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THE MOLECULAR STRUCTURE OF DI(μ-1-PROPYNYL)BIS(DIMETHYLALUMINIUM), $[(CH_3)_2Al(\mu\text{-}C{\equiv}CCH_3)]_2$, DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The electron scattering pattern of di(μ-1-propynyl)-bis(dimethylaluminium) (I) has been recorded from s = 2.50 to 36.50 $Å^{-1}$ with a nozzle temperature of 88±6 °C.

Models of $\underline{D}_{2h}$ symmetry (with the C≡C bonds perpendicular to the Al•••Al vector) were not compatible with the electron diffraction data. A model of $\underline{C}_{2h}$ symmetry could be brought into satisfactory agreement with the data. The structure parameters obtained by least squares calculations on the intensity data suggest that (I) may be regarded as consisting of two somewhat distorted $(CH_3)_2AlC{\equiv}CCH_3$ units which are joined by donation of π-electrons from the C≡C bond of each unit into an empty atomic orbital on the Al atom of the other unit.

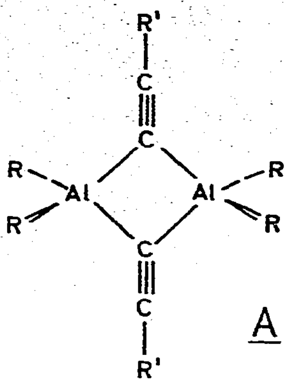
Introduction

The structure of the trimethylaluminium dimer has been determined by X-ray crystallography [1,2,3] and by gas phase electron diffraction [4]. When the hydrogen atoms of the two bridging methyl groups are excluded, the molecular symmetry is $\underline{D}_{2h}$ or very nearly so, and the (approximate) threefold symmetry axes of the bridging methyl groups bisect the Al-Al vector [3]. The structure indicates that each bridging methyl group interacts equally with both Al atoms, and the structure is rationalized as involving two three-center two-electron bonds [1].

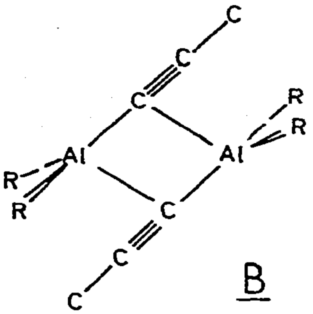
The molecular structure of dimeric dimethyl(phenyl)-aluminium, di(μ-phenyl)bis(dimethylaluminium), is also close to $\underline{D}_{2h}$ with the planes of the bridging phenyl groups perpendicular to the Al-Al vector [5]. This structure too can be rationalized on the basis of three-center two-electron bonds, though it is commonly assumed that the structure is stabilized by delocalization of the π electrons of the phenyl rings into empty non-bonding orbitals of appropriate symmetry centered on the Al atoms [6].

Dimethyl(phenylethynyl)aluminium is dimeric in benzene with the phenylethynyl groups in the bridging position [7,8]. The slowness of the exchange of methyl groups with trimethylaluminium indicates that the phenylethynyl bridges have particularly high thermodynamic stability [8,9]. By analogy with the known structures of dimeric trimethylaluminium and dimeric dimethyl(phenyl)aluminium it has been assumed that the molecular structure of di(μ-phenyl ethynyl)bis(dimethyl-aluminium) would have $\underline{D}_{2h}$ symmetry as indicated for Model $\underline{A}$:

It was therefore somewhat surprising when an X-ray diffraction investigation of di(μ-phenylethynyl)bis(diphenyl-aluminium) by Stucky, Eisch and coworkers [10] showed that - in the crystalline phase at least - the molecular structure deviates considerably from $\underline{D}_{2h}$ symmetry. Rather the structure found (model $\underline{B}$ above) may be described as consisting of two



A



B

distinct monomer units joined by long bonds between the Al atom of one monomer unit and the C_α atom of the phenylethynyl group in the other unit.

Since it was not clear whether the greater stability of structure B was due to crystal packing forces, or to the presence of phenyl rings in conjugation with the C≡C bonds, or to a combination of both causes, we decided to investigate the dimethyl(1-propynyl)aluminium dimer [11] by means of gas phase electron diffraction.

Experimental and data processing

The sample of dimethyl(1-propynyl)aluminium was a gift from Mr. W. Haaf, Mr. W. Storm and Dr. H. Lehmkuhl. It had been synthesized from $NaC{\equiv}CCH_3$ and $(CH_3)_2AlCl$ in *n*-hexane and purified by sublimation at 25-30 °C and $5x10^{-4}$ torr. The melting point was 50-52 °C (lit. 53-54 °C [11]). IR and H^1-NMR spectra were identical to those reported by Schneider [11].

