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STUDIES OF ALKYLMETAL ALKOXIDES OF ALUMINIUM, GALLIUM AND INDIUM

IV*. THE MOLECULAR STRUCTURE OF DIMETHYLALUMINIUM t-BUTOXIDE DIMER BY GAS PHASE ELECTRON DIFFRACTION

ARNE HAALAND* and ODDVAR STOKKELAND

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

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Summary

The electron diffraction data for gaseous dimethylaluminium t-butoxide dimer are consistent with a molecular model of effective D_{2h} symmetry. The Al_2O_2 ring is planar and the three valencies of the O atoms are lying in a plane. The t-butyl groups undergo nonhindered or slightly hindered internal rotation. The most important bond distances and valence angles are: Al—O = 1.864(6), Al—C = 1.962(15), O—C = 1.419(12), C—C = 1.533(5) Å, ∠Al—O—Al = 98.1(0.7), ∠C—Al—C = 121.7(1.7) and ∠O—C—C = 110.4(0.5)°.

Dimethylaluminium t-butoxide, Me_2AlO-t-Bu, is dimeric in freezing benzene [2]. The ^1H NMR spectrum in benzene [3] or CCl_4 [2] consists of two sharp peaks of relative area close to 3/2.

Previously we have determined the molecular structure of trimeric Me_2AlOMe in the gas phase by electron diffraction [4]. The central Al_3O_3 ring was found to be nonplanar, but the three valencies of the O atoms were lying in a plane or very nearly so. The planarity of the O atoms might be rationalized by invoking dative $p\pi$—$d\pi$ O—Al bonding or by steric interactions of the type Al···C(O) [5].

More recently we have carried out ab initio molecular orbital calculations on the model compound $(H_2AlOH)_2$ [6]. The calculations indicated that the equilibrium conformation of this molecule is one in which the O—H bonds are bent 25° out of the plane of the Al_2O_2 ring, but the energy of a planar confor-

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* For part III see ref. 1.

mation is only 0.35 kcal mol^{-1} higher. There was no indication for the formation of dative $p\pi$—$d\pi$ bonds between O and Al in the equilibrium or in the planar conformation.

We now report the molecular structure of dimeric Me_2AlO-t-Bu by means of gas phase electron diffraction.

Experimental and calculation procedure

Me_2AlO-t-Bu was prepared from trimethylaluminium and t-butanol in benzene [2, 3] and purified by sublimation. The uncorrected melting point was 80-81°C (lit. [3] 80-82°). The electron scattering pattern was recorded on Balzers Eldigraph KD-G2. The nozzle temperature was about 90°C. Exposures were made with nozzle to photographic plate distances of 50 cm and 25 cm. Five plates from the first set and six from the second were photometered and the data corrected and processed as described by Andersen et al. [7].

The modified molecular intensity points obtained from the 50 cm plates are shown in Fig. 1A, the modified molecular intensity points obtained from the 25 cm plates are shown in Fig. 2A.

Theoretical intensity curves were calculated from:

$$I^{\mathrm{AlC}}(s) = \sum_{\mathrm{i}\neq\mathrm{j}} \frac{|\mathrm{f_i}(s)| \cdot |\mathrm{f_j}(s)|}{|\mathrm{f_{Al}}(s)| \cdot |\mathrm{f_C}(s)|} \cos(\eta_\mathrm{i}(s) - \eta_\mathrm{j}(s)) \frac{\sin(R_{\mathrm{ij}}s)}{R_{\mathrm{ij}}} \exp(-\tfrac{1}{2}l_{\mathrm{ij}}^2 s^2)$$

