Journal of Organometallic Chemistry, 54 (1973) 77–86

ON THE MOLECULAR STRUCTURE OF DIMETHYLALUMINIUM FLUORIDE TETRAMER, $[(CH_3)_2AlF]_4$

G. GUNDERSEN, T. HAUGEN and ARNE HAALAND
Department of Chemistry, University of Oslo (Norway)
(Received September 15th, 1972)

SUMMARY

$(CH_3)_2AlF$ has been studied by gas phase electron diffraction. The compound is tetrameric under the experimental conditions. The main molecular parameters are R(Al–C) 1.947 (4), R(Al–F) 1.810 (3) Å, < C–Al–C 131.2 (1.9)°, < F–Al–F 92.3 (1.2)° and < Al–F–Al 146.1 (2.6)° the Al_4F_4 ring being puckered. The factors determining the degree of association of compounds of the type R_2AlX (X = F, OR′, NR'_2, Cl, SR′ and PR'_2) are discussed, and it is suggested that Pitzer strain may be a significant factor in some cases.

INTRODUCTION

Dialkylaluminium fluorides, R_2AlF, with R = methyl, ethyl, n-propyl or isobutyl, were first synthesized by Köster and Ziegler[1]. The most thoroughly studied member of the series is $(C_2H_5)_2AlF$[2]: This compound is tetrameric (as indicated by its molecular weight) in freezing and boiling benzene. No dependence of the degree of association on the concentration could be detected. The proton NMR spectrum of $(C_2H_5)_2AlF$ in benzene or cyclopentane solution shows all the ethyl groups to be equivalent; cooling to −60° produces no broadening or splitting of the signals. Fluorine NMR spectra likewise show all the fluorine atoms to be equivalent. On the basis of the NMR data, and of the infrared absorption spectrum (in absence of solvent) which contained no lines corresponding to bridging ethyl groups, Laubengayer and Lengnick[2] concluded that the tetramer consists of an eight-membered ring of alternating aluminium and bridging-fluorine atoms.

$(CH_3)_2AlF$, too, is tetrameric in freezing benzene [3]. Weidlein and Krieg[3] have recorded the infrared and Raman spectra of $(CH_3)_2AlF$ and $(C_2H_5)_2AlF$ without solvent in the range 250–3000 cm^{-1}. Because of the small number of lines observed, and because of the apparent operation of the mutual exclusion principle, they suggested that the molecular symmetry is D_{4h}, *i.e.* that the eight-membered ring is planar.

In the anionic complex $K[(C_2H_5)_3AlFAl(C_2H_5)_3]$, the < Al–F–Al valence angle is 180° [4]. In crystalline polymeric $(CH_3)_2SnF_2$[5], also, the valence angle at the bridging fluorine atoms is 180°, and the fluorine valence angle in polymeric $(CH_3)_3SnF$ is very large[6]. It therefore seemed probable that the high degree of association of $(CH_3)_2AlF$ as compared to $(CH_3)_2AlOCH_3$ ($n = 3$)[7] and $(CH_3)_2AlCl$ ($n = 2$)[7] is due to the requirement of an $<$Al–F–Al angle of nearly 180°.

In an effort to determine the molecular structure of $[(CH_3)_2AlF]_4$, we have undertaken a gas phase electron diffraction study. Since the gas phase molecular weight was unknown, the possibility that the gas jet might contain significant amounts of trimeric or dimeric species had to be kept in mind, even though the fact that the molecular weight of $(C_2H_5)_2AlF$ in benzene solution is independent of concentration and temperature show that the tetrameric unit is particularly stable.

It was hoped that comparison of the structure of tetrameric $(CH_3)_2AlF$ with the structures of other associated species of the type R_2AlX ($X = NR'_2$, OR', PR''_2, SR' and Cl) would yield information about the factors influencing the degree of association of such compounds.

