Complexes of Organoaluminium Compounds. Part VI.[1] Crystal and Molecular Structures of *cis*- and *trans*-Cyclotri-μ-methylamido-tris-(dimethylaluminium) and of Cyclodi-μ-dimethylamido-bis(dimethylaluminium)

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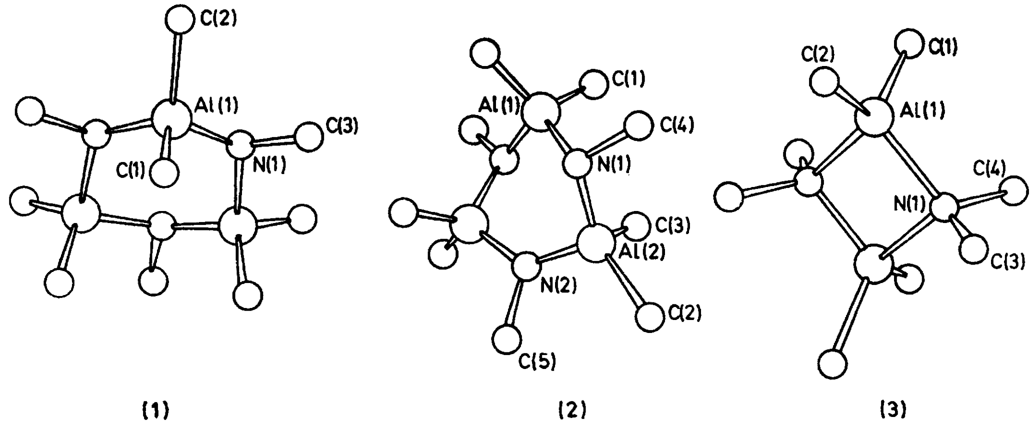
Two stereoisomers of cyclotri-μ-methylamido-tris(dimethylaluminium), have been characterized by single-crystal *X*-ray studies from diffractometer data. The rhombohedral *cis*-isomer (1) crystallizes in space group *R*3 with a = 9·983 ± 0·004 Å, α = 104° 39′ ± 3′, and Z = 2. The molecules have crystallographic symmetry C_3 with six-membered $(AlN)_3$ rings in the chair conformation. All methyl substituents on nitrogen atoms are equatorial. The mean molecular dimensions are: Al–N 1·940 ± 0·005, Al–C, 1·973 ± 0·005, and N–C 1·504 ± 0·010 Å; N–Al–N 102·1 ± 0·4, C–Al–C 116·9 ± 0·4, Al–N–Al 122·3 ± 0·4, C–Al–N 109·4 ± 0·3, and Al–N–C 108·6 ± 0·4°. The monoclinic *trans*-isomer (2) crystallizes in space group *C*2/*c* with a = 11·897 ± 0·008, b = 15·904 ± 0·012, c = 9·778 ± 0·007 Å, β = 107° 50 ± 3′, and Z = 4. The molecules have the same molecular dimensions as those of the rhombohedral isomer, but the configuration at one of the nitrogen atoms is reversed, and the conformation of the $(AlN)_3$ rings is of the skew-boat type. Crystals of cyclodi-μ-dimethylamido-bis(dimethylaluminium) (3) are monoclinic, space group $P\,2_1/a$, with a = 12·770 ± 0·012, b = 8·104 ± 0·007, c = 7·655 ± 0·009 Å, β = 117° 39′ ± 3′, and Z = 2. The molecules have four-membered $(AlN)_2$ rings, molecular symmetry which approximates to D_{2h}, and dimensions: Al–N 1·958 ± 0·005, Al–C 1·950 ± 0·008, and N–C 1·509 ± 0·010 Å; N–Al–N 88·3 ± 0·3, C–Al–C 115·7 ± 0·5, Al–N–Al 91·7 ± 0·2, C–N–C, 107·6 ± 0·6, C–Al–N 112·4 ± 0·3, and Al–N–C 114·3 ± 0·4°.

The structures were refined to *R* values of 5·5 [(1), 996 reflections], 12·1 [(2), 621 reflections], and 6·9% [(3), 525 reflections].

IT has been suggested[2] that the molecular complexities of organometallic compounds $(R^1{}_2M^1M^2R^2R^3)_n$, with small rings of alternate Group III atoms M^1 and Group V atoms M^2, are determined by balances between several factors. These include ring strain, steric hindrance between the groups R^{1-3}, and entropy differences between oligomers. In order to examine these factors in more detail for a particular pair of atoms M^1, M^2 and to find the effects of the configuration of the groups R^2, R^3 on ring conformation, we have determined the crystal and molecular structures of several compounds in which $M^1 = Al$ and $M^2 = N$; two of these compounds were shown to be stereoisomers of cyclotri-μ-methylamido-tris(dimethylaluminium), $(Me_2AlNHMe)_3$ [(1) *cis*-; (2), *trans*-][3] and another was cyclodi-μ-dimethylamido-bis(dimethylaluminium), $(Me_2AlNMe_2)_2$ (3). After our study of $(Me_2AlNMe_2)_2$ was complete, an independent *X*-ray determination of the structure, which agrees well with ours, was described.[4]



(1) (2) (3)

FIGURE 1 The molecular structures

The structures of compounds (1)—(3) are closely related. Each shows discrete molecules (Figure 1) with rings of alternate aluminium and nitrogen atoms. The molecular complexities in the solid are the same as those found cryoscopically in benzene or in the vapour.[5,6] Atomic co-ordinates and thermal parameters are shown in Tables 1—3. The elucidation

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[3] K. Gosling, G. M. McLaughlin, G. A. Sim, and J. D. Smith, *Chem. Comm.*, 1970, 1617.