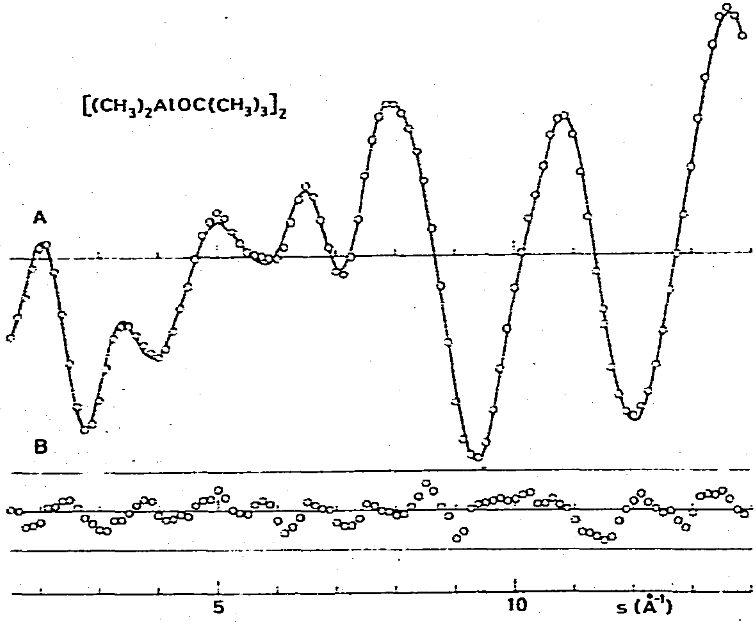

Fig. 1.A. ○: Experimental modified molecular intensity points from s = 1.500 Å^{-1} to 13.875 Å^{-1}. Full line: Theoretical intensity curve calculated for best model. B. ○: Difference points. The two full lines indicate the estimated uncertainty (three standard deviations) of the experimental values. *Note*: The scale of B is twice that of A.

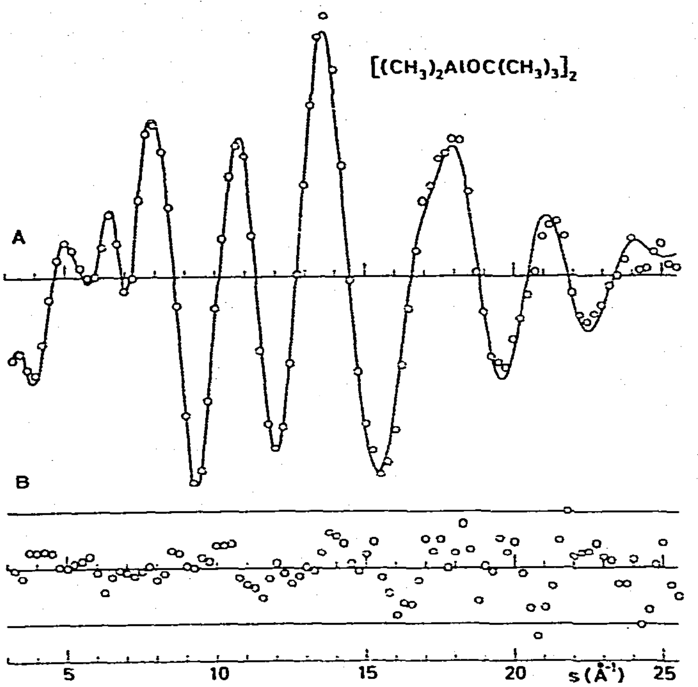

Fig. 2. A. ○: Experimental modified molecular intensity points from s = 3.250 Å^{-1} to 25.500 Å^{-1}. Full line: Theoretical intensity curve calculated for best model. B. ○: Difference points. The two full lines indicate the estimated uncertainty (three standard deviations) of the experimental values. *Note*: The scale of B is twice that of A.

The sum extends over all atom pairs 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 [7].

The molecular structure was refined by least-squares calculations on the intensity data under the constraints of a geometrically consistent r_a structure and with a separately refined scale factor for each nozzle-to-plate distance. Initial refinements are made with a diagonal-, the final refinements of the best model with a non-diagonal-weight matrix [8]. The standard deviations obtained were expanded to take into account an estimated uncertainty of 0.1% in the electron wavelength.

Radial distribution curves were calculated by Fourier inversion of experimental and calculated intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$. The experimental intensity functions were then spliced to each other and to the theoretical curve calculated for the best model below s = 1.500 Å^{-1}.

Structure refinement

A molecular model of $(Me_2AlO\text{-}t\text{-}Bu)_2$ is shown in Fig. 3. It was assumed that: (i) Except for Me groups in the t-Bu group the molecular symmetry is D_{2h}. This implies that the Al_2O_2 ring is planar and that the three valencies of the O atom are lying in a plane. (ii) The t-Bu groups have C_{3v} symmetry with the