EXPERIMENTAL AND CALCULATION PROCEDURE

The sample of $(CH_3)_2AlF$ was a gift from Dr. Weidlein, and was redistilled before use. The electron scattering pattern was recorded on the Oslo electron diffraction unit[8], with the sample reservoir at about 60° and a nozzle temperature of about 70°. $(CH_3)_2AlF$ is thermally stable below 200° [1]. Exposures were made at nozzle-to-photographic-plate distances of about 48 and 30 cm.

Four apparently faultless plates from the first set, and five from the second, were photometered and processed in the usual way[9]. The resulting modified molecular intensity points are shown in Figs. 1 and 2.

Theoretical intensity curves were calculated from:

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

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. $f_j(s) = |f_j(s)| \cdot \exp[i \cdot \eta_j(s)]$ is

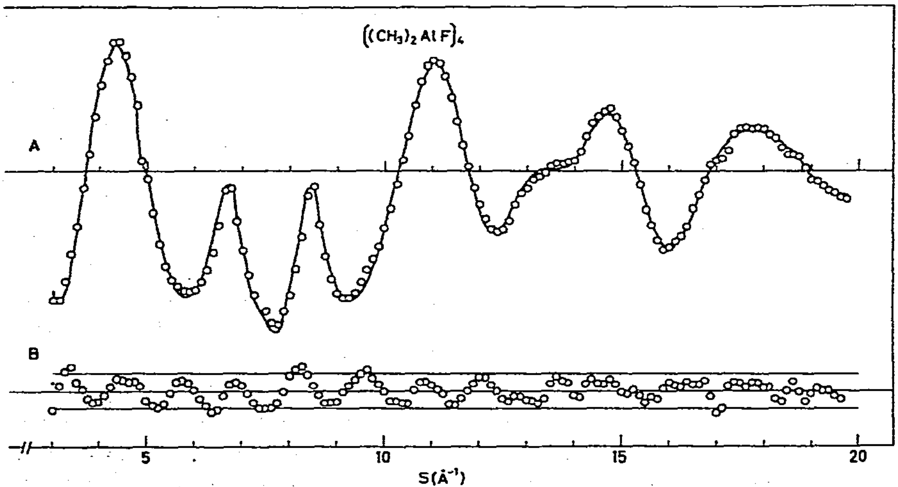

Fig. 1. A. ○; Experimental modified molecular intensity points from $s = 3.00$ to 19.75 Å^{-1}. Point density 8 points per Å^{-1}. Full line; theoretical modified molecular intensity curve calculated for the best model. B. ○; Difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. Note: The scale of B is twice that of A.

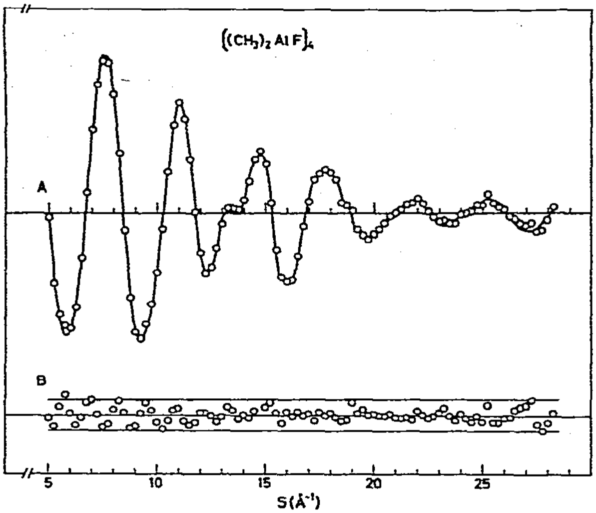

Fig. 2. A. ○; Experimental modified molecular intensity points from $s=5.00$ to $28.25\ \text{Å}^{-1}$. Point density 4 points per Å^{-1}. Full line; theoretical modified molecular intensity curve calculated for the best model. B. ○; Difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. Note: The scale of B is twice that of A.

the complex atomic scattering factor of atom *j*. It has been calculated for Al, F, C and H by the partial wave approximation with a program written by Peacher[10]. The scattering potentials of Al, F and C have been found by non-relativistic Hartree–Fock calculations[11,12].

