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THE MOLECULAR STRUCTURE OF DIMETHYLALUMINIUM THIOMETHOXIDE DIMER, $[(CH_3)_2AlSCH_3]_2$, AS DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The molecular structure of $[(CH_3)_2AlSCH_3]_2$ has been determined by gas phase electron diffraction. The scattering pattern is consistent with a molecular model of C_{2h} symmetry with the $CH_3(S)$ groups in the *trans* configuration. The main molecular parameters are Al—S = 2.370(3), Al—C = 1.945(4), and S—C = 1.811(10) Å; ∠Al—S—Al = 94.5(0.6), ∠C—Al—C = 128.6(2.5) and ∠Al—S—C = 106.1(1.2)°.

Dimethylaluminium thiomethoxide $(CH_3)_2AlSCH_3$, first prepared by Davidson and Brown, is dimeric in the gas phase [1] and in benzene solution [2].

An X-ray diffraction investigation by Brauer and Stucky [3] has shown crystalline $(CH_3)_2AlSCH_3$ to consist of infinite linear polymers with thiomethoxy groups bridging dimethylaluminium groups. The ^{27}Al NQR spectrum of the solid has been measured and discussed by Dewar et al. [4].

We have determined the molecular structure of the dimethylaluminium thiomethoxide dimer in the gas phase for comparison with the structure of the polymer and with the structure of the dimethylaluminium chloride dimer, which has also been determined by gas phase electron diffraction [5].

Experimental and calculation procedure

$(CH_3)_2AlSCH_3$ was prepared from $(CH_3)_3Al$ and CH_3SH in benzene and purified by sublimation. The electron scattering pattern was recorded on

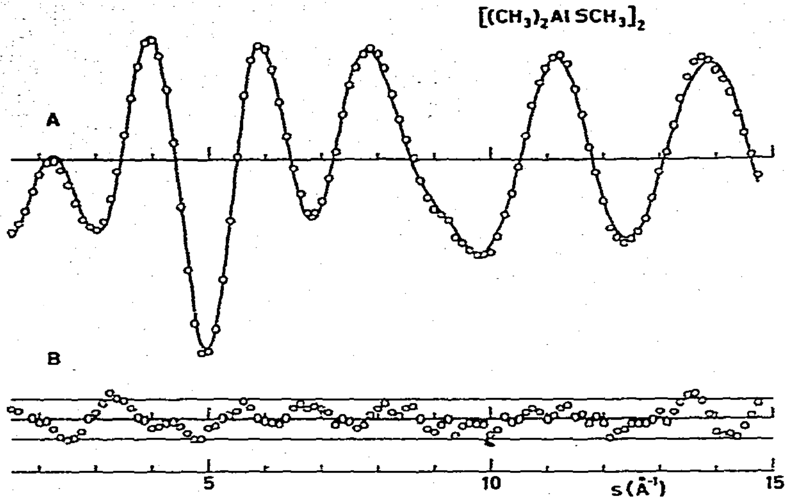

Fig. 1. A. o: Experimental modified molecular intensity points from $s = 1.500$ Å^{-1} to $s = 14.750$ Å^{-1}. Full line: Theoretical intensity curve calculated for model of C_{2h} symmetry with the parameter values listed in Tables 1 and 2. B. o: Difference points. The two full lines indicate the estimated uncertainty (three standard deviations) of the experimental values. *Note*: The scale of B is twice that of A.

Balzars Eldigraph KD G2. The nozzle temperature was about 130°C, corresponding to vapour pressure of about 23 Torr [1]. Exposures were made with nozzle to photographic plate distances of about 50 cm and 33 cm. The optical densities of three plates from the first set and two plates from the last were recorded, converted into intensities and processed in the usual way [6]. The modified molecular intensity points obtained from the 50 cm plates are shown in Fig. 1, those obtained from the 33 cm plates in Fig. 2.