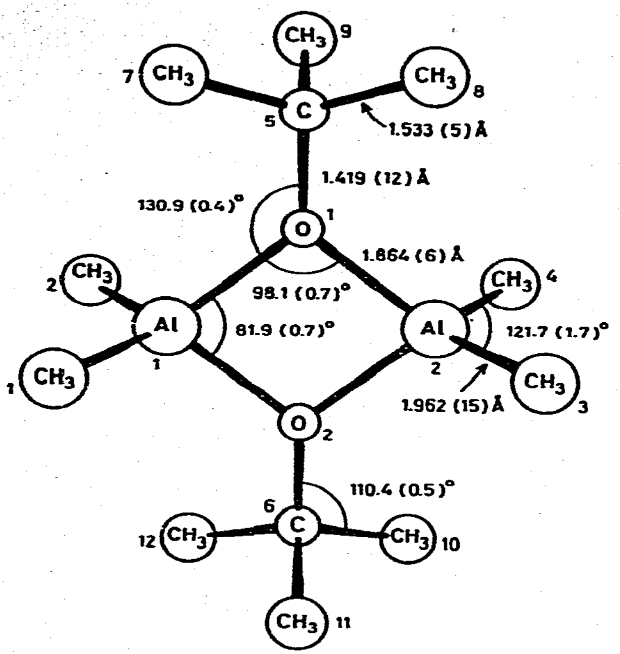

Fig. 3. Molecular model of $(Me_2AlO\text{-}t\text{-}Bu)_2$, symmetry C_{2h}.

threefold axes coinciding with the C—O bonds. (iii) All Me groups have C_{3v} symmetry with the threefold axes coinciding with the C—C or Al—C bonds. The ∠C—C—H valence angle is equal to the corresponding angle in $(CH_3)_3CCl$, 110.8° [9], ∠Al—C—H is equal to the corresponding angle in $[(CH_3)_3Al]_2$, 112.1° [10]. All C—H bond distances are equal. (iv) The angle of rotation of the Me groups about the C—C and Al—C bonds is such that the H atoms are staggered with respect to the bonds radiating from the C(O) or Al atoms respectively.

If the orientation of the t-Bu groups with respect to rotation about the C—O bonds is as indicated in Fig. 3, the molecular symmetry is C_{2h}, and the molecular structure is determined by eight independent parameters, e.g. the five bond distances C—H, C—C, C—O, Al—O and Al—C and the three valence angles ∠Al—O—Al, ∠C—Al—C and ∠O—C—C.

$(Me_2AlO\text{-}t\text{-}Bu)_2$ is with its 46 atoms one of the largest molecules that have been investigated by gas phase electron diffraction, and the number of interatomic distances (not counting H···H distances) is greater than one hundred. As a consequence only a very limited number of vibrational amplitudes could be refined. The remainder were fixed at what happened to be reasonable valves compared to similar amplitudes in t-BuCl [9], $(Me_2AlOMe)_3$ [4] and $(Me_2AlCl)_2$ [11] as indicated in Table 1.

Least-squares refinement of the eight unknown structure parameters with a diagonal weight matrix converged to give an R-factor of $R_2 = 12.65$ [8]. The calculated radial distribution curve showed serious disagreement with the experimental curve in the region above 3.2 Å.

The model was then modified to contain non-planar O atoms; the two C—O bonds were assumed to be bent out of the plane of the Al_2O_2 ring in such a way that the two t-Bu groups are *trans* to each other, as are the Me(S) groups in $(Me_2AlSMe)_2$ [12]. The molecular symmetry remains C_{2h}. Least-squares refinements were carried out for a series of fixed values for the angle α between the O—C bonds and the Al_2O_2 plane. The R factor was found to increase with α from $R_2 = 12.65$ for $\alpha = 0°$ to $R_2 = 16.04$ for $\alpha = 10°$ and even higher for $\alpha = 20°$ and $\alpha = 30°$.

Finally, least-squares refinements were carried out on a model with planar O atoms and non-hindered ($V = 0$) rotation of the t-Bu groups about the O—C bonds, i.e. the gas jet was assumed to contain an even distribution of molecules with all orientations of the t-Bu groups. The effective symmetry of the whole molecule is then D_{2h} and the molecular structure is determined by the same eight parameters as before. The refinements led to convergence with $R_2 = 6.36$. In our view the difference in R-factors is so large as to allow us to rule out the other models.

Finally the free rotation model was refined with a non-diagonal weight matrix to give the structure parameters listed in Tables 1 and 2. The estimated standard deviations obtained have been multiplied by a factor of 2.0 in order

TABLE 1

INTERNUCLEAR DISTANCES AND ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (l) OF $(Me_2AlO\text{-}t\text{-}Bu)_2$

Estimated standard deviations are given in parentheses in units of the last digit. The distances are listed as r_a. For numbering of the atoms consult Fig. 3.