The electron scattering pattern was recorded on the Oslo electron diffraction unit [12] with a nozzle temperature of 88±6 °C. The reported vapor pressure of $(CH_3)_2Al(C{\equiv}CCH_3)$ is 15 torr at 93 °C [11]. Exposures were made with nozzle to photographic plate distances of 48 and 25 cm. The optical densities of four plates from the first set and six plates from the second were processed using the programs described by Andersen et al. [13]. The resulting modified molecular intensity points are shown in Fig. 1.

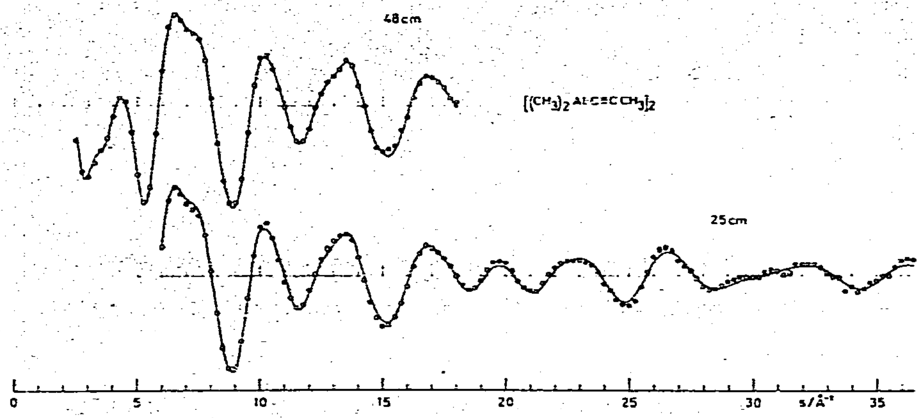


Fig. 1. o : experimental modified molecular intensity points for $[(CH_3)_2Al(\mu\text{-}C\equiv CCH_3)]_2$ from s = 2.50 to 18.00 A^{-1} (upper curve) and from s = 6.00 to 36.50 A^{-1} (lower curve). In the upper curve only every second experimental point is shown. Full lines : theoretical intensity curves calculated for best model.

Structure refinement

A radial distribution curve calculated for a model of di(μ-1-propynyl)bis(dimethylaluminium) of D_{2h} symmetry (model A) is compared to a radial distribution curve calculated by Fourier inversion of the experimental modified molecular intensity data in Fig. 2 A. The agreement is very poor. Attempts to improve the agreement by refinement of the model failed, and it was concluded that this model could be ruled out. (Before going on, we wish to point out that since the disagreement between the two curves in Fig. 1 A is due to differences in the positions of the peaks at r>3.5 A, and not to differences

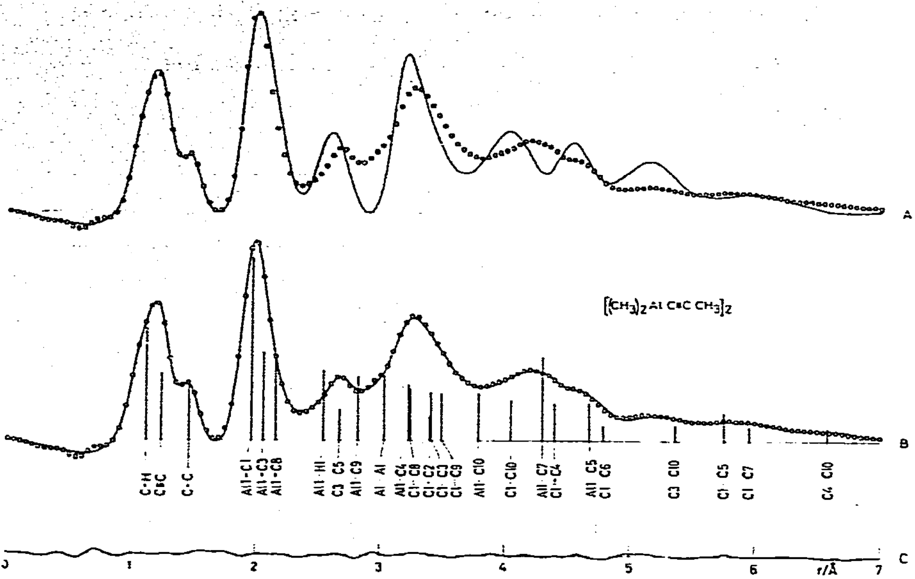


Fig. 2. o : experimental radial distribution curve for $[(CH_3)_2Al(\mu\text{-}C{\equiv}CCH_3)]_2$. A, full line : theoretical radial distribution curve calculated for model of $\underline{D}_{2h}$ symmetry (A). B, full line: theoretical curve calculated for best model of symmetry $\underline{C}_{2h}$. C, full line : difference between the experimental curve and the theoretical curve calculated for best model.

in area, the disagreement cannot be due to partial dissociation into monomers).

