

On the Molecular Structure of Trimethylamine Alane, $\text{H}_3\text{AlN}(\text{CH}_3)_3$

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The molecular structure of $\text{H}_3\text{AlN}(\text{CH}_3)_3$ has been determined by gas phase electron diffraction. The main molecular parameters are $\text{Al}-\text{H}=1.560(11)$ Å, $\text{Al}-\text{N}=2.063(8)$ Å, $\text{N}-\text{C}=1.476(3)$ Å, $\text{C}-\text{H}=1.108(3)$ Å, and $\angle\text{N}-\text{Al}-\text{H}=104.3(1.1)^\circ$, $\angle\text{Al}-\text{N}-\text{C}=109.0(0.3)^\circ$, and $\angle\text{N}-\text{C}-\text{H}=107.6(0.7)^\circ$. The $\text{Al}-\text{N}$ bond distance in this complex is significantly shorter than the $\text{Al}-\text{N}$ bond distance in $(\text{CH}_3)_3\text{AlN}(\text{CH}_3)_3$ and significantly longer than the $\text{Al}-\text{N}$ bond distances in $(\text{BH}_4)_3\text{AlN}(\text{CH}_3)_3$ and $\text{Cl}_3\text{AlN}(\text{CH}_3)_3$.

Trimethylamine alane, $\text{H}_3\text{AlN}(\text{CH}_3)_3$, was first synthesized by Wiberg and coworkers.¹ The compound is monomeric in the vapour phase^{2,3} and in hydrocarbon solution.

Recently Anderson *et al.* determined the molecular structure of $(\text{CH}_3)_3\text{AlN}(\text{CH}_3)_3$ by gas phase electron diffraction.⁵ They found that the $\text{Al}-\text{C}$ bond distance in the complex is significantly longer than in free monomeric trimethylaluminium, and that the $\text{N}-\text{C}$ bond distance in the complex is significantly longer in free trimethylamine. The $\angle\text{N}-\text{Al}-\text{C}$ valence angle in the complex is 102° while free trimethylaluminium is planar. The $\text{Al}-\text{N}$ bond distance in $(\text{CH}_3)_3\text{AlN}(\text{CH}_3)_3$, 2.10 Å, is significantly longer than in $\text{Cl}_3\text{AlN}(\text{CH}_3)_3$, 1.96 Å.⁶ It was suggested that the difference is due to the inductive effect⁷ of the more electronegative chlorine atoms. In an attempt to study further the effect of different substituents on the aluminium atom on the structure of such complexes we have now determined the molecular structure of $\text{H}_3\text{AlN}(\text{CH}_3)_3$.

EXPERIMENTAL AND CALCULATION PROCEDURE

Trimethylamine alane was prepared as described by Ruff.⁸ The electron scattering pattern was recorded on the Oslo electron diffraction unit⁹ with the sample reservoir at about 75° and a nozzle temperature of about 95° . Exposures were made with nozzle to photographic plate distances of 48 cm and 20 cm. The optical densities of six plates from the first set were recorded at $\Delta s=0.125$ Å⁻¹ intervals, the optical densities of three plates from the last set were recorded at $\Delta s=0.250$ Å⁻¹ intervals. (The scattering parameter

$s = (4\pi/\lambda) \sin(\theta/2)$ where λ is the electron wavelength and θ the diffraction angle.) The optical densities were converted into intensities and the data processed in the usual way.¹⁰

The modified molecular intensity points obtained from the 48 cm plates are shown in Fig. 1A and the modified intensity points obtained from the 20 cm plates are shown in Fig. 2A.

Theoretical intensity curves were calculated from

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

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, N, C, and H by partial wave approximation with a program written by Peacher and Wills.¹¹ The scattering potentials of Al, N, and C have been found by non-relativistic Hartree-Fock calculations.¹² Radial distribution (RD) functions were calculated by Fourier inversion of experimental and 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 then to the theoretical curve obtained for the best model below $s = 2.250 \text{ \AA}^{-1}$.