Radial distribution functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function $\exp(-k\cdot s^2)$. The experimental intensity functions obtained with different nozzle-to-plate distances were combined to give a composite intensity function, to which—after a satisfactory molecular model had been found—the theoretical curve calculated for the model below s $3.00\ \text{Å}^{-1}$ could be fitted.

The molecular structure was initially refined by least squares calculations on the intensity data with a diagonal weight matrix. After a satisfactory model had been obtained, the bond distances and valence angles were refined with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle-to-plate distance[13]. The standard deviations obtained were expanded to take into account an estimated uncertainty of 1.4 ppt in the electron wavelength.

STRUCTURE ANALYSIS

A molecular model of $[(CH_3)_2AlF]_4$ is shown in Fig. 3. In the following account the C and H atoms are assumed to be numbered according to the methyl group to which they belong.

A radial distribution (RD) curve obtained by Fourier inversion of the experimental intensity data is shown in Fig. 4. Here the peak at 1.1 Å must correspond to the C–H bond distances. The peak at 1.85 Å is composite; it consists of an Al–F bond distance peak near 1.82 Å (the Al–F bond distance in K $[(C_2H_5)_3AlFAl(C_2H_5)_3]$[4])

and an Al–C bond distance peak near 1.96 Å.

The three peaks at 2.65, 3.15 and 3.47 Å must contain the peaks corresponding to the nonbonded distances Al(5)–H(1) (expected near 2.60 Å), F(3)–F(4), C(1)–F(3) and C(1)–C(2) as well as the distances from F(3) and C(2) to the hydrogen atoms bonded to C(1).

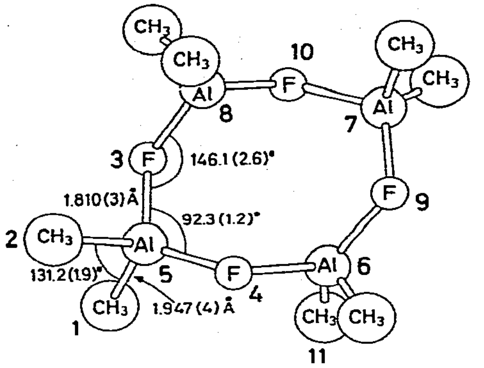

Fig. 3. Molecular model of $[(CH_3)_2AlF]_4$.

If the < Al–F–Al valence angles are 180°, the Al(5)–Al(6) distance peak should be found near 3.65 Å. In fact this value is very near a *minimum* in the RD curve. If it is assumed that the Al(5)–Al(6) peak is part of the broad peak at 3.47 Å, it follows that < Al–F–Al is about 145°. Since a planar eight-membered ring then only can be attained if < F–Al–F is about 125°, the RD curve immediately indicates that the symmetry of the molecule is lower than D_{4h}. This indication is confirmed by the appearance of the RD curve in the region beyond 3.6 Å, where it consists of a maze of unresolved peaks. If the symmetry is as high as D_{4h} one would expect a few individual peaks to be discernable.

Nevertheless several attempts were made to refine a model of D_{4h} symmetry from different initial parameters. However, agreement between experimental and theoretical intensity curves was always bad, and comparison of experimental and theoretical RD curves showed that agreement could only be obtained for the region below $r = 2.3$ Å, *i.e.* in the region determined by the bond distances.

Attempts were then made to refine a non-planar model of C_{4v} symmetry. The agreement between experimental and theoretical intensity data improved considerably, but remained unsatisfactory. The bond distances and valence angles obtained were close to those listed in Table 1. Comparison of experimental and theoretical RD curves (Fig. 4) showed that good agreement had been obtained in the region below $r = 3.6$ Å, *i.e.* in the region determined by the bond distances and the valence angles, but that the agreement was poor in the region above $r = 3.6$ Å. Clearly the model was incorrect as regards the relative position of the Me_2AlF_2 tetrahedra, *i.e.* as regards the conformation of the ring.

