

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Structure of the Hydrides of Boron. VI.  $\text{AlB}_3\text{H}_{12}$ BY J. Y. BEACH AND S. H. BAUER<sup>1</sup>

To the varied compounds of hydrogen and boron, a most interesting group was added recently through the researches of Professor H. I. Schlesinger and co-workers.<sup>2</sup> The known members are  $\text{AlB}_3\text{H}_{12}$ ,  $\text{BeB}_2\text{H}_8$  and  $\text{LiBH}_4$ . In this paper we report an electron diffraction investigation of the first of these compounds. We have deduced a probable configuration, and have determined the interatomic distances in  $\text{AlB}_3\text{H}_{12}$ .

The sample was generously furnished by Dr. A. B. Burg, to whom we wish to give sincere thanks. With the material at  $20^\circ$ , we obtained eight diffraction photographs of varying densities. The essential features of the pattern are sketched in Fig. 1, curve A. The maxima and minima are evenly spaced and their magnitudes decrease uniformly as the angle of scattering increases. Their diameters, measured by means of the usual visual procedure, and the estimated intensities, are given in Table I.

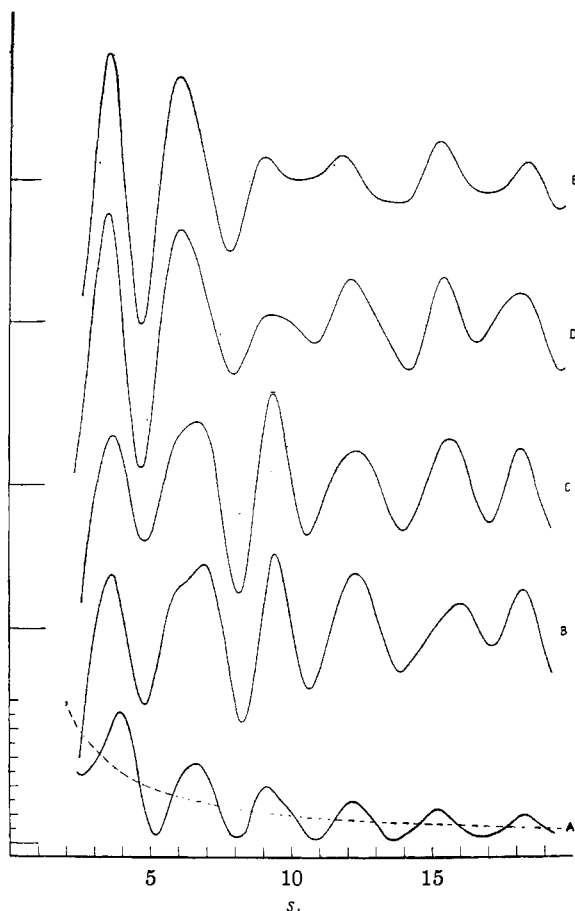


Fig. 1.—Curve A, visual appearance of the photographs, theoretical intensity curves: Curve B,  $\text{H}_3\text{Al}(\text{BH}_3)_3$ , B-Al-B tetrahedral, H-Al-H  $80^\circ$ , Al-B 2.14 Å., Al-H 1.20 Å.; Curve C, same as Curve B except that Al-H is 1.28; Curve D, planar  $\text{Al}(\text{BH}_4)_3$ , B atoms trigonal bipyramids, Al-B = 2.15 Å., B-H = 1.20 Å., Curve E, same as Curve D except that B-H = 1.28 Å. and Al-B-H is  $85^\circ$ .

(1) At Cornell University, Ithaca, N. Y.

