A critical, experimental test of these equations has been made, by measuring $K_D = (Cl/A)_i \cdot (A^-/Cl^-)_o$ as a function of X^i_{Cl} for perchlorate-chloride and trichloroacetate-chloride exchange using Dowex-2, a quaternary base anion exchanger. (The quaternary ammonium perchlorates are somewhat insoluble; the trichloroacetate forms ion-pairs to a marked extent, while the chloride appears to form ion-pairs to a smaller extent). The curves shown in Fig. 1 were calculated assuming $K_m = 0.12$ for perchlorate, $K_m = 0.4$ for trichloroacetate, $K_m = 1.2$ for chloride. According to the theory the value of K_D at $X^i_A - \rightarrow 1$, is the same as K_m for that ion. Values taken for K'_m are 0.04 for perchlorate and trichloroacetate, and 0.4 for chloride. The resin phase contains about 250 g. of water per mole of exchange capacity. Pressure–volume effects were neglected in these calculations, since they are small for these systems.

The experimental points fit the calculated curve based upon K_m well; the K'_m curves obviously do not apply. For loosely cross-linked gels where translational degrees of freedom may exist, a trend from K_m to K'_m may be anticipated. A series of papers dealing with ion-pair phenomena is in preparation.

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RECEIVED MAY 14, 1951

ON THE STRUCTURE OF STABLE PENTABORANE

Sir:

We have found several arrangements of the boron atoms which appear to be capable, with appropriate disposition of the hydrogen atoms, of giving complete agreement with the electron diffraction pattern of gaseous B_5H_9, whereas neither the model reported by Bauer and Pauling[1] nor the planar five-membered ring proposed by Pitzer[2] is satisfactory. Of the satisfactory arrangements, however, only the tetragonal pyramid, originally proposed and later discarded in the original electron diffraction study[1] but recently further advocated by Pauling,[3] has the high symmetry suggested by the spectrum[4] and entropy.[5] For this arrangement, which we at first thought unsatisfactory,[6] the position and shape of the radial distribution peak at about 2.57 Å. (Fig. 1), as well as intensive analysis of the pattern by trial and error, eventually led us to the structure shown in Fig. 2, which is of the type that had been suggested to us by King and Lipscomb[7] on the attractive grounds outlined in the following communication by Dulmage and Lipscomb. The parameter values

B_1–B_2 = 1.70 Å.
B_2–B_2 = 1.80
B_2–H_2 = 1.23
B_2–H_3 = 1.36
∠ B_1–B_2–H_2 = 120°
external dihedral ∠ $B_1B_2B_2$–$B_2B_2H_3$ = 185°.

which are surely close to the final values to be obtained from our data, give excellent agreement, qualitative and quantitative (12-feature average deviation for q/q_0, 0.008, with $\overline{q/q_0}$ adjusted to 1.000). Limits of error, not yet completely determined, are large for the two angle values and about ±0.03 Å. and ±0.05 Å. for the B–B and B–H distances, respectively.