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.¹³

STRUCTURE ANALYSIS

It was assumed that

- (i) $\text{H}_3\text{AlN}(\text{CH}_3)_3$ has C_{3v} symmetry;
- (ii) the methyl groups have C_{3v} symmetry with the threefold axes coinciding with the N-C bonds;
- (iii) the angle of rotation of the methyl groups about the C-N bonds is such that the hydrogen atoms are staggered with respect to the bonds radiating from the nitrogen atom.

A molecular model in which the hydrogen atoms of the acceptor and the carbon atoms of the donor are staggered with respect to rotation about the Al-N bond is shown in Fig. 3. With this model the molecular geometry is determined by seven independent parameters, *i.e.* by the C-H, N-C, N-Al and Al-H bond distances and the $\angle \text{N-Al-H}$, $\angle \text{Al-N-C}$ and $\angle \text{N-C-H}$ valence angles.

Unfortunately it proved impossible to refine the lengths and vibrational amplitudes of the N-C and Al-H bonds simultaneously. The vibrational amplitude of the N-C bond was therefore fixed at the value found in free trimethylamine, $l(\text{N-C}) = 0.045 \pm 0.003 \text{ \AA}$.¹⁴ In $(\text{CH}_3)_3\text{AlN}(\text{CH}_3)_3$ $l(\text{N-C}) = 0.042(6) \text{ \AA}$.⁵ Refinements were also carried out with $l(\text{N-C}) = 0.042 \text{ \AA}$ and $l(\text{N-C}) = 0.048 \text{ \AA}$. The other parameters then changed less than one standard deviation. The vibrational amplitude of the $\text{N}\cdots\text{H}_4$ distance could not be refined and was fixed at $l(\text{N}\cdots\text{H}_1) = 0.120 \text{ \AA}$. Separate refinements with $l(\text{N}\cdots\text{H}_1) = 0.090 \text{ \AA}$ and $l(\text{N}\cdots\text{H}_1) = 0.150 \text{ \AA}$ lead to insignificant changes in the other parameters. The vibrational amplitudes of all $\text{H}\cdots\text{H}$ distances were fixed at estimated values and not refined.

The seven structure parameters and twelve vibrational amplitudes were refined by least squares calculations on the intensity data with a non-diagonal weight matrix. The parameters obtained and their estimated standard deviations are given in Table 1. The standard deviations have been expanded to include an estimated uncertainty of 1.4 ppt in the electron wavelength.

Table 1. Structure parameters of $H_3AlN(CH_3)_3$ with estimated standard deviations. Carbon and hydrogen atoms are numbered like the methyl group to which they belong (see Fig. 3).

	R (Å)	l (Å)
Al—H	1.560(11)	0.085(13)
Al—N	2.063(8)	0.084(9)
N—C	1.476(3)	0.045 ^a
C—H	1.108(3)	0.065(3)
Al...C ₄	2.900(3)	0.111(3)
N...H ₁	2.877(18)	0.120 ^b
N...H ₄	2.096(10)	0.097(15)
C ₄ ...H ₁	3.271(20)	0.114(13) ^c
C ₄ ...H ₃	4.126(13)	0.084(13) ^c
C ₄ ...C ₅	2.417(3)	0.070(2)
Al...H ₄ (gauche)	3.003(11)	0.164(12) ^d
Al...H ₄ (trans)	3.898(4)	0.104(12) ^d
C ₄ ...H ₅ (gauche)	2.637(10)	0.165(10) ^e
C ₄ ...H ₅ (trans)	3.385(6)	0.105(10) ^e
$\angle H-Al-N$	104.3(1.1) ^{o f}	
$\angle Al-N-C$	109.0(0.3) ^{o f}	
$\angle N-C-H$	107.6(0.7) ^{o f}	

^a Assumed equal to the corresponding amplitude in $N(CH_3)_3$ (see text). ^b Assumed value (see text). ^c These amplitudes were assumed to differ by 0.030 Å. ^d These amplitudes were assumed to differ by 0.060 Å. ^e These amplitudes were assumed to differ by 0.060 Å. ^f The angles have not been corrected for shrinkage.

Modified molecular intensity curves calculated from these parameters are shown in Figs. 1 and 2. Agreement with the experimental data is seen to be satisfactory. An experimental radial distribution curve is shown in Fig. 4A, the difference between this curve and one calculated from the parameters of Table 1 is shown in Fig. 4B. Again the agreement is satisfactory. For interpretation of the radial distribution curve one should consult Table 1.