Refinements were then carried out on a model similar to the one found for di(μ-phenylethynyl)bis(diphenylaluminium) by X-ray crystallography [10] (model B). This model is shown in more detail in Fig. 3 A. It was assumed that: (i) The molecule has $\underline{C}_{2h}$ symmetry. (ii) All methyl groups are identical and have $\underline{C}_{3v}$ symmetry with the threefold axes coinciding with the C-Al or C-C bonds. (iii) The angle of rotation of the terminal methyl groups about the C-Al bonds is such that one C_1-H bond is <u>anti</u> the Al_1-C_2 bond. (iv) The angle of rotation

Table 1. Bond distances, valence angles, and root mean square vibrational amplitudes of $[(CH_3)_2AlC{\equiv}CCH_3]_2$. (Estimated standard deviations in parentheses) [a]

	r_a/A	ℓ/A	
C—H (mean)	1.110(3)	0.082(4)	
C≡C	1.229(4)	0.039(5)	
C—C	1.454(4)	0.048(4)	
Al_1—C_1	1.956(5)	0.060(3)	
Al_1—C_3	2.050(15)	0.088(15)	
Al_1—C_8	2.153(27)	0.187(31)	
Al---Al	3.03(3)	0.15(3) [b]	
Al_1---C_9	2.82(2)	0.15(3) [b]	
Al_1---C_4	3.22(1)	0.09(1) [c]	
Al_1---C_{10}	3.79(3)	0.20(2) [d]	
Al_1---C_7	4.30(2)	0.20(2) [d]	
Al_1---C_5	4.68(1)	0.11(1) [c]	
Al_1---H_1	2.54(2)	0.149	(assumed)
C_3---C_5	2.67(1)	0.064	(assumed)
C_3---C_8	2.92(3)	0.140	(assumed)
C_1---C_8	3.23(2)	0.15(3) [b]	
C_1---C_3	3.40(2)	0.140	(assumed)
C_1---C_9	3.49(4)	0.20(2) [d]	
C_1---C_{10}	4.04(6)	0.20(2) [d]	
C_1---C_4	4.40(2)	0.23(4) [e]	
C_1---C_5	5.75(2)	0.33(4) [e]	

(cont)

(cont)

$\angle \mathrm{Al{-}C{-}H}$	108.5(1.7)° [f]
$\angle \mathrm{C{-}C{-}H}$	108.5(1.7)° [f]
$\angle \mathrm{C_1{-}Al_1{-}C_2}$	120.8(1.6)°
$\angle \mathrm{C_1{-}Al_1{-}C_3}$	116.2(0.9)°
$\angle \mathrm{Al_1{-}C_3{-}C_4}$	158.3(1.9)°
$\angle \mathrm{C_3{-}C_4{-}C_5}$	167.8(1.6)°
$\angle \mathrm{C_8{-}Al_1{-}C_1}$	103.6(0.9)°
$\angle \mathrm{C_8{-}Al_1{-}C_3}$	88.0(1.0)°
$\angle \mathrm{Al_2{-}C_3{-}C_4}$	109.7(1.3)°

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a) For numbering of the atoms consult Fig.3 A. The distances are given as r_a. The angles have not been corrected for shrinkage. b) These amplitudes were assumed equal. c) These amplitudes were assumed to differ by 0.020 Å. d) These amplitudes were assumed equal. e) These amplitudes were assumed to differ by 0.100 Å. f) Assumed equal.

of the methyl groups in the bridges is such that one C_5-H bond is *anti* the C_3-C_4 bond.

