

On the Molecular Structure of Dimethylaluminium Hydride Dimer, $[(\text{CH}_3)_2\text{AlH}]_2$

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The molecular structure of $[(\text{CH}_3)_2\text{AlH}]_2$ has been determined by gas phase electron diffraction. The electron scattering pattern is consistent with a model of D_{2h} symmetry. The main molecular parameters are $R(\text{C}-\text{H})=1.117(5)$ Å, $R(\text{Al}-\text{C})=1.947(3)$ Å, $R(\text{Al}-\text{H bridge})=1.676(19)$ Å, $R(\text{Al}-\text{Al})=2.617(6)$ Å and $\angle \text{C}-\text{Al}-\text{C}=118.5(0.9)^\circ$ and $\angle \text{Al}-\text{H}-\text{Al}=102.6(1.6)^\circ$. The nature of the bonding is discussed.

Dimethylaluminium hydride, $(\text{CH}_3)_2\text{AlH}$, first synthesized by Wartik and Schlessinger, is a colorless highly viscous liquid at room temperature.¹ While the high viscosity suggests that the compound is polymeric in the liquid state, it is trimeric in hydrocarbon solvents at room temperature.¹ The vapour at 80°C consists of about equal amounts of trimeric and dimeric species, and at 170°C the molecular weight corresponds to a dimeric species only.¹

It has been assumed that the dimer has a hydrogen bridged structure analogous to that of tetramethyldiborane² and that the trimer has a structure consisting of a six-membered ring of alternating aluminium and bridging hydrogen atoms. The latter model is in agreement with the IR absorption spectrum of trimeric diethylaluminium hydride in cyclohexane solution,³ and recent self consistent field molecular orbital calculations support the view that hydrogen atoms form stronger bridges between aluminium atoms than do methyl groups.⁴ The heat of association per hydrogen bridge bond has been estimated⁵ to 15–20 kcal mol⁻¹ as against 10.1 ± 0.15 kcal mol⁻¹ per methyl bridge bond in trimethylaluminium dimer.⁶

The mass spectrum of dimethylaluminium hydride has been investigated by two groups.^{7,8}

EXPERIMENTAL AND CALCULATION PROCEDURE

The dimethylaluminium hydride was prepared according to the method of Wartik and Schlessinger¹ and identified by its infrared and mass spectra. The electron scattering

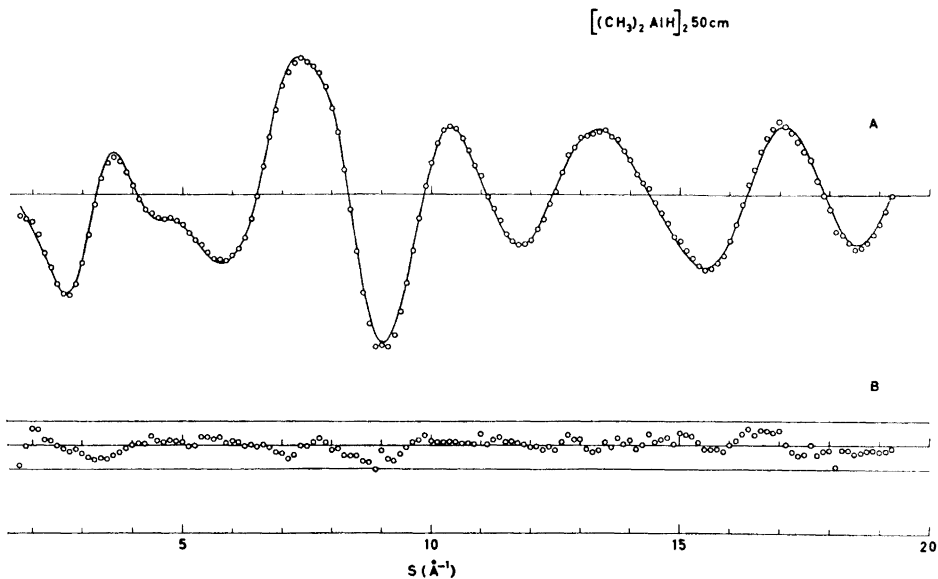


Fig. 1. A. \circ ; experimental modified molecular intensity points from $s=1.750 \text{ \AA}^{-1}$ to $s=19.250 \text{ \AA}^{-1}$. Point density 8 points per \AA^{-1} . Full line; theoretical modified molecular intensity curve calculated from the parameters in Table 1. B. \circ ; difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. *Note:* The scale of B is twice that of A.

