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On the Molecular Structure of the Complex Trimethylaluminium—Trimethylamine, $(CH_3)_3AlN(CH_3)_3$

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The molecular structure of $(CH_3)_3AlN(CH_3)_3$ has been determined by gas phase electron diffraction. The main molecular parameters are Al–C = 1.987(5) Å, Al–N = 2.099(10) Å, N–C = 1.474(3) Å, and ∠C–Al–N = 102.3(0.3)° and ∠Al–N–C = 109.3(0.4)°. The changes in the structure of acceptor and donor on formation of the complex are discussed.

The complex trimethylaluminium trimethylamine was first synthesized by Davidson and Brown [1] by direct union of the components. The heat of formation of the gaseous complex from the gaseous components

$$(CH_3)_3Al(g) + N(CH_3)_3(g) = (CH_3)_3AlN(CH_3)_3(g) + \Delta H_f(g)$$

can be calculated from the thermodynamic data collected by Eyman and coworkers [2,3] and the heat of sublimation of the crystalline complex determined by Davidson and Brown,[1]

$$\Delta H_f(g) = -30.69 \pm 0.29 \text{ kcal mol}^{-1}$$

(Eyman and coworkers [3] having exchanged the heat of sublimation with heat of vaporization of the liquid complex, incorrectly obtains $\Delta H_f(g) = -32.29$ kcal mol^{-1}). The complex is not noticeably dissociated in the gas phase below 150°C.[1]

Trimethylaluminium forms weaker complexes with ethers than with amines: The heat of formation of the gaseous complex with dimethylether [3] is $\Delta H_f(g) = 21.92 \pm 0.18$ kcal mol^{-1}. The molecular structure of this compound has not been determined, but the molecular structure of a very similar compound, the 2 : 1 complex of trimethylaluminium with dioxane, has been determined by Atwood and Stucky.[4]

Replacement of the methyl groups in trimethylaluminium by more electronegative substituents, *e.g.* by chlorine atoms, increases the acceptor strength. The heat of formation of the crystalline complex $Cl_3AlN(CH_3)_3$ [5] from the

gaseous components is -64.5 kcal mol^{-1}. The heat of sublimation of this complex is unknown, but on the basis of the heats of sublimation of $(CH_3)_3AlN(CH_3)_3$,[1] 12.5 kcal mol^{-1}; $(CH_3)_2ClAlN(CH_3)_3$,[1] 14.4 kcal mol^{-1}; and $Br_3Al.pyridine$,[6] 19.9 kcal mol^{-1} we might assume that $\Delta H_{subl} = 17 \pm 2$ kcal mol^{-1}. The heat of formation of gaseous $Cl_3AlN(CH_3)_3$ then becomes $\Delta H_f(g) = -47.5 \pm 2.0$ kcal mol^{-1}.

After formation of these complexes the former lone pair electrons on the donor occupy a two center molecular orbital between the aluminium atom and the nitrogen or oxygen atom on the donor. In this way negative charge is transferred from the donor to the acceptor. The bonding in the donor should therefore be intermediate between that found in the isolated donor and that found in analogous positive ions, while the bonding in the acceptor should be intermediate between that found in the isolated acceptor and that found in analogous negative ions. The stronger the complex the closer the bonding in donor and acceptor should approach the ionic limit. It is therefore of interest not only to compare the molecular structure of a complex like $(CH_3)_3AlN(CH_3)_3$ with the structure of $(CH_3)_3Al$ [7] and $N(CH_3)_3$,[8] but also with the structure of the ions $[(CH_3)_4Al]^{-1}$,[9] and $[N(CH_3)_4]^{+1}$.[10]

