H bond distance the comparison of Table I leads to 1.17 Å., which is, however, determined to a large extent by the assumed model. The radial distribution curve also leads to the value 1.17 Å. We have not endeavored to test the possibility of distortion of the four-membered ring from a square. From experience with other substances we would estimate from the agreement shown by model R that the angles are equal to within about 10° and the B–B distances are equal to within about 5%.

At present discussion of the electronic structure of the boron hydrides is still speculative. We might point out that the structure

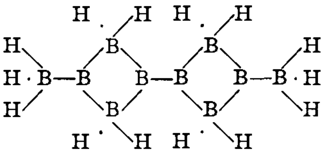


for B_5H_9, involving electron-pair bonds between boron atoms and electron-pair or one-electron bonds between boron and hydrogen atoms,[13] with no more than one one-electron bond per boron atom, is closely similar to the structure  suggested for B_2H_6 by Sidgwick[14] and Pauling,[15] and that these structures are supported by the observed interatomic distances, which correspond to single bonds.

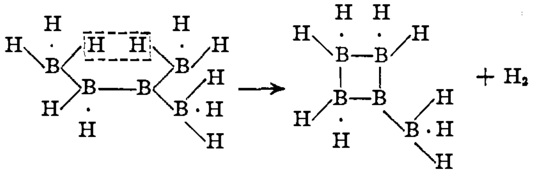
Starting with the basic assumption that a four-membered ring of boron atoms such as is found in B_5H_9 brings about a stability of the hydride as contrasted with a straight or forked chain arrangement which introduces in the other boranes a characteristic lack of stability, we tentatively suggest the related structures



(or the corresponding 1,2-structure) and



for B_6H_{10} and $B_{10}H_{14}$, respectively. Of the entire class of hydrides these show the closest analogies to B_5H_9 in most chemical properties. These structures are compatible in the main with the chemical behavior of the substances. Besides the factor of stability we may mention that the number of molecules of ammonia these boranes add is reported to be equal to the number of one-electron bonds present in the above structures. Further, the reported synthesis of B_5H_9 from B_5H_{11} is reasonably accounted for in the following way



and a similar reaction can be written for the formation of B_6H_{10} from B_6H_{12}. The facts that B_5H_{11} is produced under very similar but milder conditions than is B_5H_9[16] and that under the less stringent circumstances the higher hydride is always present along with the lower one lend strong support to the above equation.

We wish to thank Dr. Anton B. Burg for giving us the pentaborane and for a number of interesting communications, and Dr. L. O. Brockway for the use of the electron diffraction apparatus and for his aid during the investigation.

Summary

From the study of electron diffraction photographs of B_5H_9 it is concluded that the substance

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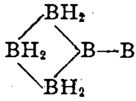
[13] There is, of course, resonance between the B:H and B·H bonds, making the hydrogen atoms equivalent. In these formulas we have used a line to represent an electron-pair bond and a dot to represent a one-electron bond.

[14] N. V. Sidgwick, "The Electronic Theory of Valency," London, 1929, p. 103.

[15] L. Pauling, THIS JOURNAL, **53**, 3225 (1931).

[16] A. Stock and W. Mathing, *Ber.*, **69**, 1456 (1936).

has the structure  $\overset{\mathrm{BH_2}}{\underset{\mathrm{BH_2}}{\mathrm{BH_2}\rangle\mathrm{B{-}BH_3}}}$, the fifth boron atom being coplanar with the square four-membered ring. The values found for interatomic distances are B–B = 1.76 ± 0.02 Å. and B–H = 1.17 ± 0.04 Å.