Refinements were also carried out on a model in which the hydrogen atoms of the acceptor and the carbon atoms of the donor were eclipsed with respect to rotation about the Al—N bond. The agreement obtained was slightly better than for the staggered model; the square error sum decreased by 4%. The Al—H bond distance increased to 1.580(12) Å, the $\angle N-Al-H$ angle

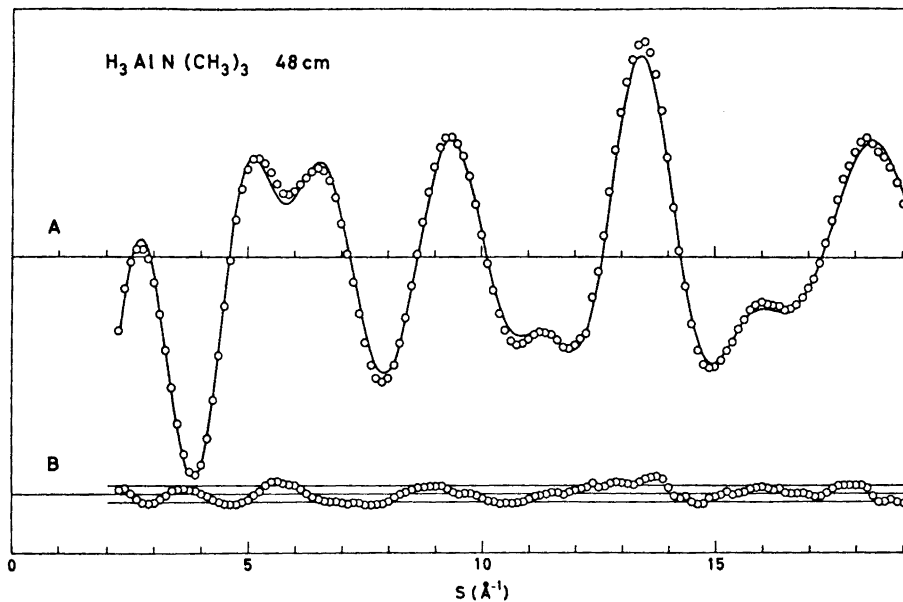


Fig. 1. A. \circ , experimental modified molecular intensity points from $s=2.25 \text{ \AA}^{-1}$ to $s=19.00 \text{ \AA}^{-1}$. The point density is eight points per \AA^{-1} . Full line, theoretical curve calculated from the parameters in Table 1. B. \circ , difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points.

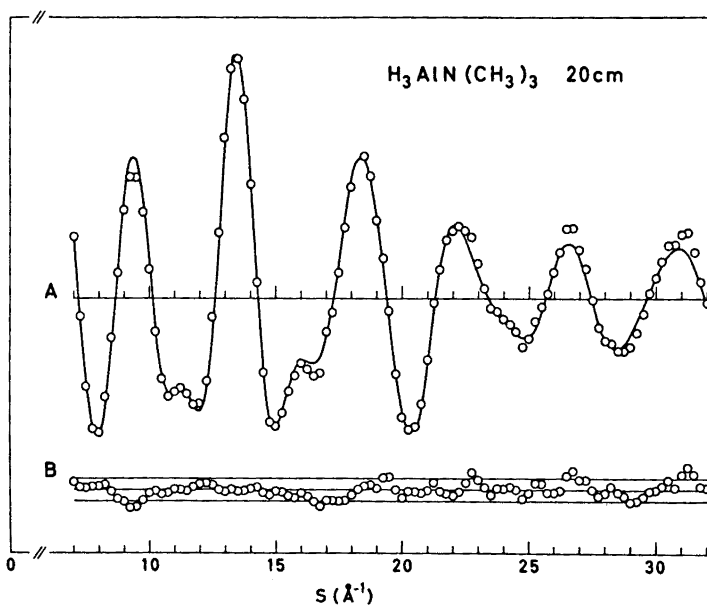


Fig. 2. A. \circ , experimental modified molecular intensity points from $s=7.00 \text{ \AA}^{-1}$ to $s=32.00 \text{ \AA}^{-1}$. The point density is four points per \AA^{-1} . Full line, theoretical modified molecular intensity curve calculated from the parameters in Table 1. B. \circ , difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points.