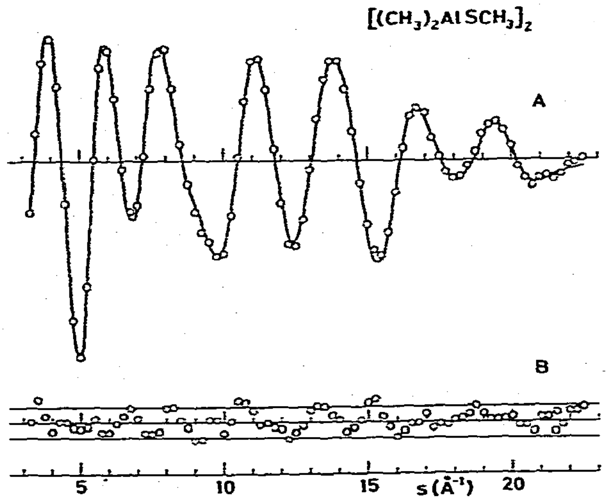

Fig. 2. A. o: Experimental modified molecular intensity points from $s = 3.250$ Å^{-1} to $s = 22.500$ Å^{-1}. Full line: Theoretical intensity curve calculated for model of C_{2h} symmetry with the parameter values listed in Tables 1 and 2. B. o: Difference points. The two full lines indicate the estimated uncertainty (three standard deviations) of the experimental values. *Note*: The scale of B is twice that of A.

Theoretical intensity curves were calculated from

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

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 [6].

The molecular structure was refined by least-squares calculations on the intensity data under the constraints of a geometrically consistent r_a structure, with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle-to-plate distance [7]. 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 analysis

A molecular model of $[(CH_3)_2AlSCH_3]_2$ with the two $CH_3(S)$ in a *trans* configuration is shown in Fig. 3. It was assumed that: (i) The molecular symmetry is C_{2h}. This implies that the Al_2S_2 ring is planar. (ii) All C—H bond distances are equal. (iii) All methyl groups have C_{3v} symmetry with the symmetry axes coinciding with the Al—C or S—C bonds. (iv) The angle of rotation of the methyl groups about the Al—C and S—C bonds is such that the H atoms are staggered with respect to the bonds radiating from the Al and S atoms respectively.

The molecular symmetry C_{2h} implies that the two Al atoms and the four C(Al) atoms lie in a plane, but this plane is not necessarily perpendicular to the Al_2S_2 ring plane. The angle between the Al_2C_4 plane and a plane perpendicular

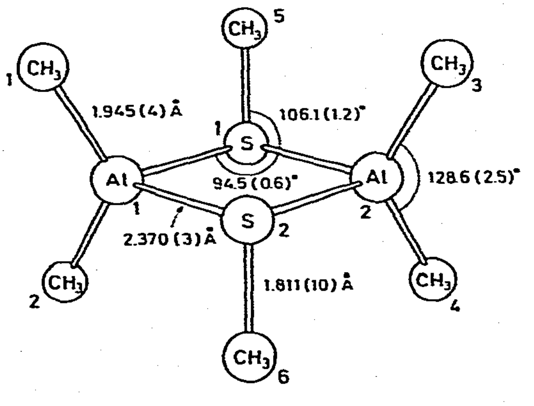

Fig. 3. Molecular model of $[(CH_3)_2AlSCH_3]_2$.

to the ring was denoted by α and defined as positive when the $C_1 \cdots C_5$ distance is increased.

After the assumptions (i) to (iv) have been made, the molecular structure is determined by ten independent parameters, i.e. by the four bond distances Al—S, Al—C, S—C and C—H, the five valence angles ∠Al—S—Al, ∠C—Al—C, ∠Al—S—C, ∠Al—C—H and ∠S—C—H and the angle α defined above. The angle ∠S—C—H was assumed to be equal to the mean ∠S—C—H angle in $(CH_3)_2S$, 108.7° [8].

In order to achieve convergence it was necessary to limit drastically the number of vibrational amplitudes to be refined by least-squares calculations on the intensity data along with the nine remaining structure parameters. Several of the main amplitudes were therefore assigned values or assumed to be equal as indicated in the footnotes to Table 1.