(2) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, 61, 536 (1939); and private communications.

| Max. | Min. | Intensity | $s_0$ | $s_0/s_0$ (Curve E) |
|------|------|-----------|-------|---------------------|
| 1    |      | 25        | 3.93  | (0.916)             |
|      | 2    | -19       | 5.18  | (.923)              |
| 2    |      | 14        | 6.62  | .932                |
|      | 3    | -10       | 8.09  | .933                |
| 3    |      | 8         | 9.11  | 1.013               |
|      | 4    | -5        | 10.83 | 0.960               |
| 4    |      | 3         | 12.18 | .988                |
|      | 5    | -2        | 13.62 | 1.035               |
| 5    |      | 1         | 15.19 | 1.026               |
|      | 6    | 0.3       | 18.28 | 1.023               |
|      |      | Mean      |       | 0.995               |

$$0.995 \times 2.15 = 2.14 \text{ \AA.}$$

$$.995 \times 1.28 = 1.27$$

A modified radial distribution<sup>3</sup> curve is shown in Fig. 2. The principal peak is at 2.16 Å. Since 2.14 Å. is the sum of the covalent radii of aluminum and boron, whereas directly bonded boron atoms would be approximately 1.76 Å. apart, an intense peak at the former distance and the lack of an appreciable peak at the latter clearly indicates that the Al atom is central, and that the three boron atoms are directly bonded to it. If a B atom were at the center and the Al atom and the other two B atoms were bonded to it the principal peak in the radial distribution function should occur at about 2.9 Å. corresponding to the two equal long Al-B distances. As the principal peak does not occur at this distance models of this type are immediately ruled out. Accordingly no theoretical intensity curves were calculated for such models. The B-Al-B angle can be determined from the second highest peak in the radial distribution function at 3.73 Å. This distance is equal to  $\sqrt{3}$  times 2.16 which indicates strongly

(3) V. F. H. Schomaker, paper presented to the Am. Chem. Soc. at Baltimore, April, 1939.