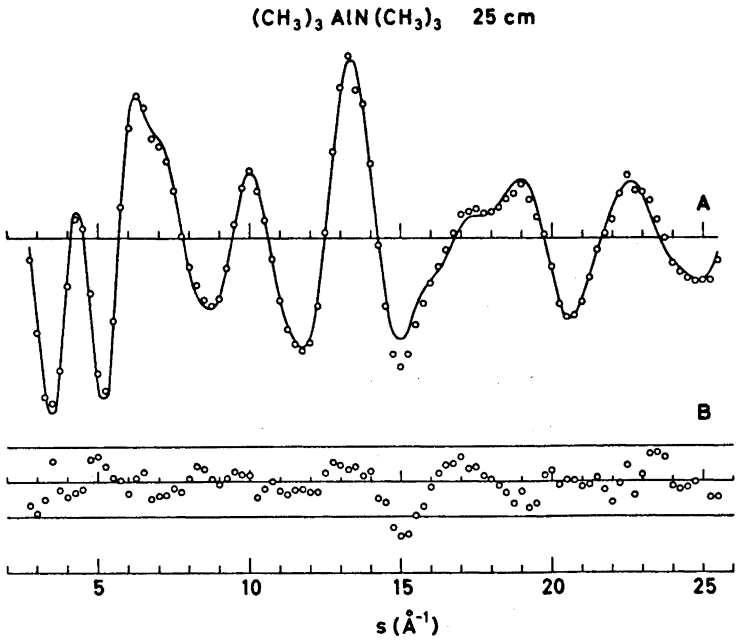

Fig. 1. A. ○; experimental modified molecular intensity points from $s = 1.250$ Å^{-1} to $s = 14.875$ Å^{-1}. The point density is eight points per Å^{-1}. Full line; theoretical modified molecular intensity curve calculated from the parameters in Table 1. B. ○; difference points. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. *Note:* The scale of B is twice that of A.

EXPERIMENTAL AND CALCULATION PROCEDURE

Trimethylaluminium trimethylamine was prepared according to the method of Davidson and Brown [1] and identified by its mass spectrum. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2 with the sample reservoir at 65°C (corresponding to a vapour pressure of about 15 mm [1]) and a nozzle temperature of about 80°C. Exposures were made with nozzle-to-photographic plate distances of 50 cm and 25 cm. The optical densities of four 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 $s = (4\pi/\lambda)\sin(\theta/2)$ when λ is the electron wavelength (determined by diffraction from solid ZnO) and θ the diffraction angle). The optical densities were converted into intensities and the data processed in the usual way.[11]

The modified molecular intensity points obtained from the 50 cm plates are shown in Fig. 1A and the modified molecular intensity points obtained from the 25 cm plates are shown in Fig. 2A. Theoretical intensity curves were calculated from

$$I^{\mathrm{AIC}}(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_{\mathrm{Al}}(s)||f_{\mathrm{C}}(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}l^2_{ij}s^2)$$

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, N, C, and H by the partial wave approximation with a program written by Peacher.[12] The scattering potentials of Al, N, and C have been found by non-relativistic Hartree-Fock calculations.[13,14]

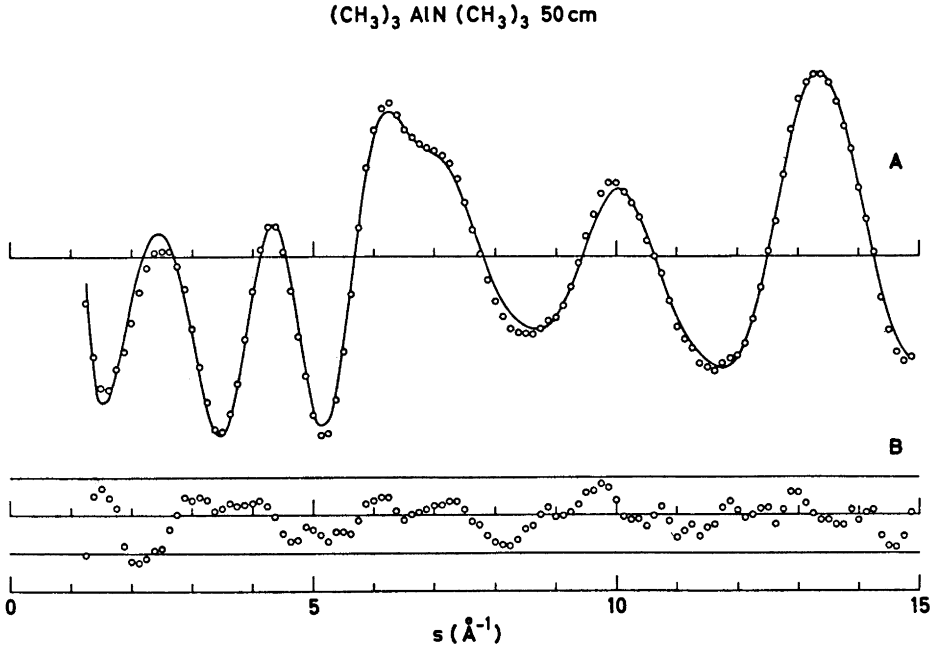

Fig. 2. A. O; experimental modified molecular intensity points from $s = 3.75$ Å^{-1} to $s = 25.50$ Å^{-1}. The point density is four points per Å^{-1}. Full line; theoretical modified molecular intensity curve, calculated from the parameters in Table 1. B. O; difference points. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. *Note:* The scale of B is twice that of A.