Using as start parameters ∠Al—S—Al = 95° and the other bond distances and valence angles at values close to those obtained for the polymeric compound by X-ray crystallography, the refinement converged to the values listed in Tables 1 and 2. The estimated standard deviation listed for l(Al—C) has been

TABLE 1

INTERNUCLEAR DISTANCES AND ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (l) OF $[(CH_3)_2AlSCH_3]_2$

Estimated standard deviations 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)
Independent distances		
Al—S	2.370(3)	0.073(3)
Al—C	1.945(4)	0.025(22)
S—C	1.811(10)	0.055 [a]
C—H (mean)	1.101(6)	0.054(9)
Dependent distances		
Al···Al	3.48(2)	0.106 [b]
$Al_1 \cdots C_3$	4.67(2)	0.35(3) [c]
$Al_1 \cdots C_5$	3.36(3)	0.150 [d]
$Al_1 \cdots H_1$	2.55(3)	0.149 [e]
S···S	3.22(2)	0.077 [f]
$S_1 \cdots C_1$	3.61(1)	0.07(1) [g]
$S_1 \cdots C_2$	3.42(2)	0.07(1) [g]
$S_1 \cdots C_6$	4.29(3)	0.35(3) [c]
$S_1 \cdots H_5$	2.40(1)	0.110 [h]
$C_1 \cdots C_2$	3.51(4)	0.133 [i]
$C_1 \cdots C_3$	5.17(6)	0.37(4) [j]
$C_1 \cdots C_4$	6.25(3)	0.160 [b]
$C_1 \cdots C_5$	3.64(3)	0.250 [d]
$C_1 \cdots C_6$	4.77(1)	0.37(4) [j]
$C_5 \cdots C_6$	5.75(5)	0.150 [d]

[a] Assumed to be 0.005 Å greater than the calculated S—C amplitude in $(CH_3)_2S$ at 25° [13]. [b] Assumed equal to the corresponding amplitude in $[(CH_3)_2AlCl]_2$ [5]. [c] Assumed equal. [d] Assumed value. [e] Assumed equal to the corresponding amplitude in $[(CH_3)_3Al]_2$ [14]. [f] Assumed equal to the Cl···Cl amplitude in $[(CH_3)_2AlCl]_2$ [5]. [g] Assumed equal. [h] Assumed equal to the corresponding amplitude in $(CH_3)_2S$ [13]. [i] Assumed equal to the corresponding amplitude in $(CH_3)_3Al$ [14]. [j] Assumed equal.

TABLE 2

BOND ANGLES OF $[(CH_3)_2AlSCH_3]_2$ (THIS WORK) AND POLYMERIC $(CH_3)_2AlSCH_3$ [3]
Estimated standard deviations in parentheses

	$[(CH_3)_2AlSCH_3]_2$	$[(CH_3)_2AlSCH_3]_x$
Indenpendent angles (°)		
∠Al—S—Al	94.5(0.6)	103.0(0.1)
∠C—Al—C	128.6(2.5)	122.0(0.4)
∠Al—S—C	106.1(1.2)	103.7(0.3)
∠Al—C—H	110.7(2.0)	
∠S—C—H	108.7 [a]	
α [b]	6.9(0.4)	
Dependent angles (°)		
∠S—Al—S	85.5(0.6)	100.1(0.1)
$\angle S_1—Al_1—C_1$	113.0(1.8)	110.8(0.3)
$\angle S_1—Al_1—C_2$	104.0(1.8)	106.4(0.3)
γ [c]	65.9(2.0)	

[a] Assumed equal to mean ∠S—C—H angle in $(CH_3)_2S$ [8]. [b] α is the angle between the Al_2C_4 plane and a plane perpendicular to the Al_2S_2 ring. [c] γ is the angle between S—C bond and the Al_2S_2 ring plane.

doubled to account for the large correlation with l(S—C), the correlation coefficient being $\rho = 0.91$. The generalized R-factor was $R_3 = 14.75$ [7].