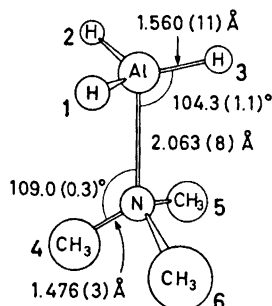


Fig. 3. Molecular model of $\text{H}_3\text{AlN}(\text{CH}_3)_3$.

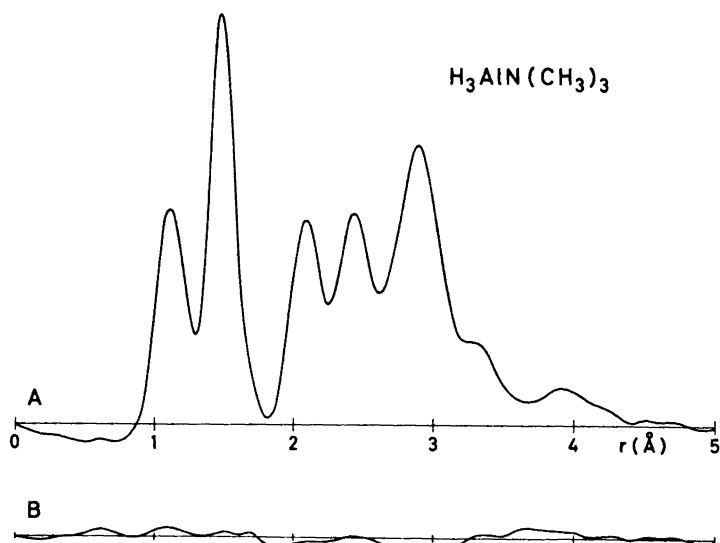


Fig. 4. A. Experimental radial distribution curve. Artificial damping constant $k=0.002 \text{ \AA}^2$. B. Difference between the experimental radial distribution curve and a theoretical curve calculated from the parameters in Table 1.

to $120.6(0.7)^\circ$. The other parameters changed with less than one standard deviation. When the $\angle \text{N}-\text{Al}-\text{H}$ angle was fixed at 108° , the square error sum was 25 % higher than for a staggered model and serious disagreement with the experimental radial distribution curve appeared around 3.3 \AA . An eclipsed model with $\angle \text{N}-\text{Al}-\text{H}$ equal to or less than 108° can therefore be ruled out. Because of the large $\angle \text{N}-\text{Al}-\text{H}$ angle required by an eclipsed model and because chemical experience would seem to favor a staggered model, we regard the better fit obtained with an eclipsed model as an artifact introduced by systematic errors in our method of analysis, *e.g.* the neglect of shrinkage and anharmonicity, and prefer to base our discussion of the structure on the parameters obtained by refinement of the staggered model.

DISCUSSION

After the formation of a complex of the type $X_3AlN(CH_3)_3$ the former lone pair electrons of the amine occupy a two center molecular orbital between the aluminium and nitrogen atoms. In this way negative charge is transferred from the donor to the acceptor. The bonding – and hence the structure – of the donor, should therefore be intermediate between that found in the isolated donor, $N(CH_3)_3$, and that found in analogous positive ions, *e.g.* $N(CH_3)_4^+$. Similarly the bonding – and hence the structure – of the acceptor should be intermediate between that found in the isolated acceptor AlX_3 , and that found in analogous negative ions, *e.g.* X_4Al^- .

As the substituent X becomes more electronegative, increased polarization of the Al–X bonds helps to remove charge from the metal atom. The acceptor strength increases⁷ and one should observe a decrease in the Al–N bond distance and increased deformation of the donor molecule.