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 then to the theoretical curve obtained for the best model below $s = 1.25$ Å^{-1}.

The molecular structures were 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.[15]

STRUCTURE ANALYSIS

It was assumed that

(i) $(CH_3)_3AlN(CH_3)_3$ has C_{3v} symmetry;
(ii) All C – H bond distances are equal;
(iii) All methyl groups have C_{3v} symmetry with the threefold axes coinciding with the C – Al or C – N bond;
(iv) The angle of rotation of the methyl groups about the C – Al and C – N bonds is such that the hydrogen atoms are staggered with respect to the bonds radiating from the aluminium and nitrogen atoms.

A molecular model in which the carbon atoms of donor and acceptor are staggered with respect to rotation about the Al – N bond is shown in Fig. 3. It was found that models where the carbon atoms were eclipsed or where there was essentially nonhindered rotation about the Al – N bond could not be brought into agreement with the electron diffraction data. The molecular structure is then determined by eight independent parameters, *viz.* by the C – H (mean), Al – C, Al – N, and N – C bond distances and the ∠Al – C – H, ∠C – Al – N,

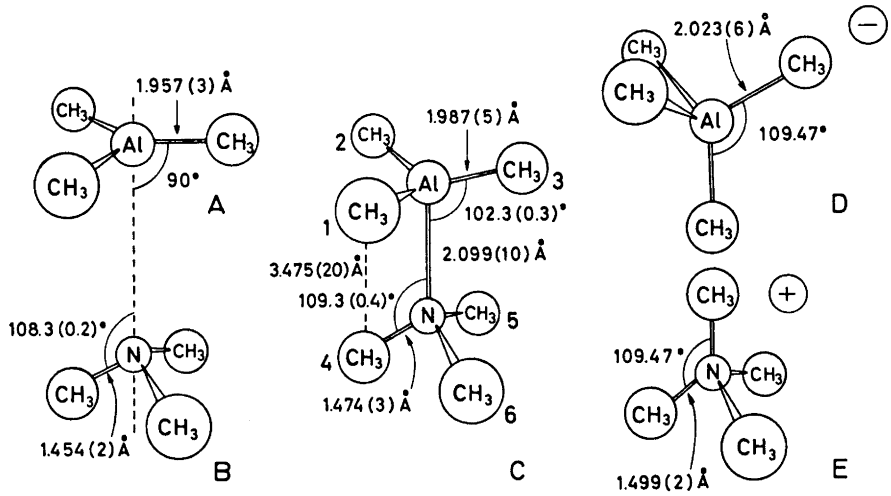

Fig. 3. Molecular structures of $(CH_3)_3Al$[7] (A), $N(CH_3)_3$[8] (B), $(CH_3)_3AlN(CH_3)_3$ (C), and the tetrahedral ions $[(CH_3)_4Al]^-$ (D) and $[N(CH_3)_4]^+$ (E). The Al – C bond distance in $[(CH_3)_4Al]^-$ has been taken from the crystal structure of $LiAl(C_2H_4)_4$,[9] the N – C bond distance in $[N(CH_3)_4]^+$ from the crystal structure of $[N(CH_3)_4]F.4H_2O$.[10]

$\angle$Al−N−C, and $\angle$N−C−H valence angles. As large amplitude intramolecular motion, particularly libration about the Al−N bond, could lead to average values for the distances $C_1 \cdots C_4$ and $C_1 \cdots C_5$ (see Fig. 3) that are significantly different from those calculated from the equilibrium geometry, these distances too were refined as independent parameters.

Unfortunately it proved impossible to refine the lengths and vibrational amplitudes of the Al−C and Al−N bonds simultaneously. The vibrational amplitude of the Al−C bond was therefore fixed at the value found in monomeric trimethylaluminium,[7] l(Al−C) = 0.061(1) Å. Refinements were also carried out with l(Al−C) = 0.058 Å and l(Al−C) = 0.064 Å. The other parameters then changed less than one standard deviation. The amplitude of the $N-H_4$ distance (hydrogen atoms being numbered according to the methyl group to which they belong) could not be refined and was fixed at the value found in trimethylamine,[8] 0.097 ± 0.010 Å.