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

An experimental radial distribution curve is shown in Fig. 4A, the difference between this curve and one calculated for this model is shown in Fig. 4B. Inspection of the radial distribution curve makes it clear why so few vibrational

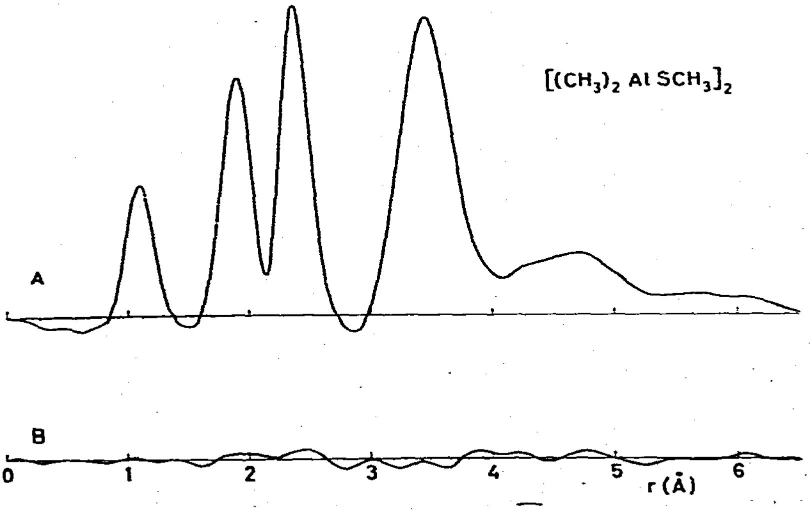

Fig. 4. A. Experimental radial distribution curve. Artificial damping constant k = 0.004 Å². B. Difference between experimental curve and theoretical curve calculated for model with C_{2h} symmetry with the parameter values listed in Tables 1 and 2.

amplitudes could be refined along with the nine structure parameters; the curve contains only five peaks.

Refinement with other start parameters led to another stable least-squares minimum with ∠C—Al—C = 136.1(1.4)°, ∠Al—S—C = 111.5(1.2)° and α = 5.5 (2.3)°. The other parameters refined to values that differed from those listed in Tables 1 and 2 by less than one standard deviation. The generalized R-factor was R_3 = 13.64. Inspection of the table of dependent distances showed that this second model was obtained by re-arrangement and interchange of the relative magnitude of the closely spaced Al···C and S···C nonbonded distances around 3.4 and 4.5 Å.

Refinements were also carried out on a model of C_{2v} symmetry with the two CH_3(S) groups in the *cis* configuration. The Al_2S_2 ring is then no longer planar by symmetry, and the angle between the two Al_2S planes was denoted by β. The angle between the line bisecting ∠C—Al—C and the AlS_2 plane was assumed equal to zero.

When the assumptions (ii) to (iv) above are made, the molecular structure of the *cis* model, like that of the *trans* model, is determined by ten parameters, e.g. the four bond distances and five valence angles listed for the *trans* model and the angle β.

These were refined by least-squares calculations on the intensity data in the same way as for the *trans* model. Only one least squares minimum could be found with ∠C—Al—C = 140.2(0.7)°, ∠Al—S—C = 114.4(0.9)°, and β = 3.8(3.3)°. The other structure parameters obtained differed from those listed in Tables 1 and 2 by less than two standard deviations. R_3 = 13.23.

Discussion

As described in the last section, least-squares refinement of the structure of $[(CH_3)_2AlSCH_3]_2$ led to three models which gave satisfactory agreement between calculated and observed intensities. The first model has C_{2h} symmetry and the CH_3(S) groups in the *trans* configuration as shown in Fig. 3 and the structure parameters shown in the Figure and listed in Tables 1 and 2. The second model differed from the first in the values assigned to the two valence angles ∠C—Al—C = 136.1(1.4)° and ∠Al—S—S = 111.5(1.2)°. The third model has C_{2v} symmetry and the CH_3(S) groups in the *cis* configuration, ∠C—Al—C = 140.2(0.7)° and ∠Al—S—C = 114.4(0.9)°.