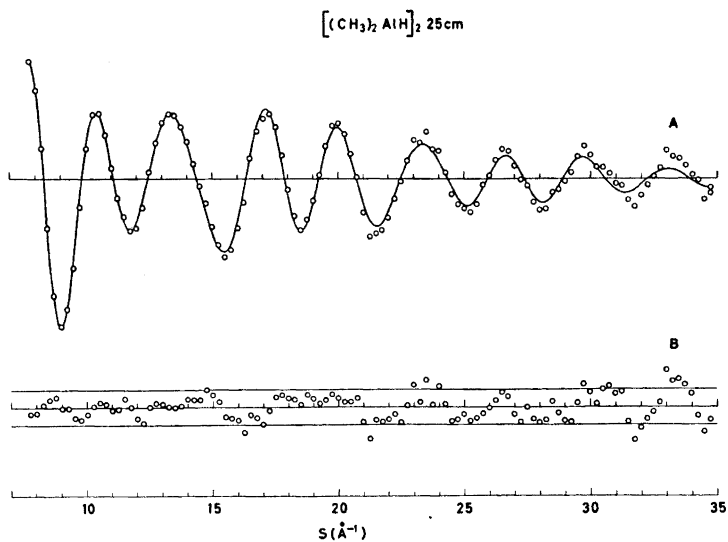


Fig. 2. A. \circ ; experimental modified molecular intensity points from $s=7.750 \text{ \AA}^{-1}$ to $s=34.750 \text{ \AA}^{-1}$. Point density 4 points per \AA^{-1} . Full line; theoretical modified molecular intensity curve calculated from the parameters in Table 1. B. \circ ; difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. *Note:* The scale of B is twice that of A.

pattern was recorded on the Oslo electron diffraction unit⁹ with the sample reservoir at 75° (corresponding to a vapor pressure of about 35 mmHg¹) and a nozzle temperature of 170°C. Exposures were made at nozzle-to-photographic plate distances of about 48 cm and about 26 cm.

Four apparently faultless plates from the first set and three from the second were photometered and processed in the usual way.¹⁰ The resulting modified molecular intensity points obtained from the two sets are shown in Figs. 1 and 2.

Theoretical intensity curves were calculated from:

$$I^{\text{AlC}}(s) = \sum_{i \neq j} \frac{|f_i(s)| |f_j(s)|}{|f_{\text{Al}}(s)| |f_{\text{C}}(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}l_{ij}^2 s^2)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, l_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j . It has been calculated for Al, C, and H by the partial wave approximation with a program written by Peacher and Wills.¹¹ The scattering potentials of Al and C have been found by non-relativistic Hartree-Fock calculations.^{12,13}

Radial distribution (RD) functions were calculated by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$. The experimental intensity functions obtained for different nozzle-to-photographic plate distances were then first spliced to each other and to the theoretical curve obtained for the best model below $s = 1.75 \text{ \AA}^{-1}$.

The molecular structure was refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the intensity values obtained for each nozzle-to-plate distance.¹⁴ The standard deviations obtained were expanded to take into account an estimated uncertainty of 1.4 ppt in the electron wavelength.

STRUCTURE ANALYSIS

A molecular model of dimethylaluminium hydride dimer (I) is shown in Fig. 3. It was assumed that:

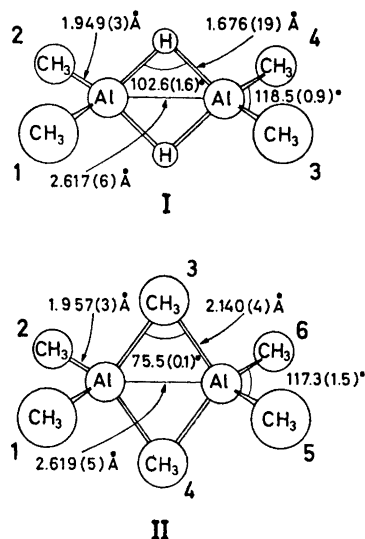


Fig. 3. Molecular structures of $[(\text{CH}_3)_2\text{AlH}]_2$ (I) and $[(\text{CH}_3)_3\text{Al}]_2$ (II).¹⁵

- (i) The molecular symmetry is D_{2h} .
- (ii) The methyl groups have C_{3v} symmetry with the threefold axes coinciding with the Al–C bonds.
- (iii) The methyl groups are staggered with respect to the Al–C bonds radiating from the aluminium atoms.