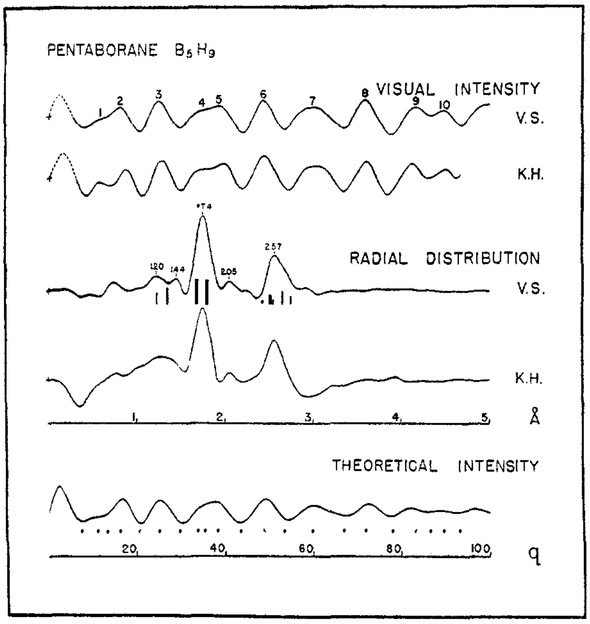

Fig. 1.—Visual, radial distribution and theoretical intensity curves. Theoretical intensity curve for the following model B–H_{av}/B–B_{av} = 1.275/1.74, B_1–B_2/B_2–B_2 = 1.69/1.79, B_2–H_1/B_2–H_3 = 1.20/1.35, ∠ B_1–B_2–H_1 = 125°, external ∠ plane B_1–B_2–B_2, plane B_2–B_2–H_3 = 190°.

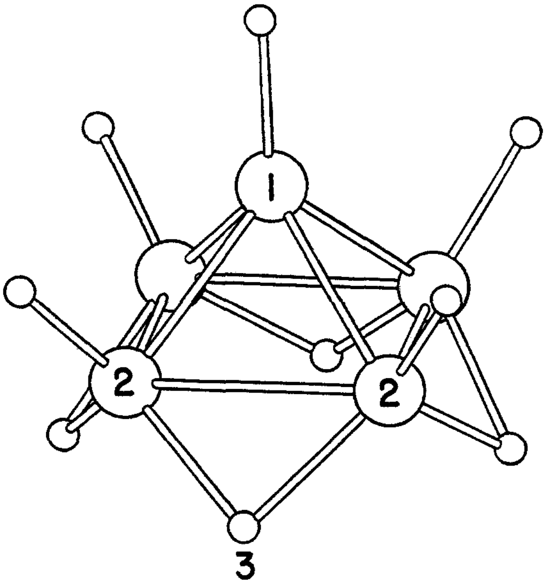

Fig. 2.—B_5H_9, diagram of the structure.

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

(2) K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

(3) Private communication.

(4) Private communications from Professor K. S. Pitzer and from Dr. G. C. Pimentel.

(5) W. J. Taylor, C. W. Beckett, J. Y. Tung, R. B. Holden, and H. L. Johnston, *Phys. Rev.*, **79**, 234 (1950).

(6)(a) V. Schomaker, *J. chim. phys.*, **46**, 252 (1949); (b) K. Hedberg, V. Schomaker, M. E. Jones, *Abstracts*, Chicago Meeting, A. C. S., September 1950. Substantially the present result was given at the meeting, however.

(7) M. V. King and W. N. Lipscomb, private communication.

We are indebted to Professor H. I. Schlesinger and Dr. I. Shapiro for samples of pentaborane and to the Office of Naval Research (Contract N6onr 24423) for support during most of this investigation.

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RECEIVED JUNE 7, 1951

THE MOLECULAR STRUCTURE OF PENTABORANE

Sir:

If one compares the recently-determined structures of boron carbide[1] and decaborane[2] on the one hand with the structure of calcium boride[3] and possible structures of pentaborane on the other, the most reasonable structure of B_5H_9 (M. V. King and W. N. Lipscomb, unpublished) that can now be predicted is a tetragonal pyramid of molecular symmetry C_{4v}, such as that shown in Fig. 1. Apparently a molecule of this structure was overlooked in the earlier electron diffraction study,[4] because a recent study by Hedberg, Jones and Schomaker[5] shows that the electron diffraction pattern is consistent with such a model, but is also not inconsistent with some quite different, but chemically less reasonable, models.

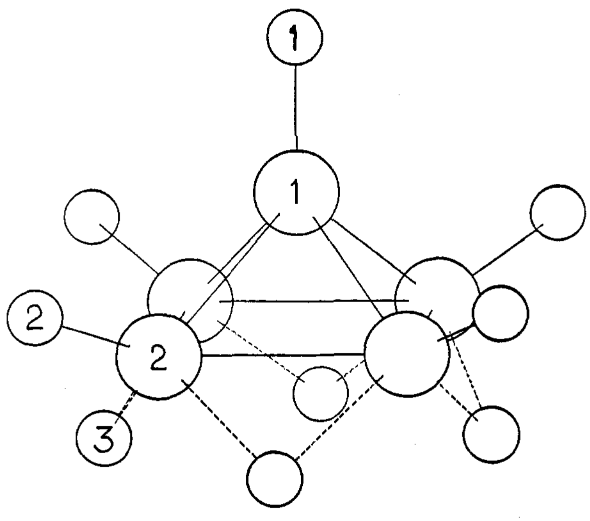

Fig. 1.—The pentaborane molecule: boron and hydrogen atoms are represented by large and small circles, respectively.