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of the structure of crystals of compound (1) yields molecular parameters (Table 4) for two crystallographically independent molecules, which are identical within experimental error. Each molecule has crystallographic symmetry C_3, so the $(AlN)_3$ rings are required to be in the chair conformation. The distances between the Al_3 and N_3 planes are 0·540(9) and 0·534(7) Å for the two molecules. The *X*-ray data were not sufficiently complete for the location of all the hydrogen atoms, so the positions given in Table 1 are tentative. *X*-Ray data for *trans*-$(Me_2AlNHMe)_3$, (2), were more

TABLE 1

Fractional atomic co-ordinates,* with standard deviations in parentheses, and thermal parameters for *cis*-$(Me_2AlNHMe)_3$, (1)

	x/*a*	*y*/*b*	*z*/*c*
Al(1)	0·21341(65)	0·38460(64)	0·14224(63)
Al(2)	0·75509(61)	0·61492(63)	0·86271(64)
N(1)	0·38437(85)	0·32001(87)	0·16938(85)
N(2)	0·68322(70)	0·77794 †	0·90381(69)
C(1)	0·0509(10)	0·2425(11)	−0·0317(10)
C(2)	0·2815(11)	0·5886(10)	0·1459(11)
C(3)	0·4315(12)	0·3175(11)	0·0362(12)
C(4)	0·5981(11)	0·4385(10)	0·7144(12)
C(5)	0·8503(12)	0·5926(13)	1·0493(12)
C(6)	0·5699(11)	0·7438(12)	0·9753(12)
H(1)	0·074	0·244	−0·132
H(2)	−0·045	0·257	−0·042
H(3)	0·035	0·132	−0·028
H(4)	0·374	0·651	0·246
H(5)	0·315	0·588	0·051
H(6)	0·193	0·631	0·140
H(7)	0·344	0·269	−0·060
H(8)	0·506	0·261	0·036
H(9)	0·491	0·429	0·049
H(10)	0·472	0·379	0·263
H(11)	0·646	0·357	0·685
H(12)	0·507	0·397	0·753
H(13)	0·545	0·461	0·613
H(14)	0·929	0·694	1·019
H(15)	0·775	0·564	1·102
H(16)	0·909	0·512	1·029
H(17)	0·500	0·628	0·923
H(18)	0·509	0·809	0·955
H(19)	0·617	0·763	1·088
H(20)	0·769	0·854	1·000

* Hydrogen positions were not refined. † Not refined.

Anisotropic temperature factors are of the form

$$T = \exp[-10^{-4}(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$$

with parameters as follows:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Al(1)	112	109	102	37	33	40
Al(2)	128	114	127	36	42	51
N(1)	121	123	113	41	49	45
N(2)	129	146	119	44	53	46
C(1)	149	214	121	32	21	43
C(2)	198	158	241	70	97	108
C(3)	232	197	222	107	158	112
C(4)	194	139	233	20	73	54
C(5)	239	283	195	126	82	143
C(6)	224	243	229	114	146	127

TABLE 2

Fractional atomic co-ordinates, with standard deviations in parentheses, and thermal parameters for *trans*-$(Me_2AlNHMe)_3$, (2)

	x/*a*	*y*/*b*	*z*/*c*	*B*/Å²
Al(1)	0·0000	0·1169(4)	0·2500	*
Al(2)	−0·0919(4)	0·2997(3)	0·3481(5)	*
N(1)	−0·0111(10)	0·1940(7)	0·3995(12)	4·9
N(2)	0·0000	0·3485(10)	0·2500	4·0
C(1)	0·1505(17)	0·0517(13)	0·3243(21)	8·8
C(2)	−0·0820(17)	0·3639(12)	0·5223(21)	8·1
C(3)	−0·2511(16)	0·2827(11)	0·2086(19)	7·5
C(4)	−0·0567(16)	0·1449(11)	0·5070(19)	7·3
C(5)	0·0405(29)	0·4382(20)	0·2905(38)	7·2

* Anisotropic temperature factors are of the form given in Table 1 with parameters as follows:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Al(1)	94	45	240	3	34	74
Al(2)	86	50	140	8	38	6

TABLE 3

Fractional atomic co-ordinates,* with standard deviations in parentheses, and thermal parameters for $(Me_2AlNMe_2)_2$ (3)

	x/*a*	*y*/*b*	*z*/*c*
Al(1)	0·04280(18)	0·07970(29)	0·38281(32)
N(1)	0·0858(5)	0·0750(8)	0·6622(8)
C(1)	0·1644(7)	−0·0202(13)	0·3290(14)
C(2)	−0·0142(9)	0·2943(12)	0·2628(14)
C(3)	0·0747(10)	0·2377(12)	0·7486(15)
C(4)	0·2076(7)	0·0081(15)	0·7922(13)
H(1)	0·166	0·042	0·197
H(2)	0·150	0·150	0·299
H(3)	0·252	−0·004	0·454
H(4)	−0·030	0·292	0·132
H(5)	0·052	0·390	0·341
H(6)	−0·094	0·329	0·274
H(7)	0·003	0·281	0·687
H(8)	0·141	0·322	0·758
H(9)	0·093	0·210	0·903
H(10)	0·216	−0·080	0·726
H(11)	0·221	−0·019	0·933
H(12)	0·276	0·101	0·801