The remaining molecular parameters were refined by least squares calculations on the intensity data with a non-diagonal weight matrix.[15] The main molecular parameters obtained and their estimated standard deviations are shown in Table 1.

Table 1. Structure parameters of $(CH_3)_3AlN(CH_3)_3$ with estimated standard deviations. Carbon and hydrogen atoms are numbered like the methyl groups to which they belong (see Fig. 3). The distances are given as r_a. The angles have not been corrected for shrinkage.

	R (Å)	l (Å)
C−H(mean)	1.106(4)	0.083(6)
Al−C	1.987(5)	0.061(assumed)
Al−N	2.099(10)	0.078(18)
N−C	1.474(3)	0.042(6)
Al···C_4	2.937(9)	0.105(9)
Al−H_1	2.608(6)	0.095(12)
N···C_1	3.184(34)	0.095(21)
N···H_4	2.150(42)	0.097(assumed)
$C_1 \cdots C_2$	3.362(17)	0.067(13)
$C_1 \cdots C_4$	3.506(16)	0.176(15)
$C_1 \cdots C_5$	4.470(15)	0.130(13)
$C_4 \cdots C_5$	2.409(9)	0.058(8)
$\angle$C−Al−N	102.3(0.3)°	
$\angle$Al−N−C	109.3(0.4)°	
$\angle$Al−C−H	111.8(1.0)°	
$\angle$N−C−H	112.1(2.0)°	

Modified molecular intensity curves calculated from the parameters in Table 1 are shown in Fig. 1 and Fig. 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.

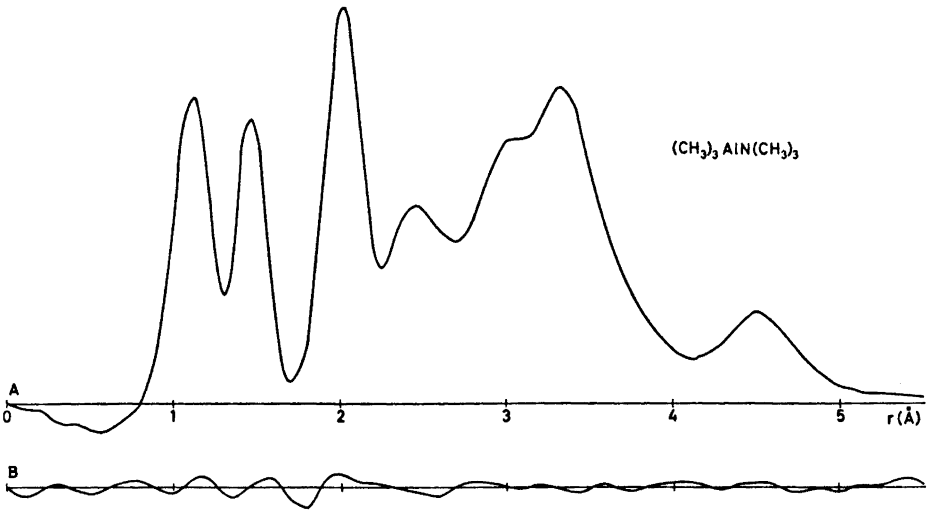

Fig. 4. A. Experimental radial distribution curve. B. Difference between the experimental radial distribution curve and a theoretical curve calculated from the parameters in Table 1. Artificial damping constant $k = 0.002$ Å^2.

DISCUSSION

The Al–N bond distance. The Al–N bond distance in $(CH_3)_3AlN(CH_3)_3$, 2.099(10) Å, may be compared to the Al–N bond distance in the complexes $(BH_4)_3AlN(CH_3)_3$ [16] and $Cl_3AlN(CH_3)_3$,[17] 1.99(1) Å and 1.96(1) Å, respectively. The trend is that expected from the inductive effect of more electronegative substituents on the aluminium atom, though the magnitude of the change may be surprising.