	R (Å)	l (Å)
Bond distances		
Al—O	1.864(6)	0.057(12)
Al—C	1.962(15)	0.060 [a]
O—C	1.419(12)	0.050 [a]
C—C	1.533(5)	0.014(29)
C—H (mean)	1.110(7)	0.059(10)
Nonbonded distances		
Al···Al	2.82(2)	0.100 [a]
$Al\cdots C_5$	2.99(1)	0.120 [a]
$Al_1\cdots C_7$ $Al_1\cdots C_8$ from $Al_1\cdots C_9$ to	3.18(1) 4.26(1)	0.200 [a] 0.120 [a]
$Al_1\cdots H_1$	2.59(1)	0.130 [a]
O···O	2.44(2)	0.100 [a]
$O_1\cdots C_1$	3.16(1)	0.120 [a]
$O_1\cdots C_6$	3.86(2)	0.120 [a]
$O_1\cdots C_7$	2.43(1)	0.063 [a]
$C_1\cdots C_2$	3.43(5)	0.130 [a]
$C_1\cdots C_3$	4.73(2)	0.700 [a]
$C_1\cdots C_4$	5.84(1)	0.200 [a]
$C_1\cdots C_5$	3.94(1)	0.130 [a]
$C_1\cdots C_7$ $C_1\cdots C_8$ from $C_1\cdots C_9$ to	3.51(1) 5.39(1)	0.200 [a] 0.200 [a]
$C_7\cdots C_8$	2.49(1)	0.071 [a]
$C_5\cdots H_7$	2.19(1)	0.200 [a]

[a] Assumed value.

TABLE 2

BOND ANGLES IN $(Me_2AlO\text{-}t\text{-}Bu)_2$
Estimated standard deviations in parentheses.

∠Al—O—Al	98.1(0.7)
∠O—Al—O	81.9(0.7)
∠C—Al—C	121.7(1.7)
∠Al—O—C	130.9(0.4)
∠O—C—C	110.4(0.5)
∠Al—C—H	112.1 [a]
∠C—C—H	110.8 [a]

[a] Assumed value, see text.

to compensate for errors introduced by assumptions (ii) to (iv) above and the fixed vibrational amplitudes.

Modified molecular intensity curves calculated for the best model are shown in Fig. 1A and Fig. 2A. The difference between experimental and calculated intensities is shown in Fig. 1B and Fig. 2B. The agreement is satisfactory.

An experimental radial distribution function is shown in Fig. 4A, the difference between this curve and a theoretical curve calculated for the best model is shown in Fig. 4B.

Molecular mechanics calculations

Some molecular mechanics calculations were carried out in order to obtain information about the equilibrium conformation of the t-Bu groups and their barrier to internal rotation. The energy of the molecule was calculated from

$$E = E_\phi + E_R$$

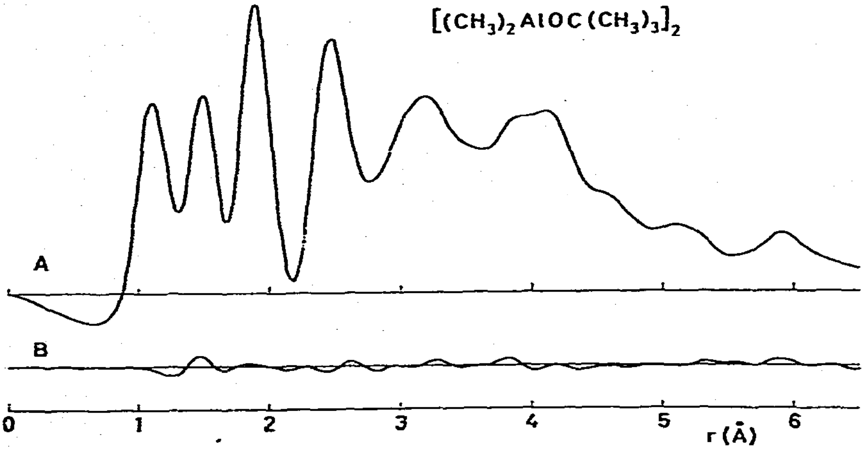

Fig. 4. Experimental radial distribution curve. Artificial damping constant k = 0.004 Å^2. B. Difference between experimental curve and theoretical curve calculated for best model.

where

$$E_\phi = \Sigma \tfrac{1}{2} V_0(1 + \cos 3\phi)$$

is the torsional strain and,

$$E_R = \Sigma[a \exp(-bR) - c/R^6]$$

is the van der Waals strain [13]. The first sum extends over the torsional angles of the six Me groups bonded to C and the four Me groups bonded to Al. The inherent torsional barrier V_0 was assumed equal to 2.65 kcal mol^{-1} for the Me(C) groups [13] and 1.00 kcal mol^{-1} for the Me(Al) groups.