The equilibrium structure is then determined by six independent parameters, *e.g.* by the C–H, Al–C, Al–H, and Al–Al bond distances and the \angle C–Al–C and \angle Al–C–H valence angles. In trimethylaluminium dimer (II) (Fig. 3) large amplitude molecular vibrations lead to average values for the $C_1\dots C_5$ and $C_1\dots C_6$ distances that differ from those calculated from the equilibrium geometry.¹⁵ The corresponding distances in the hydride (I), $C_1\dots C_3$ and $C_1\dots C_4$, were therefore refined as additional independent parameters. The structure parameters and the root mean square vibrational amplitudes (l) were refined by least squares calculations on the intensity data. Unfortunately it was not possible to refine the Al–H and Al–C bond distances and their vibrational amplitudes simultaneously. The amplitude for the Al–C bond distance was therefore not refined. The molecular parameters obtained with $l(\text{Al–C})$ fixed at the value found for the terminal Al–C distance in trimethylaluminium dimer, 0.061(2) Å,¹⁵ are shown in Table 1. The estimated standard deviations are given in parentheses. Other refinements were carried out with $l(\text{Al–C})$ fixed at 0.055 and at 0.067 Å. The change in the other molecular parameters was found to be less than one standard deviation.

Table 1. Structure parameters of $((\text{CH}_3)_2\text{AlH})_2$ with estimated standard deviations. For numbering of the atoms, consult Fig. 3 (I). The methyl hydrogen atoms are numbered like the carbon atom to which they are attached. The distances are given as r_a . The angles have not been corrected for shrinkage.

| | R (Å) | l (Å) |
|------------------------------|-------------|-----------------|
| C–H | 1.117(5) | 0.077(4) |
| Al–C | 1.947(3) | 0.061 (assumed) |
| Al–H bridge | 1.676(19) | 0.111(15) |
| Al–Al | 2.617(6) | 0.079(4) |
| \angle Al–C–H | 108.8(1.7)° | |
| \angle C–Al–C | 118.5(0.9)° | |
| \angle H–Al–H | 77.4(1.6)° | |
| $\text{Al}_1\dots\text{C}_3$ | 3.983(13) | 0.236(17) |
| $\text{Al}_1\dots\text{H}_1$ | 2.541(30) | 0.228(21) |
| $\text{Al}_1\dots\text{H}_3$ | 3.839(25) | 0.141(21) |
| $\text{Al}_1\dots\text{H}_5$ | 4.676(11) | 0.263(21) |
| $\text{C}_1\dots\text{C}_2$ | 3.350(28) | 0.167(29) |
| $\text{C}_1\dots\text{C}_3$ | 4.642(72) | 0.291(75) |
| $\text{C}_1\dots\text{C}_4$ | 5.618(30) | 0.160(22) |

Modified molecular intensity curves calculated from the parameters listed in Table 1 are shown in Figs. 1A and 2A. The difference between experimental and calculated intensities is shown in Figs. 1B and 2B. The agreement is satisfactory.

An experimental radial distribution curve is shown in Fig. 4A. For interpretation of this curve one should consult Table 1. The difference between this curve and one calculated from the parameters in Table 1 is shown in Fig. 4B. Again the agreement is satisfactory.

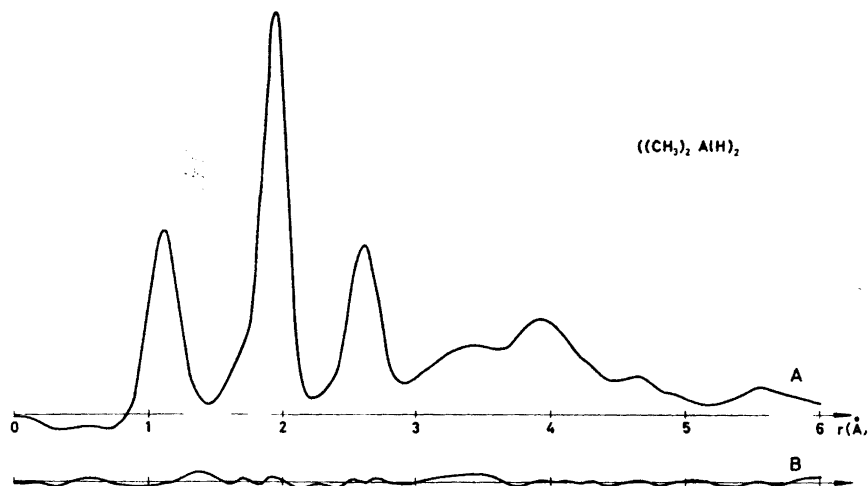


Fig. 4. A. Experimental radial distribution curve. B. Difference between the experimental radial distribution curve and the theoretical curve calculated from the parameters of Table 1. Artificial damping constants $k=0.002 \text{ \AA}^2$.

