Isomerism of Dimethyl(methylamido)aluminium: an *X*-Ray Crystallographic Study

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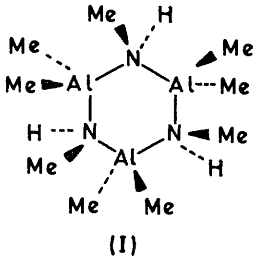
Summary Stereoisomers of $(Me_2AlNHMe)_3$ have been prepared, and have been characterized by single-crystal *X*-ray studies.

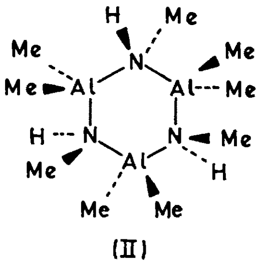
THE reaction between trimethylaluminium and methylamine at 25° (without solvent) yields products which we have separated by careful fractional sublimation into two air-sensitive solids. Both have the composition $Me_2AlNHMe$.

The less volatile solid crystallizes from hexane as needles, m.p. 110°, and the molecular weight in freezing benzene corresponds to $(Me_2AlNHMe)_3$. The crystals are rhombohedral, and have $a = 9{\cdot}983 \pm 0{\cdot}004$ Å, $\alpha = 104° \; 39' \pm 3'$, $Z = 6(Me_2AlNHMe)$, space group *R*3. *X*-Ray intensity data were obtained on a Hilger and Watts' Y290 diffractometer with Mo-K_α radiation, and the atomic parameters determined by Fourier and least-squares calculations, the analysis terminating at $R = 5{\cdot}3\%$ for 996 independent reflections. The two crystallographically unrelated trimeric molecules (I) have crystallographic symmetry C_3. The six-membered $(AlN)_3$ ring is in the chair conformation and the methyl substituents on the nitrogen atoms are equatorial. The mean molecular dimensions are: Al–N,1·953 ± 0·005 Å– Al–C, 1·980 ± 0·005 Å; N–C 1·504 ± 0·010 Å; N–Al–N, 102·1 ± 0·4; C–Al–C, 116·9 ± 0·4°; C–Al–N, 109·4 ± 0·3°; Al–N–Al, 122·3 ± 0·4°; Al–N–C, 108·6 ± 0·4°.

The more volatile solid is metastable at 20° and readily transforms to the rhombohedral form. A small crystal suitable for *X*-ray examination was eventually obtained by sublimation of the material, directly after separation of the reaction mixture, into thin-walled Pyrex capillaries. The crystal has a monoclinic unit cell with $a = 11{\cdot}897 \pm 0{\cdot}008$, $b = 15{\cdot}904 \pm 0{\cdot}012$, $c = 9{\cdot}778 \pm 0{\cdot}007$ Å, $\beta = 107° \; 50' \pm 4'$, $Z = 12(Me_2AlNHMe)$, space group *Cc*. Because of the small size of the crystal, only 621 independent intensities above background level could be measured on the diffractometer. The Patterson synthesis showed that the space group is *Cc*, rather than the alternative *C*2/*c*, and that the molecule is trimeric. The atomic parameters were adjusted by least-squares calculations which terminated at $R = 6{\cdot}7\%$. The analysis establishes that the monoclinic isomer has structure (II), and that the bond lengths and valency angles are in good agreement with those in the rhombohedral isomer (I).



(I)



(II)

TABLE

Torsion angles (deg.) about the Al–N *bonds in* $(Me_2AlNHMe)_3$

Chair conformation (I): 53, −53, 53, −53, 53, −53.
Skew-boat conformation (II): 35, −61, 20, 31, −62, 33.

The compounds (I) and (II) differ in the configuration at one of the nitrogen atoms, and are thus stereoisomers. *cis*- and *trans*-Isomers of the compounds $(H_2B{\cdot}NHR)_3$ have been characterized[1] by spectroscopic measurements.

Compound (I) has a chair conformation and compound

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(II) a skew-boat conformation. The torsion angles of the chair and skew-boat forms of the $(AlN)_3$ ring are listed in the Table. The chair form of (I) has three axial *Al*-methyl groups, three equatorial *Al*-methyl groups, and three equatorial *N*-methyl groups. The distance between the carbon atoms of axial *Al*-methyl groups is 3·81 Å, and axial–axial interactions are thus much less serious than in cyclohexanes. The chair form of (II) would have three axial *Al*-methyl groups, three equatorial *Al*-methyl groups, two equatorial *N*-methyl groups, and one axial *N*-methyl group; the extra interactions associated with the axial *N*-methyl group apparently raise the free energy of the chair conformation above that of the alternative skew-boat conformation. Since the N–N distance in the $(AlN)_3$ ring (3·02 Å) is less than the Al–Al distance (3·40 Å), an *N*-axial substituent is more directly comparable, than is an *Al*-axial substituent, with an axial substituent in cyclohexane. The compound $[Me_2AlN(CH_2)_2]_3$ also exhibits a skew-boat conformation in the solid state.[2]

The n.m.r. spectrum of $(Me_2AlNHMe)_3$ in $C_6D_5 \cdot CD_3$ is notably temperature-dependent, and probably more than one species are present in solution.

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