Calculations were first carried out with the van der Waals interactions summed over all C···C, C···H and H···H distances and the values for the parameters a, b and c recommended by Abraham and Parry [13]. The angles of rotation of the t-Bu groups were fixed at several values and for each the angles of rotation of the Me(C) and Me(Al) groups varied to minimize the energy. The lowest energy was obtained for the conformation indicated in Fig. 3. The highest energy was obtained by rotating both t-Bu groups 30° from its position. If it is assumed that the inherent barrier to rotation about the O—C bond is negligible, the effective barrier to rotation of one t-Bu is given by half the difference in the strain energies calculated for these two models. The effective barrier thus obtained is 0.61 kcal mol^{-1}.

The calculations were repeated with the van der Waals parameters a, b and c of Al, O, C and H estimated from the parameters listed by Eliel et al. [14]. Again the calculated equilibrium conformation was that shown in Fig. 3, but the calculated barrier was only 0.06 kcal mol^{-1}.

Discussion

The electron diffraction data are consistent with a model of $(Me_2AlO\text{-t-Bu})_2$ with effective D_{2h} symmetry with freely rotating t-Bu groups. This symmetry implies that the Al_2O_2 ring is planar and that the three valencies of the O atom are lying in a plane. Models with non-planar O atoms can be ruled out.

Molecular mechanisms calculations indicate that the equilibrium conformation of the molecule is that shown in Fig. 3 and that the barrier to rotation of the t-Bu groups is of the order of 0.5 kcal mol^{-1}. The electron diffraction data were collected with a nozzle temperature of about 90°C, the thermal energy available at this temperature, RT = 0.72 kcal mol^{-1}, would be sufficient to overcome a barrier of this magnitude. There is therefore agreement between the electron diffraction results and the molecular mechanics calculations. The model is also in agreement with the simple ^1H NMR spectra obtained for $(Me_2AlO\text{-t-Bu})_2$ in solution [2, 3].

$(Me_2AlO\text{-t-Bu})_2$ is therfore iso-structural with $(Br_2AlOSiMe_3)_2$ which has been studied by X-ray diffraction [15], but the Al—O bond distances in the latter compound appear to be about 0.06 Å shorter, possibly as a result of the more electronegative Br atoms.

Since ab initio molecular orbital calculations on $(H_2AlOH)_2$ [6] indicated that the equilibrium conformation of the molecule is one in which the O—H bonds are bent some 25° out of the plane of the Al_2O_2 ring and gave no indication of the formation of dative $p\pi$—$d\pi$ bonds between O and Al, the planarity of the O atoms in $(Me_2AlO\text{-}t\text{-}Bu)_2$ is best rationalized as resulting from steric repulsions of the type $Al\cdots C_5$, $Al_1\cdots Me(C)$ and $Me(Al)\cdots Me(C)$.

In the trimer $(Me_2AlOMe)_3$ [4] six $Me(Al)\cdots Me(O)$ distances are of the order of 3.5 Å or shorter. Introduction of bulky t-Bu groups of O would clearly lead to excessive van der Waals strain and Me_2AlO-t-Bu consequently forms a dimer rather than a trimer. In this dimer the shortest $Me(Al)\cdots Me(C)$ distances are 3.51 Å whether the t-Bu rotate freely or are fixed in the conformation indicated in Fig. 3. Introduction of t-Bu groups on Al would again be expected to lead to excessive van der Waals strain. t-Bu_2AlO-t-Bu is a solid which does not melt below 220°C [16]. It seems reasonable to assume that the solid consists of linear infinite polymers like those found in crystalline Me_2AlSMe [17]. Such a polymer would allow the t-Bu(Al) and t-Bu(O) groups to be situated at opposite sides of the Al_xO_x chain.

No statistically significant differences are found between the bond distances in trimeric Me_2AlOMe and dimeric Me_2AlO-t-Bu, but the endocyclic angles are of course very different. The ∠Al—O—Al angle decreases by nearly 28° from 125.8(0.4)° in the trimer to 98.1(0.7)° in the dimer, ∠O—Al—O decreases by 21° from 103.2(1.1)° in the trimer to 81.9(0.7)° in the dimer. That ∠Al—O—Al is 16° greater than ∠O—Al—O in the dimer is best explained as the result of $Al\cdots Al$ repulsions across the ring. The actual $Al\cdots Al$ distance, 2.82 Å, is smaller than in the metal.

Since the O atom is planar in both compounds, the closing of ∠Al—O—Al in the dimer leads to a noticeable increase of the ∠Al—O—C valence angle, from 116.9(0.3)° in the trimer to 130.9(0.4)° in the dimer. ∠C—Al—C on the other hand changes only by about 4°, from 117.0(0.8)° in the trimer to 121.7(1.7)° in the dimer. It seems reasonable to infer that the bonds in the Al_2O_2 ring of the dimer are highly bent.

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