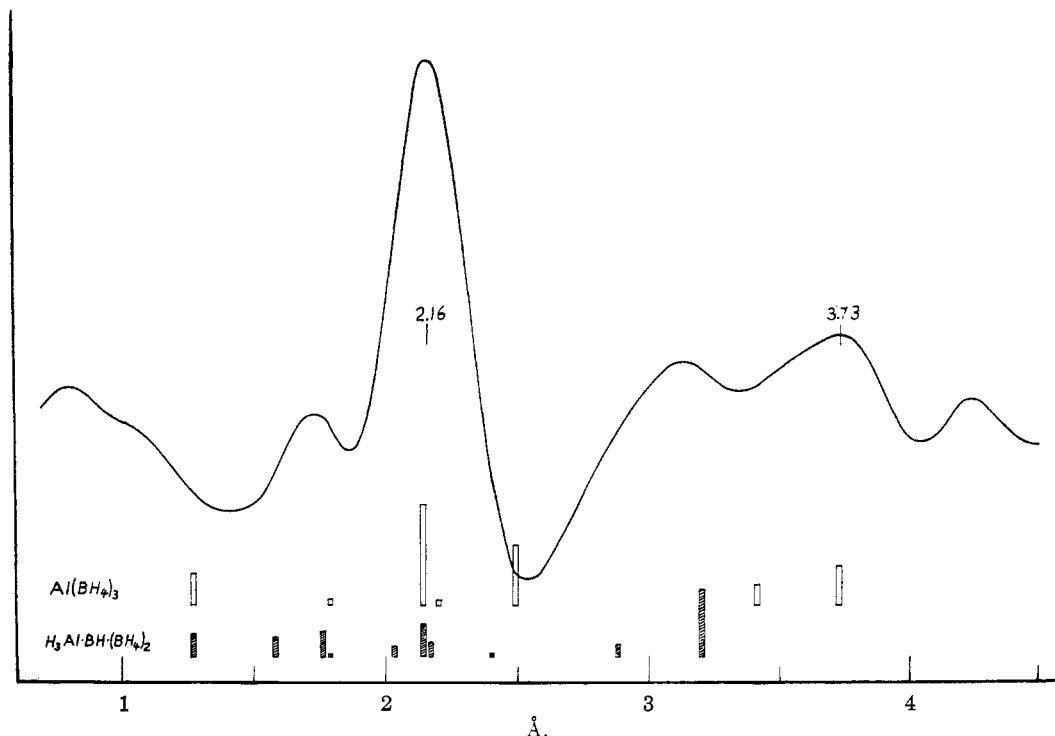


Fig. 2.—Radial distribution curve for  $\text{AlB}_3\text{H}_{12}$ . The observed peaks are compared with those expected for an  $\text{Al}(\text{BH}_4)_3$  configuration, as per Fig. 3; and with those predicted for  $\text{H}_3\text{Al}\cdot\text{BH}(\text{BH}_4)_2$ . (The line at 2.49 Å. should be at 2.40 Å.)

that the B-Al-B angle is  $120^\circ$ . The other smaller radial distribution peaks are due to Al-H and B-H distances in the molecule.

Theoretical intensity curves were calculated for nine different molecular models. In four of them the Al atom was taken to be bonded to three  $\text{BH}_3$  groups and three H atoms. The B-Al-B angle was varied from  $100$  to  $110^\circ$  and the B-H distance was varied from  $1.20$  Å. to  $1.28$  Å. Two of the curves calculated from these models are shown in Fig. 1. In both cases the first three peaks do not decrease in intensity with angle as they should. A model was considered in which the Al atom was surrounded by three  $\text{BH}_4$  groups in a plane, the four H atoms being in a plane perpendicular to the Al-B bond. The calculated curve was unsatisfactory in that there were two small maxima where the single third one should be. The curve for the same model except that the H atoms are arranged about the B atom at the corners of a trigonal bipyramid is shown in Fig. 1, curve D. This is unsatisfactory in that the third maximum is too low. To make the calculated curve agree with the photographs it was necessary to distort the trigonal bipyramid by

moving the three equatorial H atoms away from the other H atoms so that the three equal Al-B-H angles were  $85^\circ$  instead of  $90^\circ$ . The best ratio of B-H to Al-B distances was  $1.28/2.15$ . The model is shown schematically in Fig. 3. This curve is compared quantitatively with the photographs in Table I. To reproduce the photographs satisfactorily it was found necessary to introduce a temperature factor for the long Al-H distances. The temperature factor was such as to reduce the long Al-H term by one-half at  $s = 15$ .

One may therefore conclude that on the basis of electron diffraction measurements,  $\text{AlB}_3\text{H}_{12}$  has the configuration indicated by Fig. 3, with

$$\begin{aligned} \text{Al-B} &= 2.14 \pm 0.02 \text{ \AA.}; & \text{B-H} &= 1.27 \pm 0.04 \text{ \AA.} \\ \text{BAIB} &= 120 \pm 5^\circ; & \text{AlBH} &= 85 \pm 3^\circ \end{aligned}$$

The Al-B peak on the radial distribution function is displaced somewhat by the short Al-H distance. If this Al-H distance were present on the curve it would occur at  $2.40$  Å. (this point is incorrectly placed on the figure). However, the radial distribution function is not capable of resolving distances nearer together than  $0.3$  Å. especially when one distance is more important than the other. Therefore only one peak occurs

in this region, corresponding closely to the Al-B distance.

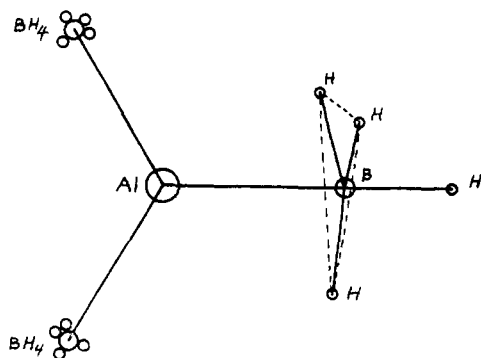


Fig. 3.—Schematic representation of  $\text{Al}(\text{BH}_4)_3$ .