DISCUSSION

The main molecular parameters of dimethylaluminium hydride dimer (I) are shown in Fig. 3 along with the corresponding parameters of trimethylaluminium dimer¹⁵ (II). Since these molecules are the first pair of analogous hydrogen- and methyl-bridged species to have their structure determined, a comparison between them is of interest.

The most conspicuous feature is the close similarity of the Al–Al distances and vibrational amplitudes in the two molecules. In I $l(\text{Al}–\text{Al})=0.079(4) \text{ \AA}$, in II $l(\text{Al}–\text{Al})=0.079(3) \text{ \AA}$. This similarity and the fact that the Al–Al distance is only 0.10 Å greater than the value calculated for a single bond by doubling the tetrahedral covalent radius of aluminium,¹⁶ and 0.24 Å smaller than the Al–Al distance in the metal¹⁷ supports the view that direct bonding between the metal atoms is of primary importance in electron deficient molecules of this kind.^{4,18,19}

Indeed, the interatomic distances indicate that the bonding between the metal atoms is as strong as or stronger than between a metal atom and a bridging hydrogen or carbon atom: The Al–H bridge distance in I is 0.17 Å longer than the single Al–H bond distance calculated from the tetrahedral covalent radius of aluminium, the covalent radius of hydrogen and Pauling's

revised version of the Schomaker-Stevenson rule.²⁰ And the Al–C bridge distance in II is 0.18 Å longer than the single terminal Al–C bond.

The same pattern is found among the other known compounds in which two metal atoms are linked through double hydrogen or methyl bridges. In diborane²¹ the B–B distance is only 0.02 Å longer than twice the covalent radius of boron, while the B–H bridge distance is 0.15 Å longer than the terminal B–H bond. In crystalline dimethylberyllium²² which consists of infinite chains of beryllium atoms linked through double methyl bridge bonds, the Be–Be distance is 0.02 Å shorter than the calculated single bond distance,¹⁶ while the Be–C bridge distance is 0.22 Å longer than the terminal Be–C distance in [(CH₃)BeOSi(CH₃)₃]₄.²³ In crystalline dimethylmagnesium,¹⁸ which has the same structure as crystalline dimethylberyllium, the Mg–Mg distance is 0.07 Å shorter than the calculated single bond distance,¹⁶ while the Mg–C bridge distance is 0.17 Å longer than the calculated Mg–C single bond distance.²⁰

Since the distance from an aluminium atom to a bridging hydrogen atom is considerably shorter than to a bridging carbon atom, the angles in the central four-membered ring are very different in I and II. It appears as if the angles are determined by the two bond distances Al–Al and Al–H bridge or Al–C bridge.

No significant differences are found between the terminal Al–C bond distances or the external $\angle C_1\text{--Al--}C_2$ valence angles in the two molecules. The C₁...C₃ and C₁...C₄ distances in (I) are found to be, respectively, longer and shorter than those calculated from the equilibrium geometry, but not significantly so.

The Al–H bond distance in I is not significantly different from the Al–H bond distance found in crystalline AlH₃,²⁴ 1.715(10) Å. In this compound the aluminium atoms is surrounded by six bridging hydrogen atoms while the shortest Al...Al distances are 3.24(1) Å.

The six Al–H bond distances in aluminium borohydride, Al(BH₄)₃,²⁵ 1.801(4) Å, are substantially longer than in I or in crystalline AlH₃. On the other hand the B–H bridge distances are 1.292(6) Å as compared to 1.339(4) Å in diborane²¹ and 1.26(2) Å in the alkali borohydrides.²⁶ Clearly the bonding in aluminium borohydride is partially ionic.

Acknowledgement. We are grateful to the Norwegian Research Council for Science and the Humanities and to the Norwegian Research Council for Science and Technology for financial support.

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Received November 9, 1971.