On the Molecular Structure of Aluminium Borohydride, $Al(BH_4)_3$

A. ALMENNINGEN, GRETE GUNDERSEN and A. HAALAND

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The electron scattering pattern from gaseous $Al(BH_4)_3$ has been recorded from 1.50 Å⁻¹ to 39.50 Å⁻¹. The molecular symmetry is either D_{3h} or slightly deformed into D_3. The anti-prismatic model is ruled out. The bond distances and valence angles are: $Al-B = 2.143 \pm 0.003$ Å, $Al-H^b = 1.801 \pm 0.006$ Å, $B-H^b = 1.283 \pm 0.012$ Å, $B-H^t = 1.196 \pm 0.012$ Å, $\angle H^bAlH^b = 73.4 \pm 0.8°$, $\angle H^bBH^b = 114.0 \pm 0.2°$, and $\angle H^tBH^t = 116.2 \pm 2.2°$.

The synthesis of aluminium borohydride, AlB_3H_{12} or $Al(BH_4)_3$, was reported by Sanderson, Burg, and Schlesinger [1] in 1940. An electron-diffraction study by Beach and Bauer [2] published the same year demonstrated that the aluminium atom is bonded to all three boron atoms and that all BAlB angles are close to 120°. The position of the hydrogen atoms, however, remained a matter of controversy until the IR spectrum was published in 1949.[3] The great similarity to the spectrum of diborane led Price [3] to conclude that the molecular structure must be as sketched in Fig. 1: Each boron atom is surrounded by four hydrogen atoms at the corners of a tetrahedron and is bonded to the aluminium atom through two hydrogen bridge bonds. If the line joining the bridge hydrogen atoms (H^b) is perpendicular to the AlB_3 plane, the molecular symmetry is D_{3h}, and the six H^b atoms form a trigonal prism around the Al atom. A model in which the six H^b atoms form a trigonal anti-prism can be obtained from the prismatic model by rotating the BH_4 tetrahedra some 50° about the Al—B bonds (the exact value depends on the magnitude of the bond lengths). The symmetry of the AlH_6^b group is then D_{3d}, but the presence of the terminal hydrogen atoms (H^t) lowers the symmetry to D_3. This is also the symmetry of all models intermediate between the prismatic and anti-prismatic. We shall refer to such models as aprismatic.

The prismatic and anti-prismatic models were first put forward by Longuet-Higgins.[4] Price considered both and concluded that the prismatic model was most probable.[3] The Raman spectrum of $Al(BH_4)_3$ has been recorded and discussed by Emery and Taylor [5] who reached the same conclusion.
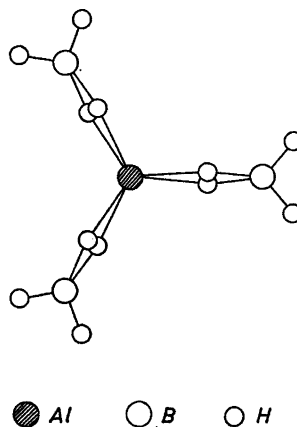
Fig. 1. The molecular structure of aluminium borohydride.

🌑 *Al*   ◯ *B*   ◯ *H*

The nuclear magnetic resonance spectrum [6] is consistent with the structure in Fig. 1, though a dynamic exchange renders bridge and terminal hydrogen atoms indistinguishable.