We have completed an X-ray diffraction study of single crystals of pentaborane. The crystals are pyroelectric, and belong to the tetragonal space group C_{4v}^9–I4mm., with two molecules in a unit cell of dimensions a = 7.16 Å. and c = 5.38 A. Evaluation of parameters from three-dimensional sections leads to the values:

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.
$H_3 \ldots H_3$ = 1.95 ± 0.09 A.
$\angle B_1.B_2.H_3 = 115 \pm 5°$
External dihedral angle between planes $B_1B_2B_2$ and $B_2B_2H_3 = 190 \pm 5°$

As in decaborane the intermolecular approaches are all between hydrogen atoms. These approaches range from 2.46 to 2.96 Å. which appear reasonable in view of the very large temperature factor in the crystal. The diagonal of the base of the pyramid has the direction of the a axis. It may be noted that the average boron-boron distance in the molecule is apparently about two per cent. smaller in the solid state than in the gaseous state, a situation previously observed only in hexamethylenetetramine.[6]

The interatomic binding in pentaborane, which is similar to decaborane, is of the 'metallic' type and in such a case we may expect Pauling's relation[7] $r = r_1 - 0.3 \log n$ to be reasonably valid. If we choose a covalent radius for hydrogen equal to 0.36 Å., then the total bond order for the molecule, which should be twelve, will depend upon the choice of the boron single-bond radius. A value of 0.78 Å. for this boron radius satisfies these conditions, thus leading to a total bond order of 12.03. The individual bond orders are $n_{12} = 0.681$, $n_{22} = 0.447$, $n'_{11} = 0.764$, $n'_{22} = 0.794$ and $n'_{23} = 0.447$, where the prime refers to B–H bonds. These orders suggest that the hydrogen atoms are somewhat positively charged and the boron atoms are somewhat negatively charged. This distribution of charge indicates a dipole moment of about 0.6 Debye. Similar calculations lead to a single-bond radius for boron of 0.79 Å. from the diborane molecule, and of 0.81 Å. from the decaborane molecule.

We wish to thank Dr. R. R. Miller of the Naval Research Laboratory and Dr. A. E. Newkirk and Dr. L. V. McCarty of the General Electric Company for samples of pentaborane. Support of this research by the Office of Naval Research and by a Fellowship (to W.J.D.) from the Minnesota Mining and Manufacturing Company is gratefully acknowledged.

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[1] G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.S.S.R.*, **32**, 432 (1941); H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943).

[2] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.* **4**, 436 (1950).

[3] L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

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

[5] K. Hedberg, M. Jones, and V. Schomaker, private communication. 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, described in the preceding letter.

[6] V. Schomaker and P. A. Shaffer, Jr., THIS JOURNAL, **69**, 1555 (1947); P. A. Shaffer, Jr., *ibid.*, **69**, 1557 (1947).

[7] L. Pauling, THIS JOURNAL, **69**, 542 (1947). The details of the present method of applying Pauling's relation were suggested to us by K. Hedberg and V. Schomaker. Following their suggestion also we have taken the revised covalent radius for hydrogen (V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1940)) corrected for the electronegativity difference between boron and hydrogen.

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RECEIVED JUNE 5, 1951

PHOTOGRAPHY IN ELECTROPHORESIS OF HEMOLYZED SERA

Sir:

The occasional necessity for the examination by electrophoresis of hemolyzed sera, or of solutions of hemoglobin or other proteins having high optical density except for red or infrared light, has presented a technical problem in photography. The customarily used mercury vapor arc lamp has strong green and yellow lines, but its red intensity