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The Molecular Structures of the 2-Butenes and the 2,3-Epoxybutanes

BY L. O. BROCKWAY AND PAUL C. CROSS

During an investigation of the reactions of the 2-butenes and some of their derivatives conducted in this Laboratory by Professor Howard J. Lucas[1,2] and his collaborators it was necessary to distinguish between the *cis* and *trans* forms of the 2-butenes and also of the 2,3-epoxybutanes. At the request of Professor Lucas these substances have been investigated by the electron diffraction method of determining the molecular structure of gas molecules. The experimental procedure has been described in detail.[3]

2-Butenes.—The two isomers of 2-butene have boiling points of 3.0 and 0.3°, respectively, at 745 mm. The compounds were photographed at a camera distance of 10.43 cm. with electrons having a wave length of about 0.06 Å. The photographs from each of the compounds show four maxima and in general are very similar in appearance. Two distinguishing features were observed, however. Photographs from the lower boiling butene show a pronounced inner maximum (preceding the first measured maximum at $s = 5.67$ in Fig. 1) which does not appear on the other photographs. The fourth minimum in the photographs of this compound is broad and flat in comparison with the sharp, distinct fourth minimum in the photographs of the higher boiling compound.

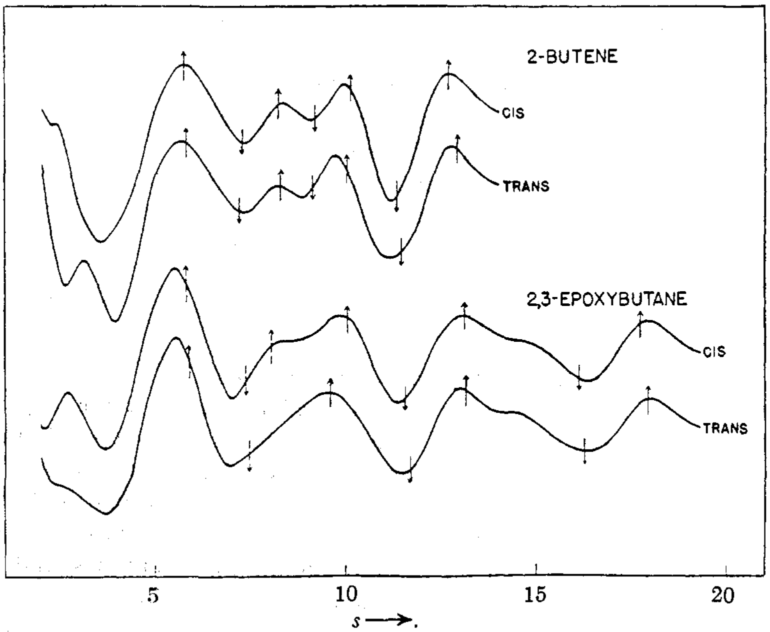

Fig. 1.—Theoretical electron diffraction curves for 2-butenes and 2,3-epoxybutanes. The arrows mark the positions of the observed maxima and minima.

Calculations of the theoretical diffraction curves were made with the aid of the formula, $I = \Sigma_i\Sigma_j Z_iZ_j \frac{\sin sr_{ij}}{sr_{ij}}$, in which r_{ij} is the distance between the *i*th and *j*th atoms; the summations extend over all of the atoms in the molecule. The curves for 2-butene in Fig. 1 are based on models in which the four carbon atoms are coplanar with a distance of 1.38 Å. between the two center atoms and 1.54 Å. for the bond distances connecting the outer atoms. The C–H distances are 1.06 Å. The angle between adjacent carbon–carbon bonds is 125° and the H_3C–C–H bond 110°. In the *cis* model the two methyl groups lie on the same side of the line joining the center atoms and on opposite sides in the *trans* model. All of the interatomic interactions were included in the calculation with the exception of those with small coefficients corresponding to the H–H separations.

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(1) W. G. Young, R. T. Dillon and H. J. Lucas, THIS JOURNAL, 51, 2528 (1929).

(2) C. E. Wilson and H. J. Lucas, *ibid.*, 58, 2396 (1936).

(3) L. O. Brockway, *Rev. Modern Phys.*, 8, 239 (1936).