There are two possible models of D_{2d} symmetry, one with the F atoms, the other (denoted with D_{2d}' in Fig. 4) with the Al atoms in the mirror planes. Attempts to refine these two models again resulted in bond distances and valence angles very similar to those listed in Table 1, but again comparison between experimental and

TABLE 1

STRUCTURE PARAMETERS[a] OF $[(CH_3)_2AlF]_4$ WITH ESTIMATED STANDARD DEVIATIONS

	$R(Å)$	$l(Å)$
C–H	1.121 (6)	0.739 (6)
Al–C	1.947 (4)	0.610 (3)
Al–F	1.810 (3)	0.601 (2)
<Al–C–H	112 (5)°	
<C–Al–C	131.2 (1.9)°	
<F–Al–F	92.3 (1.2)°	
<Al–F–Al	146.1 (2.6)°	
Al (5)–Al (6)	3.463 (10)	0.103 (8)
Al (5)–H (1)	2.58 (6)	0.16 (4)
F (3)–F (4)	2.61 (2)	0.101 (12)
F (3)–C (1)	3.01 (1)	0.123 (10)
F (3)–H (1)	3.16 (8)	0.17 (3)[b]
	3.34 (7)	0.17 (3)[b]
	3.99 (4)	0.17 (3)[b]
C (1)–C (2)	3.55 (2)	0.133[c]
C (1)–H (2)	3.87 (5)	0.17 (3)[b]
	4.42 (4)	0.17 (3)[b]

[a] For numbering of the atoms consult Fig. 3. The hydrogen and carbon atoms are numbered according to the methyl groups to which they belong. The distances are given as r_a. The angles have not been corrected for shrinkage. [b] These amplitudes were assumed equal. [c] Assumed value (see text).

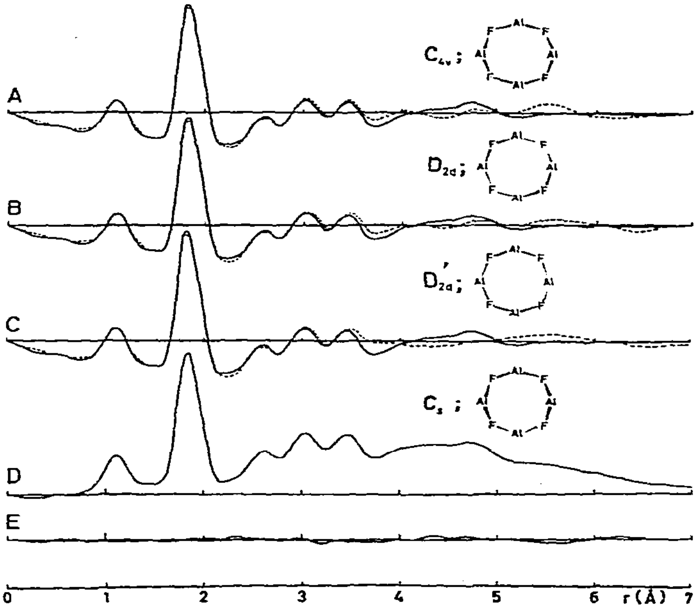

Fig. 4. A, B and C: Full line: Experimental RD curves obtained by Fourier inversion of experimental intensity curves. Broken line: Corresponding theoretical RD curves calculated for the best models of C_{4v} (A) and D_{2d} (B and C) symmetry. D: Experimental RD curve obtained by Fourier inversion of the experimental intensity curves plus the theoretical intensity curve calculated for the best model for s less than 3.00 Å^{-1}. E. Difference between curve D and a corresponding theoretical RD curve calculated for the best model. Artificial damping constants $k = 0.002$ Å^2.

theoretical RD curves showed serious disagreement in the region above $r=3.6$ Å. (Fig. 4).

The equilibrium conformation of cyclooctane is believed to have C_s symmetry[14]. It was therefore decided to refine an analogous model for $[(CH_2)_2AlF]_4$ with the mirror plane through Al(6), Al(8) and the C atoms bonded to them. In addition the following assumptions were made:

(*i*). All $(CH_3)_2AlF_2$ fragments are identical and have C_{2v} symmetry.