Anisotropic temperature factors are of the form given in Table 1 with parameters as follows:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Al(1)	81	157	242	1	56	8
N(1)	96	201	259	32	64	−34
C(1)	134	385	488	19	153	22
C(2)	193	202	481	2	71	86
C(3)	277	258	553	−132	278	−214
C(4)	88	560	330	−36	12	96

* Hydrogen positions were not refined.

TABLE 4

Interatomic distances and valency angles, with standard deviations in parentheses, for the two crystallographically independent molecules of (1)

(*a*) Intramolecular interatomic distances (Å)

Al(1)–Al(1^{I})	3·403(10)	Al(2)–Al(2^{I})	3·394(10)
Al(1)–N(1)	1·951(12)	Al(2)–N(2)	1·930(8)
Al(1)–N(1^{II})	1·931(12)	Al(2)–N(2^{II})	1·947(9)
Al(1)–C(1)	1·975(9)	Al(2)–C(4)	1·985(9)
Al(1)–C(2)	1·969(12)	Al(2)–C(5)	1·963(14)
N(1)–C(3)	1·513(16)	N(2)–C(6)	1·495(15)
N(1)–N(1^{I})	3·014	N(2)–N(2^{I})	3·023
C(1)–C(1^{I})	3·84	C(4)–C(4^{I})	3·78
C(3)–C(1)	3·54	C(6)–C(4)	3·61
C(3)–C(2)	3·48	C(6)–C(5)	3·50
C(3)–C(1^{I})	3·59	C(6)–C(4^{I})	3·58
C(3)–C(2^{I})	3·59	C(6)–C(5^{I})	3·55

(*b*) Valency angles (deg.)

N(1)–Al(1)–N(1^{II})	101·9(5)	N(2)–Al(2)–N(2^{II})	102·4(4)
N(1)–Al(1)–C(1)	110·1(5)	N(2)–Al(2)–C(4)	110·8(5)
N(1)–Al(1)–C(2)	106·5(5)	N(2)–Al(2)–C(5)	108·4(5)
C(1)–Al(1)–N(1^{II})	111·1(5)	C(4)–Al(2)–N(2^{II})	109·1(5)
C(2)–Al(1)–N(1^{II})	108·5(5)	C(5)–Al(2)–N(2^{II})	109·0(5)
C(1)–Al(1)–C(2)	117·6(6)	C(4)–Al(2)–C(5)	116·2(6)
Al(1)–N(1)–C(3)	107·0(7)	Al(2)–N(2)–C(6)	108·9(6)
C(3)–N(1)–Al(1^{I})	109·3(7)	C(6)–N(2)–Al(2^{I})	109·4(6)
Al(1)–N(1)–Al(1^{I})	122·4(5)	Al(2)–N(2)–Al(2^{I})	122·1(4)

limited than those for the *cis*-isomer (1), owing to the small size of the crystal and heavy absorption from the surrounding capillary, and it was not possible to decide unequivocally between the space groups *Cc* and *C*2/*c*.

TABLE 5

Interatomic distances, valency angles, with standard deviations in parentheses, and intermolecular separations for (2)

(*a*) Intramolecular interatomic distances (Å)

Al(1)–N(1)	1·943(13)	N(1)–N(1$^{\mathrm{I}}$)	3·014(18)
Al(2)–N(2)	1·833(8)	N(2)–N(1)	2·884(18)
Al(2)–N(1)	1·926(12)	C(4)–C(1)	3·76(3)
Al(1)–C(1)	2·002(20)	C(4)–C(1$^{\mathrm{I}}$)	3·42(3)
Al(2)–C(2)	1·959(21)	C(4)–C(2)	3·50(3)
Al(2)–C(3)	1·984(16)	C(4)–C(3)	3·81(2)
N(1)–C(4)	1·536(24)	C(5)–C(2)	3·27(5)
N(2)–C(5)	1·518(34)	C(5)–C(3)	4·13(4)
Al(1)–Al(2)	3·349(7)	C(5)–C(2$^{\mathrm{I}}$)	3·45(5)
Al(2)–Al(2$^{\mathrm{I}}$)	3·322(8)	C(5)–C(3$^{\mathrm{I}}$)	3·52(4)

(*b*) Valency angles (deg.)