The molecular structure is then determined by twelve independent parameters, *e.g.* the C-H, C≡C, C-C, Al_1-C_1, Al_1-C_3 and Al_1-C_8 bond distances and the valence angles $\angle$Al-C-H = $\angle$C-C-H, $\angle C_1$-Al_1-C_2, $\angle C_1$-Al_1-C_3, $\angle Al_1$-C_3-C_4, $\angle C_3$-C_4-C_5, and $\angle C_8$-Al_1-C_3. These twelve structure parameters and ten root-mean-square vibrational amplitudes (ℓ) (including the amplitudes of all bond distances) were refined by least-squares calculations on the intensity data under the constraints of a geometrically consistent r_a structure using programs written by H.M. Seip [13]. The asymmetry parameter of the

C-H bond distance was fixed at $\kappa = 1.8\times10^{-5}$ A^3, other asymmetry parameters were ignored [14]. The final refinements were carried out with a diagonal weight matrix and a separately refined scale factor for each nozzle to plate distance. The molecular parameters obtained and their estimated standard deviations are listed in Table 1. The standard deviations have been doubled to take into account the additional uncertainty due to correlation in the experimental data [15] and introduced by the assumptions (i) to (iv) above and the assumptions made regarding the vibrational amplitudes that could not be refined as independent parameters (see Table 1).

Modified molecular intensity curves calculated for the best model are shown in Fig. 1. A radial distribution curve calculated for the best model is compared to an experimental curve in Fig. 2 B and C. The agreement is seen to be satisfactory.

Discussion

The molecular structure of di(μ-1-propynyl)bis(dimethylaluminium) (I) (Fig. 3 B and Table 1) deviates considerably from $\underline{D}_{2h}$ symmetry. This is most clearly seen by comparing the angles $\angle Al_1-C_3-C_4 = 158.3(1.9)^{o}$ and $\angle Al_2-C_3-C_4 = 109.7(1.3)^{o}$. The Al···Al distance, 3.03(3) A, which is significantly longer than the Al···Al distances in dimeric trimethylaluminium, 2.619(5) A [4] or di(μ-phenyl)bis(dimethylaluminium), 2.687(3) A [5], also indicates that the bridge bonding in (I) is different from the bridge bonding in the other two species.

Below we compare some bond distances and valence angles in I to the corresponding parameters in di(μ-phenylethynyl)bis(diphenylaluminium) (II) as determined by X-ray

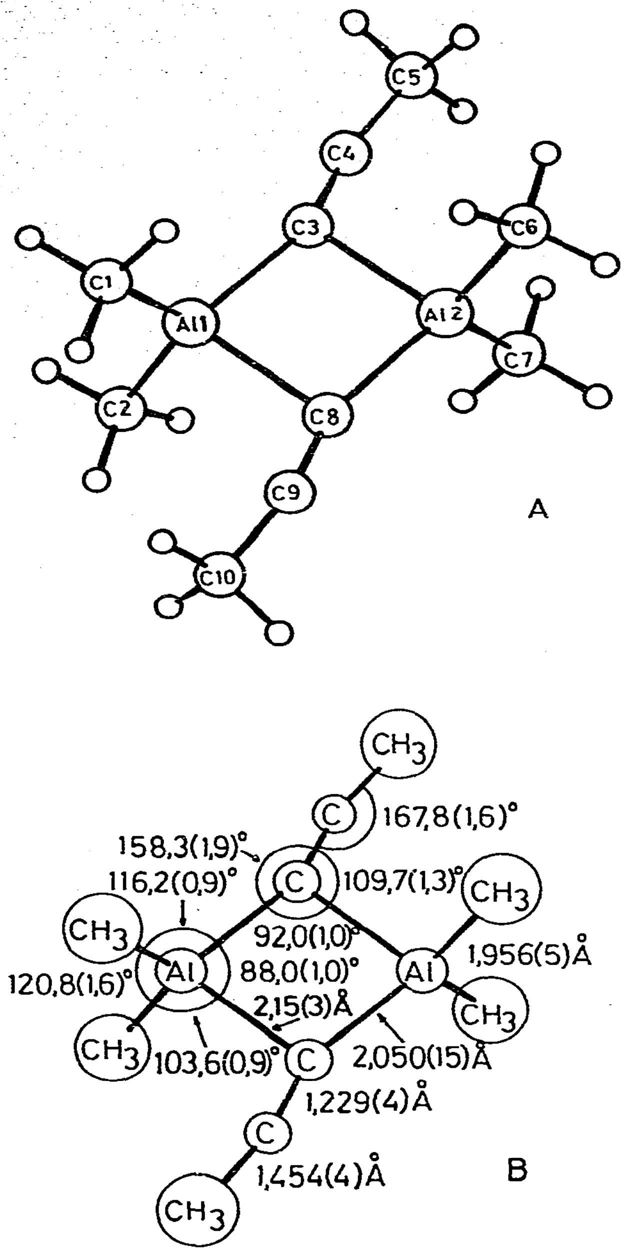


Fig. 3. Molecular models of $[(CH_3)_2Al(\mu\text{-}C\equiv CCH_3)]_2$.