(*ii*). All methyl groups have C_{3v} symmetry with the threefold axes coinciding with the Al–C bonds.

(*iii*). The angle of rotation of the methyl groups about the Al–C bonds is such that the H atoms are staggered with respect to the bonds radiating from the Al atoms.

(*iv*). The four <Al–F–Al valence angles are identical.

It follows that the four F atoms are lying at the corners of a square. Al(5), Al(7) and Al(10) were assumed to lie above the plane of the F atoms, Al(6) below.

The molecular structure is then determined by eight independent parameters, *e.g.* by the three bond distances, Al–F, Al–C and C–H, the four valence angles, < F–Al–F, < C–Al–C, < Al–C–H and < Al–F–Al, and the angle between the plane through F(3), F(10) and Al(8) and the F_4 plane.

Refinement of these structure parameters along with the major vibrational amplitudes gave a square-error sum that was less than half of that obtained with the other models described above, and comparison of experimental and theoretical RD curves (Fig. 4) showed satisfactory agreement over the entire range.

The bond distances and valence angles obtained were again similar for those listed in Table 1. The angles between the F_4 plane and the planes through Al(8), F(3) and F(10), through Al(5), F(3) and F(4) and through Al(6), F(4) and F(9) were 13°, 30° and −69° respectively. We do not believe, however, that this model is unique in being in agreement with the experimental data. It seems probable that equally good agreement could be obtained with other models of low symmetry.

In conclusion, the bond distances, the valence angles, and the vibrational amplitudes of all interatomic distances that are independent of the conformation of the ring 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 data obtained for each nozzle-to-plate distance[13]. As can be seen from Table 1, all the distances that are independent of the conformation of the ring are, with the exception of one F–H and two C–H distances, shorter than 3.6 Å. Among the interatomic distances which are dependent on the conformation of the ring, only the Al(4)–F(6) = Al(4)–F(10) = 3.58 Å and F(3)–C(11) = F(10)–C(11) = 3.44 Å and eleven F–H and C–H distances are shorter than 3.7 Å. Clearly the positions of these peaks, which depend on the molecular conformation, may influence the best values obtained for the valence angles. Therefore, in order that the standard deviations of the parameters listed in Table 1 should include the uncertainty due to the uncertainty of the conformation of the ring, the vibrational amplitudes of the Al(4)–F(6) and F(3)–C(11) distances and—in the last cycle—the two distances themselves were refined as independent parameters.

Unfortunately it proved impossible to refine the amplitude of the C(1)–C(2) distance. The molecular parameters obtained with l[C(1)–C(2)] fixed at the value found in trimethylaluminium monomer, 0.133(5) Å, are listed in Table 1. Other refinements were carried out with l[C(1)–C(2)] fixed at 0.113 and 0.143 Å. The shift in the other parameters was much smaller than their standard deviations.

Modified molecular intensity curves calculated for the best model are shown in Figs. 1a and 2a. The difference between experimental and calculated intensities is shown in Figs. 1b and 2b.

DISCUSSION

If radial distribution curves calculated for monomeric, dimeric, trimeric and tetrameric species of $(CH_3)_2$ AlF are scaled to each other in such a way that the areas under the bond distance peaks are equal, the integrated areas under the curves beyond 3.6 Å would vary in the ratio 0/1/3/6. Hence if the gas jet in the diffraction region contained significant amounts of species of lower degree of association than four, the integrated area under the experimental RD curve beyond 3.6 Å would be less than the area under the curve calculated for a tetrameric species regardless of the model chosen for the latter. Conversely, the fact that the RD curve calculated for tetrameric species of C_s symmetry is in good agreement with the experimental curve, allows us to conclude that the concentration of species of degree of association lower than four must have been negligible, and this conclusion is valid even if the C_s model is incorrect.