N(1)–Al(1)–N(1$^{\mathrm{I}}$)	101·7(6)	N(2)–Al(2)–N(1)	100·1(6)
N(1)–Al(1)–C(1)	108·2(7)	N(2)–Al(2)–C(2)	110·3(7)
N(1)–Al(1)–C(1$^{\mathrm{I}}$)	109·9(7)	N(2)–Al(2)–C(3)	107·1(6)
C(1)–Al(1)–N(1$^{\mathrm{I}}$)	109·9(7)	C(2)–Al(2)–N(1)	109·6(7)
C(1$^{\mathrm{I}}$)–Al(1)–N(1$^{\mathrm{I}}$)	108·2(7)	C(3)–Al(2)–N(1)	110·8(6)
C(1)–Al(1)–C(1$^{\mathrm{I}}$)	117·7(9)	C(2)–Al(2)–C(3)	117·4(9)
Al(1)–N(1)–C(4)	108·3(9)	Al(2)–N(2)–C(5)	117·0(6)
C(4)–N(1)–Al(2)	111·7(10)	C(5)–N(2)–Al(2$^{\mathrm{I}}$)	110·0(16)
Al(1)–N(1)–Al(2)	119·9(6)	Al(2)–N(2)–Al(2$^{\mathrm{I}}$)	129·9(9)

Nevertheless, it was firmly established that the molecule of the *trans*-isomer has a six-membered $(AlN)_3$ ring in a skew-boat conformation and differs from the molecule of the *cis*-isomer in the configuration at one of the nitrogen atoms. The most satisfactory molecular parameters (Table 5) were obtained in space group *C*2/*c*, which imposes a two-fold axis (Figure 2) through the atoms Al(1) and N(2) and requires the hydrogen and methyl groups attached to N(2) to be disordered. The molecules are thus stacked randomly in the orientation of Figure 2 and in the orientation obtained by a rotation of 180°. Since the space group has a glide plane, half the molecules in the structure have a conformation which is the mirror image of that shown in Figure 2. The C_2 axis requires that the atoms N(2), N(1), Al(1), N(1$^{\mathrm{I}}$) (Figure 2) in the skew-boat ring are coplanar. The two remaining atoms of the ring Al(2) and Al(2$^{\mathrm{I}}$) lie on either side of this plane at a distance of 0·917(10) Å.

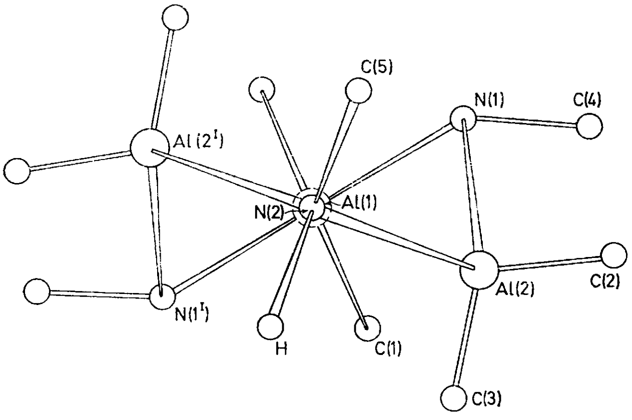

FIGURE 2 The molecular structure of (2), viewed along the pseudo-twofold axis. In the crystal, the atoms C(5) and H are disordered

Molecular parameters for the dimer $(Me_2AlNMe_2)_2$ (3) are given in Table 6. The molecules have crystallographic symmetry C_i. The angles between the mean plane of the ring and the planes defined by the atoms C(1), Al(1), C(2) and C(3), N(1), C(4), are 90·2(5) and 89·2(5)°. The molecular symmetry is thus D_{2h} within experimental error.

TABLE 6

Interatomic distances, valency angles, with standard deviations in parentheses, and intermolecular separations for (3)

(*a*) Intramolecular distances (Å)

Al(1)–N(1)	1·948(7)	Al(1)–Al(1$^{\mathrm{I}}$)	2·809(4)
Al(1)–N(1$^{\mathrm{I}}$)	1·967(7)	N(1)–N(1$^{\mathrm{I}}$)	2·726(7)
Al(1)–C(1)	1·956(12)	C(3)–C(2)	3·38(2)
Al(1)–C(2)	1·945(9)	C(4)–C(1)	3·33(2)
N(1)–C(3)	1·511(13)	C(3)–C(1$^{\mathrm{I}}$)	3·33(2)
N(1)–C(4)	1·508(10)	C(4)–C(2$^{\mathrm{I}}$)	3·36(2)

(*b*) Valency angles (deg.)

N(1)–Al(1)–N(1$^{\mathrm{I}}$)	88·3(3)	Al(1)–N(1)–Al(1$^{\mathrm{I}}$)	91·7(2)
N(1)–Al(1)–C(1)	111·9(3)	Al(1)–N(1)–C(4)	114·5(6)
N(1)–Al(1)–C(2)	113·0(4)	Al(1)–N(1)–C(2)	115·3(5)
C(1)–Al(1)–N(1$^{\mathrm{I}}$)	112·3(4)	C(4)–N(1)–Al(1$^{\mathrm{I}}$)	114·2(6)
C(2)–Al(1)–N(1$^{\mathrm{I}}$)	112·6(4)	C(3)–N(1)–Al(1$^{\mathrm{I}}$)	113·2(6)
C(1)–Al(1)–C(2)	115·7(5)	C(4)–N(1)–C(3)	107·6(6)