EXPERIMENTAL AND CALCULATION PROCEDURE

Aluminium borohydride was synthesized by the procedure outlined by Schlesinger and coworkers [1] and purified by sublimation. The electron-diffraction pattern from the gas at about 20°C was recorded on the Oslo apparatus.[7]
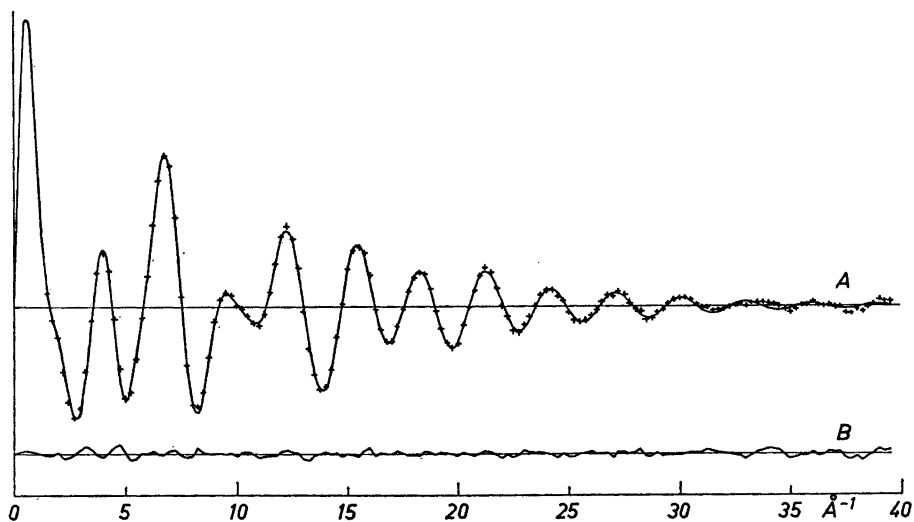

Fig. 2. A. Theoretical modified molecular intensity curve of Al(BH₄)₃ computed from the parameters in Table 1, part A with experimental values drawn in. B. Difference curve.

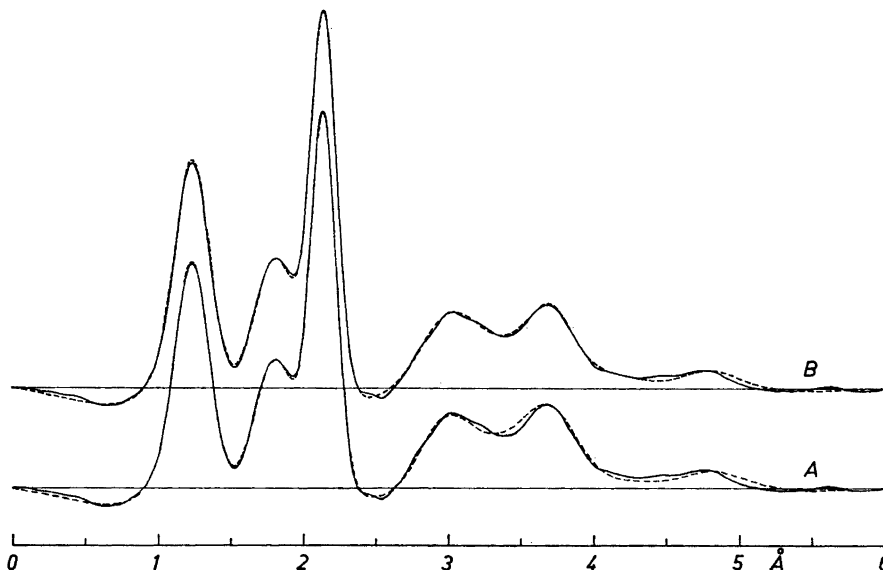*Fig. 3.* Radial distribution curves of Al(BH$_4$)$_3$. ———— experimental, – – – – theoretical; A, computed from the parameters in Table 1 part A, and B, computed from the parameters in part B. $k = 0.001$ Å^2.

The temperature in the reservoir was $-20°$C. Exposures were made with two nozzle to photographic plate distances, the two sets of plates thus obtained covered the diffraction ranges $s = 1$ Å^{-1} to 20 Å^{-1} and 7 Å^{-1} to 40 Å^{-1}. The diffraction parameter $s = (4\pi\sin\theta)/\lambda$, where θ is half the diffraction angle and λ the electron wavelength. Three apparently faultless plates from the first set and five from the second were micro-photometered and used for this study.

The experimental data were corrected and processed in the usual way.[8] The resulting modified molecular intensity points from $s = 1.50$ Å^{-1} to 39.50 Å^{-1} are shown in Fig. 2. The interval between the points is 0.25 Å^{-1}. A radial distribution (RD) curve obtained by Fourier inversion of the observed intensity is shown in Fig. 3 (full line).