It is found that the electron diffraction data are incompatible with a model containing a planar eight-membered ring or with models containing puckered rings of C_{4v} or D_{2d} symmetry. Since the RD curves calculated for models of C_{4v} or D_{2d} symmetry all are considerably higher than the experimental curve in the region 3.6 to 4.0 Å, and considerably lower in the region 4.2 to 4.8 Å, the existence of a mixture of molecules in two or three of these conformations can likewise be ruled out.

Satisfactory agreement with the electron diffraction data is obtained for a model of C_s symmetry. It should not be concluded, however, that this is the only possible model. It seems probable that equally good agreement could be obtained with other models of low symmetry. For this reason we refrain from a closer description of the C_s model.

The bond distances and valence angles of tetrameric $(CH_3)_2AlF$ and their estimated standard deviations are listed in Table 1. The bond distances are not unusual: the Al–C bond distance is not significantly different from the Al–C bond distances in monomeric $(CH_3)_3Al$[15], 1.957(3) Å, or trimeric $(CH_3)_2AlOCH_3$[16], 1.957(3) Å, both of these molecules having been studied by electron diffraction. Nor, probably, is it significantly different from the Al–C bond distance in trimeric $(CH_3)_2$-$AlNHCH_3$[17], as determined by X-ray diffraction, 1.973(5) Å; the operational definition of a bond distance is somewhat different for the two methods. The Al–F bond distance in $[(CH_3)_2AlF]_4$ is very similar to the Al–F(bridge) bond distance in $K[(C_2H_5)_3$-$AlFAl(C_2H_5)_3]$[4], 1.820(3) Å, both are significantly longer than the Al–F(terminal) bond distance in gaseous monomeric AlF_3[18], 1.63±0.01 Å.

The valence angles of $[(CH_3)_2AlF]_4$ are listed in Table 2 along with the analogous angles in $[(CH_3)_2AlOCH_3]_3$[16], $[(CH_3)_2AlN(CH_2)_2]_3$[19] and $[(CH_3)_2$-$AlNH(CH_3)]_3$[17]. All these molecules are non-planar, and may therefore be assumed to be relatively free from angle strain. It is seen that all compounds are characterized by wide <C–Al–C and narrow <X–Al–X (X = bridging atom) angles, and that the deviation from tetrahedral angles increases in the order $N \approx O < F$. It would appear

TABLE 2

AVERAGE VALENCE ANGLES IN NONPLANAR ASSOCIATED SPECIES OF THE TYPE $(R_2ALX)_n$ (X=F, OR′ or NR'_2)

	$[(CH_3)_2AlF]_4$	$[(CH_3)_2AlOCH_3]_3$	$[(CH_3)_2AlN(CH_2)_2]_3$	$[(CH_3)_2AlNHCH_3]_3$
< C–Al–C	131.2 (1.9)°	117.3 (0.8)°	113.4 (1.1)°	116.9 (0.4)°
< X–Al–X	92.3 (1.2)°	103.2 (1.1)°	102.3 (0.8)°	102.1 (0.4)°
< Al–X–Al	146.1 (2.6)°	125.8 (0.4)°	120.0 (0.4)°	122.3 (0.4)°

that the *s* character is concentrated in those hybrid atomic orbitals on the Al atom that are pointing towards the relatively electropositive C atoms, leaving hybrid orbitals of predominant *p* character pointing towards the electronegative bridging atoms[20]. The effect is, of course, enhanced by the fact that the bridging atoms carry a formal charge of +1.

The four compounds compared in Table 2 are also characterized by wide <Al–X–Al angles that increase in the order N< O< F. Similar wide angles have previously been found where N or O is bonded between two Si atoms: Thus in $[(CH_3)_2SiO]_4$[21] (which is isoelectronic with $[(CH_3)_2AlF]_4$) < Si–O–Si = 142°, in disilylether[22] < Si–O–Si = 144°. In $[(CH_3)_2SiNH]_4$[23], which may be regarded as isoelectronic with $[(CH_3)_2SiOCH_3]_3$, < Si–N–Si = 132°, in $(SiH_3)_2NCH_3$[24] < Si–N–Si = 125°. In the latter compound the N atom and the three atoms bonded to it lie in one plane, as do the O atom and its three neighbours in $[(CH_3)_2AlOCH_3]_3$. In disilylmethane[25], however, the < Si–C–Si angle is 114°, only two degrees larger than the < C–C–C angle in propane.