Since the mean aluminium–nitrogen bond lengths in (1) and (3) are 1·940(11) and 1·958(5) Å there is no significant difference between Al–N distances in four- and six-membered rings; similarly, no significant difference was found for the Si–N distances in the compounds $(Me_2SiNSiMe_3)_2$ and $(Me_2SiNSiMe_3)_3$.[7] In view of the low accuracy in the structure determination of compound (2), the low value of 1·90 Å for the mean Al–N distance in that compound is probably not significantly different from the distances in compounds (1) and (3). There are few structure determinations available for comparison of compounds having $(AlN)_n$ rings with quaternary aluminium and nitrogen atoms. Al–N distances of 1·91 Å were found[8] in $[Me_2AlN(CH_2)_2]_3$, which has a skew-boat ring like (2), and 1·90—1·94 Å in the cage compound $Al_4Cl_4(NMe_2)_4(NMe)_2$ which has bridging dimethylamido-groups in six-membered rings constrained in the chair conformation.[9] An Al–N distance of 1·916 Å was found in $[Ph_2AlN{:}CPh{\cdot}C_6H_4Br]_2,2C_6H_6$;[10] molecules of this compound have four-membered $(AlN)_2$ rings, but the nitrogen atoms are trigonal, rather than quaternary as in $(Me_2AlNMe_2)_2$, (3). Mean aluminium–carbon distances are 1·973 in (1), 1·982 in (2), and 1·950 Å in (3), and

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[7] G. W. Adamson and J. J. Daly, *J. Chem. Soc.* (*A*), 1970, 2724; P. J. Wheatley, *J. Chem. Soc.*, 1962, 1721.

[8] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1970, **92**, 285.

[9] U. Thewalt and I. Kawada, *Chem. Ber.*, 1970, **103**, 2754.

[10] W. S. McDonald, *Acta Cryst.*, 1969, *B*, **25**, 1385.

exocyclic C–Al–C angles are all 116—117°. Al–C distances in the range 1·94—1·98 Å and C–Al–C angles in the range 113—123° are found in other solid compounds with dimethylaluminium groups.[8,11,12] N–C Distances (1·504—1·527 Å) are similar to those in organic compounds with quaternary nitrogen atoms.

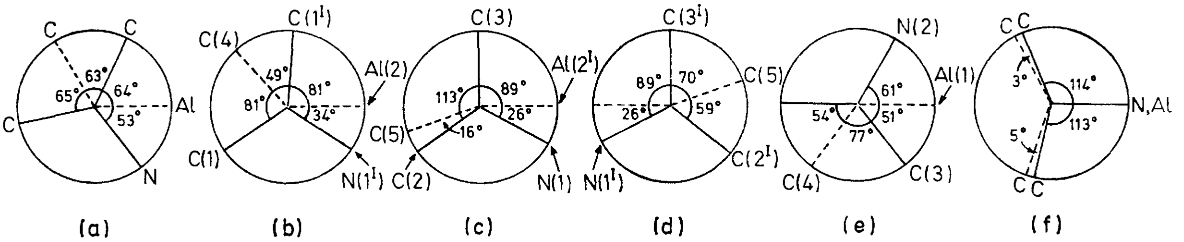

FIGURE 3 Projections along Al–N bonds, showing dihedral angles: (a) (1), mean values for four independently characterised bonds; (b)—(e) (2). The numbering of the atoms is the same as in Figures 1 and 2 and the superscripts refer to the transformation $-x, y, \frac{1}{2} - z$ of the atomic co-ordinates. Projections about the two remaining Al–N bonds are the same as (b) and (e). (f) (3), mean values for two independently characterised bonds

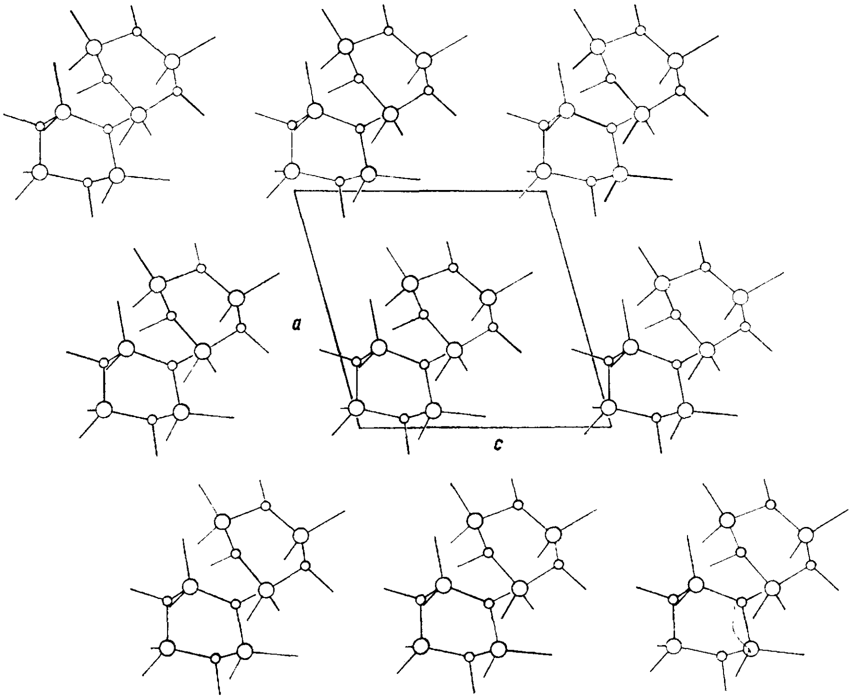

FIGURE 4 Packing diagram for (1)