A difference of the same order of magnitude has, however, been found between the Al–O distances in complexes of $(CH_3)_3Al$ and Cl_3Al with oxygen donors: In the 2 : 1 complex of $(CH_3)_3Al$ with dioxane [4] Al—O = 2.02(2) Å, while in Cl_3Al.benzoylchloride [18] Al–O = 1.819(5) Å. The B–N bond distance of the complex $Cl_3BN(CH_3)_3$ [19] is 1.575(11) Å. The molecular structure of the complex $(CH_3)_3BN(CH_3)_3$ has not been determined. This complex is largely dissociated in the gas phase, but Lide and coworkers,[20,21], on the basis of a few recorded microwave absorption lines, estimate that in this compound the B–N bond distance lies in the range 1.70 to 1.90 Å. This estimate was challenged at the time,[22] but in view of the large inductive effect now established for the Al–N and Al–O dative bond distances, the estimate of Lide and coworkers appears reasonable.

Compounds of the type $R_2Al-NR'_2$ associate through the formation of symmetrical nitrogen bridges. The Al–N bridge bonds may be regarded as 50 % covalent and 50 % dative. It is interesting to note that the Al–N bond distances found in these compounds is exactly the average of the covalent bond distances found in $Al[N(Si(CH_3)_3)_2]_3$ [23] and in the cage compound

$Al_4Cl_4[N(CH_3)_2]_4(NCH_3)_2$,[24] 1.78(2) Å and 1.79(3) Å, respectively, and the dative Al–N bond distance in $(CH_3)_3AlN(CH_3)_3$: In $[(CH_3)_2AlN(CH_3)_2]_2$ [25] the Al–N bond distance is 1.955(5) Å, in $[(CH_3)_2AlN(CH_2)_2]_3$ [25] the three crystallographically nonequivalent Al–N distances are 1.90(2) Å, 1.93(2) Å, and 1.95(1) Å.

The structure of the acceptor. The Al–C bond in $(CH_3)_3AlN(CH_3)_3$, 1.987(5) Å, is significantly longer than in isolated trimethylaluminium monomer,[4] 1.957(3) Å, but significantly shorter than the Al–C bond distance in crystalline $LiAl(C_2H_5)_4$ [9] which may be understood as consisting of Li^+ and $[Al(C_2H_5)_4]^-$ ions, 2.023(6) Å. The Al–C bond distances in the complex of $(CH_3)_3Al$ with dioxane [4] are similar, 1.96(1) Å (twice) and 1.98(2) Å. Similarly the Al–Cl distance in $Cl_3AlN(CH_3)_3$,[17] 2.11(1) Å, 2.12(1) Å, and 2.14(1) Å, are significantly longer than the Al–Cl distance in monomeric $AlCl_3$,[27] 2.06(1) Å, but they are indistinguishable from the Al–Cl distance found in $Na[AlCl_4]$,[28] 2.13 Å.

While monomeric $(CH_3)_3Al$ is planar, the ∠N–Al–C valence angle in the complex is 102.3(0.3)° which corresponds to a ∠C–Al–C angle of 114.8(0.2)°. The deformation of the acceptor in the complex with dioxane [4] is somewhat smaller; the ∠O–Al–C angles are 99.6(0.4)° (twice) and 101.9(0.6)°. The angle deformation of $AlCl_3$ in $Cl_3AlN(CH_3)_3$ [17] is greater, though the ∠N–Al–Cl angles are still less than tetrahedral; 108.1(0.5)°, 106.5(0.3)°, and 106.3(0.5)°.

The structure of the donor. The N–C bond in $(CH_3)_3AlN(CH_3)_3$, 1.474(3) Å, is significantly longer than in trimethylamine,[8] 1.454(2) Å, and significantly shorter than the N–C distance found in $[N(CH_3)_4]F.4H_2O$,[10] 1.499(2) Å. The N–C bond in $Cl_3AlN(CH_3)_3$ should be longer than in $(CH_3)_3Al(CH_3)_3$, but they have not been determined with sufficient accuracy to make a comparison meaningful.

The valence angles in trimethylamine have not been significantly altered in $(CH_3)AlN(CH_3)_3$.

The molecular conformation. The equilibrium conformation of $(CH_3)_3AlN(CH_3)_3$ is that in which the carbon atoms are staggered with respect to rotation about the Al–N bond. In this conformation the $C_1\cdots C_4$ distance calculated from the equilibrium geometry is 3.47(2) Å, and the shorterst distance between hydrogen atoms in the two methyl groups is 2.4 Å.

The amplitudes of vibration of the $C_1\cdots C_4$ and $C_1\cdots C_5$ distances show that the molecule is fairly rigidly held in the equilibrium conformation. The average values of the two distances are found to be, respectively, longer and shorter than those calculated from the equilibrium geometry, but the differences are not significant.

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