It has been assumed that these wide < Si–O–Si and < Si–N–Si angles arise from delocalization of the lone pair electrons of O or N into empty 3*d* orbitals on Si, which gives the Si–O and Si–N bonds some double bond character; such delocalization would be enhanced by increasing *p* character of the lone pair orbitals on O or N*. A similar effect might be evoked to explain the wide < Al–F–Al and < Al–O–Al angles found in $[(CH_3)_2AlF]_4$ and $[(CH_3)_2AlOCH_3]_3$, but the wide <Al–N–Al angles found in $[(CH_3)_2AlN(CH_2)_2]_3$ and $[(CH_3)_2AlNHCH_3]_3$, in which the bridging N atoms possess no lone pair electrons, suggest that there are other factors, *e.g.* repulsion between bonding electrons.

The great variation of <Al–F–Al, <Al–O–Al and <Al–N–Al angles in different molecules suggests that these angles offer little resistance to deformation: Thus the <Al–N–Al angle in $[(CH_3)_2AlN(CH_3)_2]_2$[27] is 92°, the < Al–O–Al angle in $[Br_2AlOSi(CH_3)_3]_2$[28] 96°. The < Al–F–Al angle in $(AlF_3)_2$[29] must also be less than 100°.

Coates[30] has suggested that the degree of association of organoaluminium compounds of the type R_2AlX (X = F, OR′, NR'_2, Cl, SR′ and PR'_2) is determined by a balance between entropy factors (favoring a low degree of association) and steric factors: large equilibrium < Al–X–Al angles may favor the formation of trimers or even tetramers. Steric interactions between the alkyl groups R and R′, however, increase with increasing degrees of association and may limit the degree of association

---

* For a critical review see ref. 26.

actually obtained. Since the sum of the angles $<$ Al–F–Al and $<$ F–Al–F found in $[(CH_3)_2AlF]_4$ is slightly less than 240°, it would appear that $(CH_3)_2AlF$ could form a trimer with a near-planar six-membered ring that would be free from angle strain. We suggest that the existence of a relatively stable tetramer must be due to the existence of rotational barriers about the Al–F bonds; in a planar or near-planar trimer the Al–F bonds would all be eclipsed. In $(n\text{-}C_3H_7)_2AlF$ and $(iso\text{-}C_4H_9)_2AlF$, however, interaction between the alkyl groups is sufficiently severe to lead to (apparently planar) trimers[31].

In contrast to $<$ Si–O–Si and $<$ Si–N–Si angles, $<$ Si–S–Si and $<$ Si–P–Si angles tend to be smaller than the tetrahedral angle, in fact smaller than 100° [26]. Thus $<$ Si–S–Si in $(SiH_3)_2S$[32] is 97°, $<$ Si–P–Si[32] in $(SiH_3)_3P$ is 96°. In the crystalline phase where $(CH_3)_2AlSCH_3$[34] forms infinite zig-zag chains which are presumably relatively free from angle strain, $<$ Al–S–Al $= 103°$. The tendency towards small $<$ Al–Cl–Al and $<$ Al–S–Al angles may explain why $(CH_3)_2AlCl$ and $(CH_3)_2AlSCH_3$ are dimeric[7] rather than trimeric or tetrameric in the gas phase, in $[(CH_3)_2AlCl]_2$[35] $<$ Al–Cl–Al is $91° \pm 4°$. We suggest that $(CH_3)_2AlP(CH_3)_2$ is trimeric[7] in the gas phase both because a $<$ Al–P–Al angle would tend to be larger than $<$ Al–S–Al and because a dimer would suffer from appreciably Pitzer strain: all the bonds radiating from Al and P would be eclipsed.