Interbond angles and certain intramolecular non-bonded distances (Tables 4—6) support the notion[2] that steric effects are important in determining molecular complexity. In the $(AlN)_n$ rings, the interbond angles at nitrogen are larger than those at aluminium and there is an inevitable marked contraction (from 122·3 to 91·7°) in the Al–N–Al angle from the six-membered ring in (1) to the four-membered ring in (3). Interbond angles for the trimers (1) and (2) are similar to those in $[Me_2AlN(CH_2)_2]_3$ (N–Al–N 102, Al–N–Al 120°);[8] in $Al_4Cl_4(NMe_2)_4(NMe)_2$ the N–Al–N and Al–N–Al angles are more nearly tetrahedral.[9]

The Al–Al distance in *cis*-$(Me_2AlNHMe)_3$ (1) is 3·399 Å, and axial methyl substituents at aluminium are separated by 3·813 Å. Though there is some mutual repulsion [the three Al–C(axial) bonds are not parallel], this is insufficient to cause gross deviations from the chair conformation. The N–N distance, however, is only 3·018 Å, and so mutual repulsions between axial substituents at nitrogen are likely to be more serious. The introduction of one axial substituent, as in *trans*-$(Me_2AlNHMe)_3$ (2), results in a change in ring conformation, and the replacement of methylamido- by dimethylamido-groups results in a change

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in molecular complexity exemplified by $(Me_2AlNMe_2)_2$, (3). In steroid and terpene chemistry, examples of 1,3-axial interactions causing departures from the normal cyclohexane chair conformation are well known.[13] The *N*-methyl groups in (1) are separated from the axial aluminium methyl groups by 3·58 and from the equatorial aluminium methyl groups by 3·53 Å. Both these methyl–methyl distances are shorter than the distance of *ca.* 4·0 Å calculated from the sum of van der Waals' radii, and it is clear that the methyl groups in (1), as in trimethylaluminium,[11] are quite tightly packed. Projections along Al–N bonds for the chair conformation (Figure 3a) show that bonds from adjacent aluminium and nitrogen atoms are almost exactly staggered. The torsion angles of ±53° in the $(AlN)_3$ ring are slightly smaller than those found (±56°) in an electron diffraction study of cyclohexane.[14]

The skew-boat conformation adopted by *trans*-$(Me_2AlNHMe)_3$ (2) is very flexible and a series of pseudorotations can interchange the various aluminium and nitrogen atoms. The conformations with the lowest free-energy must represent compromises between the various methyl–methyl repulsions within the molecule. Table 5 shows that there are several C–C distances in the range 3·3—3·8 Å. The conformations in the solid (that of Figure 4 and its mirror image) represent departures from a symmetrical boat in which all methyl substituents at nitrogen point outwards from the ring. The distortions allow some staggering [Figure 3(b)—(e)] between those methyl groups on adjacent aluminium and nitrogen atoms, which would be eclipsed in the symmetrical boat. Alternative skew-boat positions of the ring, easily accessible by pseudorotation, bring *N*-methyl substituents towards the centre of the molecule. In $(Me_2C{\cdot}CO)_3$[15] and $(Me_2SiNSiMe_3)_3$[7] in which alternate atoms of six-membered rings have a nearly planar distribution of bonds, methyl–methyl interactions raise the energy of the chair conformation above that of the alternative skew-boat.

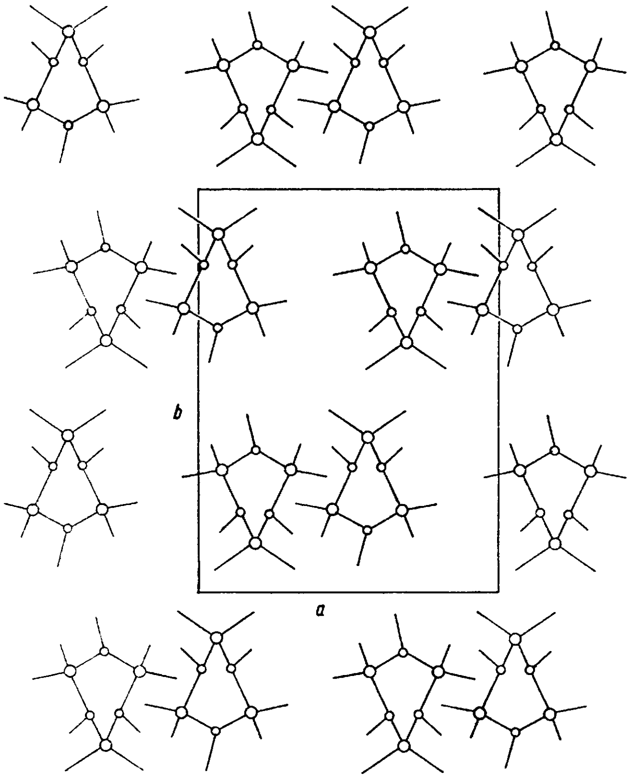

FIGURE 5 Packing diagram for (2)