The extension of this type of structure to the other two compounds in this group is obvious; in the case of  $\text{Be}(\text{BH}_4)_2$  the B-Be-B valence angle presumably is  $180^\circ$ . It is interesting to note that the deviation of the AlBH angle from  $90^\circ$  may be a consequence of the repulsion between hydrogen atoms which would be as near as  $1.8 \text{ \AA}$ . had the distortion not taken place.

The interatomic distances observed in  $\text{Al}(\text{BH}_4)_3$  find a reasonable interpretation in terms of the following electron configuration. Since the Al-B separation is equal to the sum of the covalent radii ( $\text{Al} = 1.26$ ,  $\text{B} = 0.88$ ) and the Al valence angles are  $120^\circ$ , these bonds are essentially of the  $sp^2$  type. On the other hand, the B-H distances are considerably larger than would have been expected for electron-pair bonds; indeed, they are equal to the B-H separations found in diborane, tetraborane, and the pentaborane  $\text{B}_5\text{H}_{11}$ <sup>4</sup> for which bonds one must assume a resonating system of one-electron and electron-pair bond structures. Since  $\text{Al}(\text{BH}_4)_3$ ,  $\text{Be}(\text{BH}_4)_2$  and  $\text{LiBH}_4$  have a two-electron deficiency per  $\text{BH}_4$  group, the extension of the theory proposed by Sidgwick,<sup>5</sup> Pauling,<sup>6</sup> Lewis<sup>7</sup> and Mulliken<sup>8</sup> to this group of compounds can be readily made. The ground

(4) S. H. Bauer, *THIS JOURNAL*, **59**, 1096 (1937); **60**, 805 (1938).

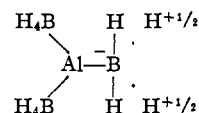
(5) N. V. Sidgwick, "The Electronic Theory of Valence," Oxford Univ. Press, London, 1929, p. 103.

(6) L. Pauling, *THIS JOURNAL*, **53**, 3225 (1931).

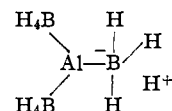
(7) G. N. Lewis, *J. Chem. Phys.*, **1**, 17 (1933).

(8) R. S. Mulliken, *ibid.*, **3**, 635 (1935).

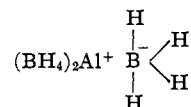
state of the aluminum compound should therefore be represented by a linear combination of the eighteen structures containing one-electron bonds



the twelve structures



and configurations of the ionic type



of course, all of these are not independent. The contribution from the ionic structures probably is not appreciable. First, the large B-H distances indicate that all the electron deficiency resides in the  $\text{BH}_4$  groups and second, the Al-B distances are just what would be expected for electron pair binding. The extent of such ionic contributions must increase however as one goes down the series,  $\text{Al}(\text{BH}_4)_3$ ,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Li}(\text{BH}_4)$ , in harmony with the observed decrease in volatility.

The available chemical data agree well with the above configuration.<sup>9</sup> Interpretation of the observed properties appears to be straightforward.

### Summary

By means of an electron diffraction study, the configuration of  $\text{AlB}_3\text{H}_{12}$  has been determined. The Al atom is bonded to three  $\text{BH}_4$  groups at angles of  $120^\circ$  making the molecule planar except for the H atoms. The boron atoms are located near the center of trigonal bipyramids formed by the four H atoms of each  $\text{BH}_4$  group and the central Al,  $\text{Al-B} = 2.14 \pm 0.02 \text{ \AA}$ .;  $\text{B-H} = 1.27 \pm 0.04 \text{ \AA}$ . From the observed interatomic distances an electron configuration for the molecule was deduced.

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RECEIVED JULY 1, 1940

(9) H. I. Schlesinger and co-workers, *THIS JOURNAL*, **62**, 3421 (1940).