Indeed, the Al–N bond distance in $H_3AlN(CH_3)_3$ is significantly shorter than the Al–N bond distance in $(CH_3)_3AlN(CH_3)_3$, 2.099(10) Å,⁵ and significantly longer than the Al–N bond distance in crystalline $(BH_4)_3AlN(CH_3)_3$, 1.99(1) Å,¹⁵ and in crystalline $Cl_3AlN(CH_3)_3$, 1.96(1) Å.⁶

As might be expected the Al–N bond distance in $H_3AlN(CH_3)_3$ is significantly shorter than the Al–N bond distance in the 1:2 complex $H_3Al(N(CH_3)_3)_2$, 2.18(1) Å.¹⁶

The N–C bond distance in $H_3AlN(CH_3)_3$ is indistinguishable from the N–C bond distance in $(CH_3)_3AlN(CH_3)_3$, 1.474(3) Å;⁵ both bond distances are significantly longer than the N–C bond distance in free trimethylamine, 1.454(2) Å,¹⁴ and significantly shorter than the N–C bond distance in crystalline $[N(CH_3)_4]F \cdot 4H_2O$, 1.499(2) Å.¹⁷ The three crystallographically independent N–C bond distances in $Cl_3AlN(CH_3)_3$ are 1.55(2) Å, 1.58(2) Å, and 1.49(2) Å, respectively.⁶ We do not feel that they have been determined with sufficient accuracy to make a comparison meaningful.

In crystalline $(BH_4)_3AlN(CH_3)_3$ at -160° to the N–C bond, distances are 1.506(10) Å (twice) and 1.547(11) Å (once).¹⁵

The angle between the threefold symmetry axis and the C–N bond is $108.3(0.2)^\circ$ in $N(CH_3)_3$,¹⁴ $109.4(0.4)^\circ$ in $(CH_3)_3AlN(CH_3)_3$,⁵ and $109.2(0.3)^\circ$ in $H_3AlN(CH_3)_3$; no significant differences are observed.

The Al–H bond distance in $H_3AlN(CH_3)_3$ is not directly comparable with the Al–H bond distance in crystalline $LiAlH_4$ as determined by X-ray diffraction (1.55 Å¹⁸): Electron diffraction measures the distance between the atomic nuclei, X-ray diffraction the distance between the centre of the electron clouds. Since the hydrogen atom has no inner shell electrons and since the bonding electrons are concentrated in the region *between* the two nuclei, the element-hydrogen bond distances obtained by X-ray diffraction tend to be shorter than those obtained by MW spectroscopy or electron diffraction. For C–H bonds the difference normally lies in the range 0.05 to 0.1 Å.¹⁹ The Al–H bond distance in $LiAlH_4$, therefore, is probably longer than in $H_3AlN(CH_3)_3$.

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REFERENCES

1. Wiberg, E., Graf, H. and Uson, R. *Z. anorg. allgem. Chem.* **272** (1953) 221.
2. Roszinski, H., Dautel, R. and Zeil, W. *Z. physik. Chem. (Frankfurt)* **36** (1963) 26.
3. Fraser, G. W., Greenwood, N. N. and Straugham, B. P. *J. Chem. Soc.* **1963** 3742.
4. Hendricker, D. G. and Heitsch, C. W. *J. Phys. Chem.* **71** (1967) 2683.
5. Anderson, G. A., Forgaard, F. R. and Haaland, A. *Acta Chem. Scand.* **26** (1972) 1947.
6. Grant, D. F., Killean, R. C. G. and Lawrence, J. L. *Acta Cryst. B* **25** (1969) 377.
7. Coates, G. E. and Wade, K. *Organometallic Compounds. The Main Group Elements*, Methuen, London 1967, Vol. 1, p. 204.
8. Ruff, J. K. *Inorg. Syn.* **9** (1967) 30.
9. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232.
10. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* **23** (1969) 3224.
11. Peacher, J. L. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4807.
12. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.
13. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Letters* **3** (1969) 617.
14. Beagley, B. and Hewitt, T. G. *Trans. Faraday Soc.* **64** (1968) 2561.
15. Bailey, N. A., Bird, P. H. and Wallbridge, M. G. H. *Inorg. Chem.* **7** (1968) 1575.
16. Heitsch, C. W., Nordman, C. E. and Parry, R. W. *Inorg. Chem.* **2** (1963) 508.
17. McLean, W. J. and Jeffrey, G. A. *J. Chem. Phys.* **47** (1967) 414.
18. Turley, J. W. and Rinn, H. W. *Inorg. Chem.* **8** (1969) 18.
19. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.

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