Theoretical intensity curves were calculated from

$$I_{\text{AlB}}(s) = \text{const} \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_{\text{Al}}(s)||f_{\text{B}}(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2)$$

$$= \text{const} \sum_{i \neq j} g_{ij/\text{AlB}}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2) \tag{1}$$

The sum extends over all atom pairs i,j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \cdot \exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j.

It has been computed for H, B, and Al by the partial wave approximation method with a program written by Peacher.[9]

Theoretical RD curves were obtained by Fourier inversion of theoretical intensity curves. The molecular structure was refined by least-squares calculations on the intensity data.[10] All parameters except H···H vibrational amplitudes (which were set equal to 0.20 Å) were refined simultaneously.

STRUCTURE ANALYSIS

A radial distribution (RD) curve obtained by Fourier inversion of the observed intensity is shown in Fig. 3 (full line). In this curve each interatomic distance R_{ij} in the molecule is represented by a peak centered at $r = R_{ij}$. The area under the peak is approximately proportional to $n_{ij}Z_iZ_j/R_{ij}$, where n_{ij} is the number of times the distance occurs and Z_i and Z_j the atomic numbers. The halfwidth of the peak is determined roughly by the root mean square amplitude of vibration, u_{ij}.

The biggest peak in the RD curve, found at 2.15 Å, must represent the three Al—B bond distances. The peak at 1.25 Å is composite, it is the sum of two closely spaced peaks representing the B—H^t and B—H^b distances. The Al—H^b distance gives a peak at 1.8 Å, the non-bonded Al···H^t distance a peak at 3.0 Å. The B···B peak is found at 3.7 Å. The two peaks representing the B···H^b distances (expected near 3.3 Å) and the shortest B···H^t distance (expected near 4.0 Å) are hidden beneath the Al···H^t and B···B peaks, but a minor peak representing the longest B···H^t distance is clearly visible at 4.8 Å. The numerous peaks representing H···H distances are all to small to be seen.

The molecular structure was first refined by least-squares calculations on the intensity data under the assumption that the molecular symmetry is D_{3h}. This implies that the BH₄ groups have symmetry C_{2v}. The molecular structure is then determined by five independent parameters, e.g. the four bond distances and the non-bonded Al···H^t distance.

The resulting parameter values and their standard deviations are given in Table 1, part A. The standard deviations include the effect of errors in the electron wavelength.[11] A theoretical intensity curve calculated from the parameters is shown in Fig. 2, a theoretical RD curve in Fig. 3A (stipled line). The agreement with the experimental curves is very good, though there are minor discrepancies between the RD curves around 3.5 and 4.5 Å. These discrepancies will be discussed in the following paragraphs.

When the formula (eqn. 1) for the theoretical intensity is derived, the effect of intramolecular motion is taken into account in the following way: For each interatomic distance R_{ij}, a radial probability function,[12] $P_{ij}(r)$, is defined such that the probability of R_{ij} being between r and $r + dr$ (at any particular instant) is $P_{ij}(r)dr$. It is then assumed that $P_{ij}(r)$ is Gaussian and centered about the equilibrium distance. Eqn. 1 is obtained as the weighted sum of the intensities for all values of R_{ij}, and the theoretical RD curve obtained by Fourier inversion of eqn. 1 consists of very nearly Gaussian peaks centered very nearly at the equilibrium distance.

The Gaussian probability distribution proves to be very good for distances between bonded atoms and adequate for short non-bonded distances. But if

Table 1. Interatomic distances, valence angles, and root mean square vibrational amplitudes of $Al(BH_4)_3$. The standard deviations include the effect of errors in the electron wavelength. The distances are given as $r_g(1)$.[12] The angles have not been corrected for shrinkage. The values for dependent parameters are enclosed in parentheses.

The best estimate of bond distances and valence angles is found in part C.