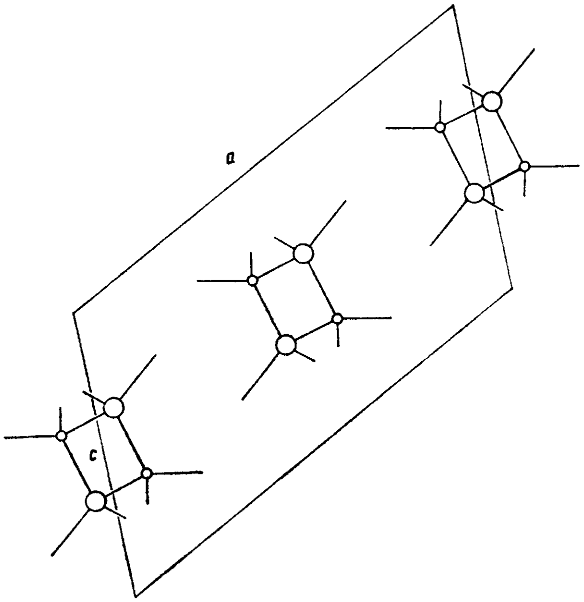

FIGURE 6 Packing diagram for (3)

Energy differences between the alternative chair and skew-boat conformations of (1) and (2) are probably not very large and the conformations found in the crystals may be determined by packing effects, for whereas the conformation of $[Me_2AlN(CH_2)_2]_3$ in the solid state is a skew-boat,[8] that of $[H_2GaN(CH_2)_2]_3$ is a chair.[16] The *cis*- and *trans*-isomers of $(H_2BNHR)_3$[17] and $(H_2GaHNR)_3$[18] have been characterized spectroscopically, and the skew-boat conformation has been postulated for the *trans*-isomers of the gallium compounds.[18]

In $(Me_2AlNMe_2)_2$ (3) the methyl substituents on adjacent aluminium and nitrogen atoms are almost eclipsed (Figure 3f). The mean shortest distance between *Al*-methyl and *N*-methyl groups is 3·352 Å. Intramolecular repulsion between substituents is apparent even though the molecules are dimeric rather than trimeric.

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Packing diagrams are shown in Figures 4—6. None of the intermolecular C–C or C–N separations is $<3{\cdot}6$ Å. The calculated densities of all these compounds are almost the same.

EXPERIMENTAL

Crystal Data.—(i) *cis*-(Me$_2$AlNHMe)$_3$ (1), $M = 261{\cdot}3$, Rhombohedral, $a = 9{\cdot}983 \pm 0{\cdot}004$ Å, $\alpha = 104° \; 39' \pm 3'$, $U = 876{\cdot}2$ Å^3, $Z = 2$, $D_c = 0{\cdot}98$, $F(000) = 288$. μ(Mo-K_α) = 2·03 cm^{-1}. Space group $R3$.

(ii) *trans*-(Me$_2$AlNHMe)$_3$ (2), $M = 261{\cdot}3$, Monoclinic, $a = 11{\cdot}897 \pm 0{\cdot}008$, $b = 15{\cdot}904 \pm 0{\cdot}012$, $c = 9{\cdot}778 \pm 0{\cdot}007$ Å, $\beta = 107° \; 50' \pm 3'$, $U = 1761$ Å^3, $Z = 4$, $D_c = 0{\cdot}98$, $F(000) = 576$. μ(Mo-K_α) = 2·02 cm^{-1}. Space group $C2/c$.

(iii) (Me$_2$AlNMe$_2$)$_2$ (3), $M = 203{\cdot}3$, Monoclinic, $a = 12{\cdot}770 \pm 0{\cdot}012$, $b = 8{\cdot}104 \pm 0{\cdot}007$, $c = 7{\cdot}655 \pm 0{\cdot}009$ Å, $\beta = 117° \; 39' \pm 3'$, $U = 703{\cdot}0$ Å^3, $Z = 2$, $D_c = 0{\cdot}955$, $F(000) = 224$. μ(Mo-K_α) = 1·73 cm^{-1}. Space group $P2_1/a$.

Crystallographic Measurements.—All three compounds react very rapidly with oxygen and so were made by vacuum line methods.[5,6] Crystals of (1) grown by sublimation consisted of bundles of fine needles. Recrystallisation from a slowly cooled solution in hexane, however, yielded better-formed needles which were mounted in thin-walled Pyrex capillaries in a nitrogen-filled dry-box. The capillaries were subsequently evacuated and sealed. When crystals of (2) were similarly mounted in the dry-box, fine whiskers, which appeared to be of the *cis*-isomer, grew from the surface. Crystals of (2), suitable for X-ray examination, were obtained, however, by sublimation of the compound, immediately after separation from the *cis*-isomer,[5] into Pyrex capillaries attached to the vacuum line. The crystal from which data were collected was sealed under vacuum and was unchanged during one year. Crystals of (3) were obtained from a solution in hexane and were mounted in Pyrex capillaries, without difficulty, in the dry-box.

For each compound, preliminary rotation, Weissenberg and precession photographs were used to find unit-cell dimensions and to obtain information about space groups. The cell dimensions were later adjusted by least-squares treatment of the θ, χ, ϕ setting angles of twelve reflections determined on a Hilger and Watts' Y 290 automatic diffractometer by use of Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). This radiation was also used for the intensity measurements, which were made by the ω—2θ scan procedure. The intensities of two standard reflections were checked periodically, and in no case was any significant change in the standard intensities observed. The scan count and the background counts were combined to give the integrated intensity I, and reflections were regarded as 'unobserved' and omitted from the structure determination if $I/\sigma(I) < 2{\cdot}8$ [compound (1)], $<2{\cdot}5$ [compound (2)] and $<2{\cdot}8$ [compound (3)]. The intensities were corrected for Lorentz-polarization effects but not for absorption, as this was small; 996 independent non-zero reflections were measured for compound (1), 621 for compound (2) and 525 for compound (3).