The ∠C—Al—C angle in the crystalline polymer, which presumably is free from angle strain, is 122.0(0.4)° [3]. The ∠S—Al—S angle is 100.1(0.1)°. For all three models of the dimers ∠S—Al—S has been reduced by 15° to about 85°, and ∠C—Al—C might consequently be expected to increase somewhat, but not more than five or six degrees: In $[(CH_3)_2AlOCH_3]_3$ ∠O—Al—O = 103.2(1.1)° and ∠C—Al—C = 117.3(0.8)° [9]. In $[(CH_3)_2AlOC(CH_3)_3]_2$ ∠O—Al—O has been reduced by 21° to 81.9(0.7)°, but ∠C—Al—C has only increased by about 4° to 121.7(1.7)° [10]. In *cis*-$[(CH_3)_2AlNHCH_3]_3$ ∠N—Al—N = 101.9(0.5)° and ∠C—Al—C = 117.6(0.6)° [11]. In $[(CH_3)_2AlN(CH_3)_2]_2$ the ∠N—Al—N angle has been reduced by 13° to 88.4(0.3)°, but ∠C—Al—C remains essentially unaltered at 115.9(0.4)° [11, 12].

A ∠C—Al—C angle near 140° in $[(CH_3)_2AlSCH_3]_2$ must therefore be regarded as highly improbable, and the *cis* model can consequently be ruled out with confidence. This must not be taken to mean that the gas jet may not have contained a small fraction of the molecules in a *cis* configuration, but the majority of the molecules must have been *trans*.

The infrared and Raman spectra of $[(CH_3)_2AlSCH_3]_2$ in benzene solution show no coincidences [2]. The structure of the dimer must therefore be centrosymmetric, i.e. the molecules must be in the *trans* configuration. The ^{1}H NMR spectra of $[(CH_3)_2AlSCH_3]_2$ in toluene or CCl_4 at 30-45°C, which consists of two peaks of relative area 2/1 [2, 3], are also in agreement with this model.

A ∠C—Al—C angle near 136° is hardly more acceptable than an angle near 140°, and we therefore base our discussion on the first *trans* model.

It has already been pointed out that ∠S—Al—S is about 15° smaller in dimeric than in polymeric $(CH_3)_2AlSCH_3$. The ∠Al—S—Al angle is less distorted; it decreases by about 8° from 103.0(0.1)° in the polymer to 94.5(0.6)° in the dimer.

The exocyxlic angles are little affected by the change in the degree of association, the ∠C—Al—C angle in the dimer is poorly determined, but appears to be a few degrees larger than in the polymer, 122.0(0.4)°. The Al_2C_4 plane is not perpendicular to the Al_2S_2 ring but has been twisted 6.0(0.4)° in such a way as to increase the distance $C_1 \cdots C_5$. The two angles $\angle S_1—Al_1—C_1 = 113.0(1.8)°$ and $\angle S_1—Al_1—C_2 = 104.0(1.8)°$ are not significantly different from the corresponding angles in the polymer, 110.8(0.3)° and 106.4(0.3)° respectively. Neither is the ∠Al—S—C angle significantly different from the angle found in the polymer.

The Al—C and S—C bond distances in the dimer are not significantly different from those of the polymer, but the Al—S bond distance appears to be longer in the dimer, possibly because of repulsions across the four membered ring.

The ∠Al—S—Al angle in $[(CH_3)_2AlSCH_3]_2$ is significantly greater than the ∠Al—Cl—Al angle in $[(CH_3)_2AlCl]_2$, 90.6(0.5)° [5]. This difference is in agreement with the valence shell electron pair repulsion model. The ∠Al—P—Al angle in a hypothetical dimer of $(CH_3)_2AlP(CH_3)_2$ would be expected to be greater than ∠Al—S—Al, and the ∠P—Al—P angle consequently even smaller than ∠S—Al—S. This may be the reason why $(CH_3)_2AlP(CH_3)_2$ forms trimers rather than dimers [1].

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