	A. D_{3h}		B. D_3	
	R (Å)	u (Å)	R (Å)	u (Å)
Al−B	2.143 ± 0.003	0.071 ± 0.001	2.143 ± 0.003	0.072 ± 0.001
Al−H^b	1.801 ± 0.004	0.125 ± 0.002	1.801 ± 0.003	0.125 ± 0.002
Al···H^t	2.966 ± 0.010	0.168 ± 0.006	2.968 ± 0.023	0.189 ± 0.009
B−H^b	1.292 ± 0.006	0.078 ± 0.005	1.290 ± 0.007	0.081 ± 0.005
B−H^t	1.187 ± 0.005	0.081 ± 0.005	1.189 ± 0.006	0.084 ± 0.005
v	0° (not ref.)		17.2 ± 2.4°	
B···B	(3.711 ± 0.005)	0.161 ± 0.007	(3.711 ± 0.005)	0.136 ± 0.005
B···H^b	(3.304 ± 0.005)	0.278 ± 0.073	(3.120 ± 0.026)	0.185 ± 0.038
B···H^b			(3.479 ± 0.023)	0.193 ± 0.026
B···H^t	(3.962 ± 0.015)	0.525 ± 0.087	(3.984 ± 0.040)	0.457 ± 0.073
B···H^t	(4.802 ± 0.009)	0.185 ± 0.018	(4.787 ± 0.012)	0.167 ± 0.015
∠H^{b}AlH^b	(74.0 ± 0.4°)		(73.8 ± 0.4°)	
∠H^{b}BH^b	(114.0 ± 0.2°)		(113.9 ± 0.2°)	
∠H^{t}BH^t	(113.3 ± 1.6°)		(113.2 ± 3.8°)	
	$\sum W(I_{obs}-I_{theor})^2 = 0.946$		$\sum W(I_{obs}-I_{theor})^2 = 0.723$	

C. Independent distances

	R (Å)	u (Å)	R_{eq}(calc D_{3h})(Å)	Shrinkage (D_{3h})(Å)
Al−B	2.143 ± 0.003	0.072 ± 0.001		
Al−H^b	1.801 ± 0.006	0.125 ± 0.002		
A···H^t	2.954 ± 0.012	0.177 ± 0.008		
B−H^b	1.283 ± 0.012	0.086 ± 0.007		
B−H^t	1.196 ± 0.012	0.089 ± 0.008		
v				
B···B	3.705 ± 0.007	0.137 ± 0.005	3.710 ± 0.010	0.005 ± 0.013
B···H^b	3.251 ± 0.016	0.235 ± 0.018	3.306 ± 0.019	0.055 ± 0.025
B···H^b				
B···H^t	4.111 ± 0.046	0.312 ± 0.033	3.936 ± 0.012	−0.175 ± 0.048
B···H^t	4.743 ± 0.016	0.155 ± 0.012	4.799 ± 0.013	0.054 ± 0.021
∠H^{b}AlH^b	(73.4 ± 0.8°)			
∠H^{b}BH^b	(114.0 ± 0.2°)			
∠H^{t}BH^t	(116.2 ± 2.2°)			
	$\sum W(I_{obs}-I_{theor})^2 = 0.596$			

the molecule undergoes large amplitude vibrations it may fail for long non-bonded distances: Assume that the equilibrium symmetry of $Al(BH_6)_3$ is D_{3h} and that the BH_4 groups carry out large amplitude vibrations about the Al−B bonds. The distance from one B atom to the far H^t atom on its neighbour is then on the average shorter than the equilibrium distance. This effect is clearly visible on the experimental RD curve Fig. 3. That the average value of R_{ij} is smaller than the equilibrium value is commonly referred to as "shrink-

age". The distance to the near H^t atom on the other hand would on the average be longer than the equilibrium value, "expansion" or "negative shrinkage". The effect on the average value of the $B\cdots H^b$ distance would be small, but the halfwidth of the peak would be great, and it might well deviate considerably from a Gaussian shape. Now, libration about the Al—B bonds is not the only conceivable large-amplitude vibration, and in the absence of a completely assigned vibrational spectrum there is no way of assessing *a priori* their effect on the average values of the large distances or the shape of their radial probability curves.

The difference between the experimental and theoretical RD curves in Fig. 3A may well be due to the inadequate theory of molecular vibrations. In order to assess the magnitude of the effect we refined the molecular structure once more, but with $B\cdots B$, $B\cdots H^b$, and the two $B\cdots H^t$ distances as independent parameters. The result of this refinement is shown in Table 1, part C. Using the four bond distances and the $Al\cdots H^t$ distance the equilibrium values of the dependent distances, $R_{eq}(calc)$, were then calculated for D_{3h} symmetry. The difference between this distance and the average distance is then listed as "shrinkage".