Structure Analysis.—(i) *Compound* (1). Initial positions for aluminium atoms were found from a three-dimensional Patterson synthesis, but location of the remaining atoms from the resulting electron density distribution (R 38%) in space group $R\bar{3}$ was difficult. We therefore tried refinement in space group $R3$. Since this does not have a specified origin, one positional parameter of one atom had to be held constant, and y/b for N(2) was chosen. Initial positions for aluminium atoms were obtained in space groups $R\bar{3}$, with the origin at the centre of symmetry. Refinement in space group $R3$ was satisfactory, and the aluminium atoms in adjacent molecules were found to be approximately related by a centre of symmetry. With structure factors based on the positions of aluminium, nitrogen and carbon atoms, R was reduced to 13·1% and with isotropic temperature factors for these atoms and two further cycles of least-squares refinement R was 8·4%. In an attempt to locate the hydrogen atoms from a difference-Fourier synthesis, peaks were found at 0·8—1·2 Å from carbon atoms, but the H–C–H angles derived from these were not completely reasonable. The best position of one hydrogen atom from each methyl group was then found from the difference-Fourier synthesis and the positions of the others calculated. Contributions from hydrogen atoms at these fixed positions with isotropic temperature factors ($B = 5{\cdot}0$) were included in the structure-factor calculations. Two cycles of least-squares refinement gave R 6·9% with all atoms isotropic; with anisotropic temperature factors assigned to aluminium atoms two further cycles of refinement gave R 6·5%, and with anisotropic temperature factors for all atoms except hydrogen, convergence was reached at R 5·5%.* The weighting scheme used was $\sqrt{w} = 1/\sigma(F)$.

(ii) *Compound* (2). A Patterson synthesis yielded initial positions for the aluminium atoms consistent with the space group $C2/c$. This space group requires, however, that the molecule possesses a two-fold axis of symmetry, which is possible only if the carbon and hydrogen atoms attached to one nitrogen atom are disordered. The first structure-factor calculations[3] were made, therefore, in space group Cc. The positions of carbon and nitrogen atoms were found from the first electron-density distribution (R 39%) and the molecule was seen to be in the skew-boat conformation. With structure factors based on all the atoms except hydrogen R was 20·5%. During least-squares refinement of this structure, it was necessary to apply a damping factor to the parameter shifts to prevent oscillation. With contributions from all atoms except hydrogen and with isotropic temperature factors, the structure refined to R 11·7%. With anisotropic temperature factors for aluminium, but not carbon or nitrogen, R was reduced to 10·7%. Calculated bond lengths and angles were reasonable, compared with those of (1), but showed unusually large standard deviations and there were discrepancies between lengths of chemically equivalent bonds. A correlation matrix showed high correlations between parameters related by a two-fold axis passing through one aluminium and one nitrogen atom of the (AlN)$_3$ ring and so the possibility that the space group is $C2/c$ was reconsidered, and the atom C(5) was disordered over two positions. Refinement in the space group $C2/c$ proceeded satisfactorily and, although R after convergence was 12·1% (higher than in Cc), reasonable standard deviations in bond lengths and angles were obtained and there was agreement between lengths of chemically equivalent

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* Observed and calculated structure factors for all three compounds are listed in Supplementary Publication No. SUP 20458 (13 pp., 1 microfiche).

bonds. A Hamilton test[19] favoured the space group *Cc*, but was not, in this case, very discriminating. In one calculation (in space group *Cc*) anisotropic temperature factors were assigned to carbon and nitrogen atoms: this reduced R to 6·7%,[3] but in view of the paucity of the X-ray data we felt that the calculation was not justified. Anisotropic temperature factors were assigned only to aluminium atoms in the calculation of the final positions and contributions from hydrogen atoms were ignored.

(iii) *Compound* (3). The positions of the aluminium atoms were deduced from a three-dimensional Patterson synthesis and the carbon and nitrogen atoms from the subsequent Fourier synthesis (R 37·9%). After isotropic least-squares refinement based on all atoms except hydrogen, R was 12·5%. The assignment of anisotropic temperature factors to aluminium (R 12·4%) and to aluminium and nitrogen atoms (R 12·2%) made little difference to the agreement between observed and calculated structure factors. The most prominent hydrogen atom of each methyl group in a difference-Fourier synthesis was fixed and the positions of the remaining hydrogen atoms were calculated. Further refinement, using contributions from hydrogens at these fixed positions with isotropic temperature factors ($B = 7·0$) reduced R to 10·0%. With anisotropic temperature factors assigned to the carbon, aluminium, and nitrogen atoms, further refinement converged at R 6·9%. The weighting scheme was $\sqrt{w} = 1·0/\sigma(F)$. The atomic positions, except those of hydrogen atoms, agree closely with those found in an independent determination.[4]

We thank the S.R.C. for financial support, Miss C. Battrick and Mrs. A. Pike for technical assistance, and Dr. K. W. Muir for helpful discussions.

[2/398 *Received*, 22*nd February*, 1972]

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