crystallography [10]. (The structure of II has only been described in a preliminary report and only a few structure parameters are given - without standard deviations) :

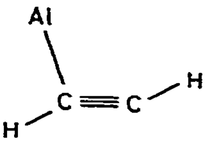
	I	II
Al_1-C_1	1.956(5) A	1.940 A
Al_1-C_3	2.050(15) A	1.992 A
Al_1-C_8	2.15(3) A	2.184 A
$C_3{\equiv}C_4$	1.229(4) A	1.207 A
C_4-C_5	1.454(4) A	1.435 A
$\angle Al_1-C_3-Al_2$	92.0(1.0)^0	91.7^0
$\angle Al_1-C_3-C_4$	158.3(1.9)^0	171.6^0

Though there are some differences, notably in the Al_1-C_3 bond distances and the $\angle Al_1-C_3-C_4$ valence angles, the structures of the two molecules are clearly quite similar.

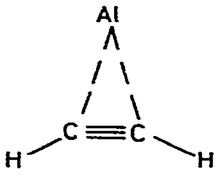
Like Stucky, Eisch and coworkers [10] we believe that the structures are best described by assuming that the Al_1-C_1 bond is a single covalent bond, and that the two monomer units are linked through dative bonding by donation of two π-electrons of the C≡C bond of one unit into an empty atomic orbital on the Al atom of the other unit. The bond distances and valence angles are in good agreement with this view: The Al-O bond distance in $(CH_3)_3AlO(CH_3)_2$ is 2.01(2) A [16], the Al-N bond distance in $(CH_3)_3AlN(CH_3)_3$ is 2.10(1) A [17]. Extrapolation to C yields an estimated Al-C dative bond distance of about 2.19 Å. The Al_1-C_1 bond distance in I is indistinguishable from the Al-C bond distance in monomeric $(CH_3)_3Al_1$ 1.957(3) A [4]. Formation of the complexes $(CH_3)_3AlN(CH_3)_3$ and $(CH_3)_3AlO(CH_3)_2$ leads to an increase in the Al-C bond distances, Al-C = 1.987(5) A and 1.973(11) A, respectively, in the two complexes. In I the elongation is confined to the Al_1-C_3 bond, but the average of the three bond distances Al_1-C_1, Al_1-C_2 and Al_1-C_3 is equal to 1.987 A. In the complexes with $N(CH_3)_3$ and $O(CH_3)_2$, $(CH_3)_3Al$ forms flat pyramids, $\angle C-Al-C$ = 115.6(0.2)^0 and 117.8(0.8)^0, respectively. In I the average of the three angles $\angle C_1-Al_1-C_2$, $\angle C_1-Al_1-C_3$ and $\angle C_2-Al_1-C_3$ is 117.7°.

Donation of π-electrons into an empty atomic orbital on Al_2 would be expected to weaken the $C_3{\equiv}C_4$ bond: In fact it is found to be significantly longer than the C≡C bond in $CH_3-C{\equiv}C-CH_3$ determined by gas phase electron diffraction, 1.206(1) Å [18]. The C-C bond distances in the two molecules are indistinguishable.

If one accepts the view of the bonding between the monomer units outlined above, the question arises as to why the structure is not such that the Al atom of one monomer unit is directly above the midpoint of the C≡C bond of the other unit; this could be accomplished by displacing one monomer unit about 0.6 Å relative to the other in the direction of the triple bond. The reason may be that C_α atom carries a larger negative charge than the C_β atom or that such a structure would require a prohibitively short $C_3 \cdots C_8$ distance. But in this connection it may also be pertinent to recall that the ESR spectrum of the matrixisolated adduct Al-atom-acetylene show the structure to be vinyl-like (C) rather than symmetric (D) [19]:



C



D

The molecular fragment $Al_1-C_3-C_4-C_5$ is nonlinear and in the trans configuration. The angles $\angle Al_1-C_3-C_4$ and $\angle C_3-C_4-C_5$ have not been corrected for shrinkage, but since these angles are determined to a large extent by the distances $Al_2 \cdots Al_1$, $Al_2 \cdots C_3$, $Al_2 \cdots C_4$ and $Al_2 \cdots C_5$, we do not believe that shrinkage corrections would amount to more than 2 or 3°.

We would suggest that the nonlinearity at C_3 is due to a rehybridization of this atom leading to an increase in the electron density in the direction of Al_2, and the nonlinearity at C_4 to a rehybridization resulting in an atomic orbital pointing (its minor lobe) in the direction of Al_2.

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