There is of course a second possible explanation for the discrepancies between the curves in Fig. 3A: The equilibrium structure may have D_3 rather than D_{3h} symmetry. It is easily seen that a change of the equilibrium structure from D_{3h} to D_3 will have much the same effect as shrinkage: The short $B\cdots H^t$ will become longer, the long $B\cdots H^t$ will become shorter. It should be noted, however, that all $H\cdots H$ distances between different BH_4 groups in the D_{3h} model are above 2.4 Å and that they change very little when the molecule is deformed into D_3. Hence a deformation cannot easily be explained as the result of van der Waals repulsion or attraction between hydrogen atoms.

If the molecular symmetry is D_3, and if it is assumed that the BH_4 groups retain their C_{2v} symmetry, the molecular structure is determined by the four bond distances, the $Al...H^t$ distance and the angle of rotation about the Al—B bonds, v. If $v = 0$, the molecular symmetry is D_{3h}. The result of a least-squares refinement of a D_3 model is shown in Table 1, part B. The weighted square error sum is intermediate between those in parts A and C. $v = 17.2°$ and as a consequence there are two different $B\cdots H^b$ distances. It is seen, however, that the vibrational amplitudes of the two distances are so large that the BH_4 groups may easily vibrate into the D_{3h} position ($B\cdots H^b = 3.30$ Å). The difference between this model and a prismatic one is therefore not very great.

A theoretical RD curve computed from the parameter values in Table 1, part B is shown in Fig. 3B (stipled line). The discrepancy near 3.5 Å has disappeared, but shrinkage must still be invoked to explain some disagreement near 4.5 Å.

The value $v = 17.2 \pm 2.4°$ would appear to rule out a model of D_{3h} symmetry. We do not wish to draw this conclusion. As long as shrinkage is neglected, we believe that even if the molecular symmetry is D_{3h} a value of v significantly different from zero might be obtained as a compensation for the omission.

Finally v was fixed at 52.2° (anti-prismatic model) and the structure refined as before. The resulting square-error sum was 1.87 and a theoretical RD curve was in very poor agreement with the experimental. This model may therefore confidently be ruled out.

CONCLUSIONS

The molecular symmetry of $Al(BH_4)_3$ is either D_{3h} (prismatic model) or slightly deformed into D_3 (aprismatic model). The anti-prismatic model is ruled out.

There are slight — though not very significant — differences between the values given for the five independent distances and their vibrational amplitudes in the three parts of Table 1. Since it is conceivable that the neglect of shrinkage has resulted in small errors in parts A and B, the best estimate of these parameters is found in part C.

REFERENCES

1. Schlesinger, H. I., Sanderson, R. T. and Burg, A. B. *J. Am. Chem. Soc.* **62** (1940) 3421.
2. Beach, J. Y. and Bauer, S. H. *J. Am. Chem. Soc.* **62** (1940) 3440.
3. Price, W. C. *J. Chem. Phys.* **17** (1949) 1044.
4. Longuet-Higgins, H. C. *J. Chem. Soc.* **1946** 139—43.
5. Emery, A. R. and Taylor, R. C. *Spectrochim. Acta* **16** (1960) 1455.
6. Ogg, R. A. and Ray, J. D. *Discussions Faraday Soc.* **19** (1955) 239.
7. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232.
8. Almenningen, A., Haaland, A. and Motzfeldt, T. *J. Organometal Chem.* **7** (1967) 97.
9. Peacher, J. L. *Ph.D. Thesis*, Department of Physics, Indiana University, Bloomington, Indiana 1965.
10. Almenningen, A., Bastiansen, O., Seip, H. M. and Seip, R. *Acta Chem. Scand.* **18** (1964) 2115.
11. Almenningen, A., Bastiansen, O., Haaland, A. and Seip, H. M. *Angew. Chem.* **20** (1965) 877.
12. Bartell, L. S. *J. Chem. Phys.* **23** (1955) 1219.