ACKNOWLEDGEMENT

We wish to thank Dr. J. Weidlein for supplying the sample, Cand. real. Arne Almenningen for collecting the electron diffraction data, and The Norwegian Research Council for Science and the Humanities for financial support.

REFERENCES

1 K. Ziegler and R. Köster, *Justus Liebigs Ann. Chem.*, 608 (1957) 1.
2 A. W. Laubengayer and G. F. Lengnick, *Inorg. Chem.*, 5 (1966) 503.
3 J. Weidlein and V. Krieg, *J. Organometal. Chem.*, 11 (1968) 9.
4 G. Allegra and G. Perego, *Acta Crystallogr.*, 16 (1963) 185.
5 E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 5 (1966) 995.
6 H. C. Clark, R. J. O'Brien and J. Trotter, *J. Chem. Soc.*, (1964) 2332.
7 N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, 64 (1942) 316.
8 O. Bastiansen, O. Hassel and E. Risberg, *Acta Chem. Scand.*, 9 (1955) 232.
9 B. Anderson, H. M. Seip, T. G. Strand and R. Stølevik, *Acta Chem. Scand.*, 23 (1969) 3224.
10 J. L. Peacher and J. C. Wills, *J. Chem. Phys.*, 46 (1967) 4807.
11 R. E. Watson and A. J. Freeman, *Phys. Rev.*, 123 (1961) 521.
12 E. Clementi, C. C. J. Roothaan and M. Yoshimine, *Phys. Rev.*, 127 (1962) 1618.
13 H. M. Seip, T. G. Strand and R. Stølevik, *Chem. Phys. Lett.*, 3 (1969) 617.
14 J. D. Dunitz, *Pure Appl. Chem.*, 25 (1971) 495.
15 A. Almenningen, S. Halvorsen and A. Haaland, *Acta Chem. Scand.*, 25 (1971) 1937.
16 D. A. Drew, A. Haaland and J. Weidlein, *Z. Anorg. Allg. Chem.*, in press.
17 G. M. McLaughlin, G. A. Sim and J. D. Smith, *J. Chem. Soc., Dalton*, (1972) 2197.
18 P. A. Akishin, N. G. Rambidi and E. Z. Zasorin, *Kristallografiya*, 4 (1959) 186.
19 J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 92 (1970) 285.
20 H. A. Bent, *J. Chem. Ed.*, 37 (1960) 616.
21 H. Steinfink, B. Post and I. Fankuchen, *Acta Crystallogr.*, 8 (1955) 420.
22 A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg and M. Traetteberg, *Acta Chem. Scand.*, 17 (1963) 2455.

23 G. S. Smith and L. E. Alexander, *Acta Crystallogr.*, 16 (1963) 1015.
24 C. Glidewell, D. W. H. Rankin, A. G. Robiette and G. M. Sheldrick, *J. Mol. Struc.*, 4 (1969) 215.
25 A. Almenningen, H. M. Seip and R. Seip, *Acta Chem. Scand.*, 24 (1970) 1697.
26 E. A. V. Ebsworth, in A. G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Marcel Dekker Inc., New York, 1968.
27 H. Hess, A. Hinderer and S. Steinhauser, *Z. Anorg. Allg. Chem.*, 377 (1970) 1.
28 M. Bonamico and G. Derry, *J. Chem. Soc. A*, (1967) 1786.
29 A. Snelson, *J. Phys. Chem.*, 71 (1967) 3202.
30 G. E. Coates and K. Wade, *Organometallic Compounds*, Vol. 1, Methuen, London 1967.
31 V. Krieg and J. Weidlein, *J. Organometal. Chem.*, 21 (1970) 281.
32 A. Almenningen, K. Hedberg and R. Seip, *Acta Chem. Scand.*, 17 (1963) 2264.
33 B. Beagley, A. G. Robiette and G. M. Sheldrick, *J. Chem. Soc. A*, (1968) 3002.
34 D. J. Brauer and G. D. Stucky, *J. Amer. Chem. Soc.*, 91 (1969) 5462.
35 L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 63 (1941) 3287.