The Crystal Structure of Dimethylphenylaluminium

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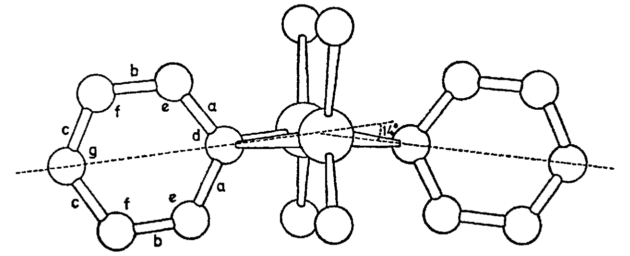
Summary A crystal structure analysis of dimethylphenylaluminium shows that the phenyl groups, which are in the bridging positions, are distorted from a regular hexagonal shape in a way similar to those in triphenylaluminium, and that whilst one third of the molecules are centrosymmetric with a planar central ring, the remainder are folded about the Al–Al line by an angle of 14°.

TRIPHENYLALUMINIUM has been shown[1] to have a dimeric structure in which the bridging phenyl groups are considerably distorted from a regular hexagonal shape. Examination of the n.m.r. spectra of mixtures of trimethylaluminium and triphenylaluminium has indicated[2] that in dimeric dimethylphenylaluminium the phenyl groups occupy the bridging positions. In order to confirm these structural features we have carried out a single crystal *X*-ray structure analysis of dimethylphenylaluminium.

Crystals of dimethylphenylaluminium are triclinic, with three dimeric molecules in the reduced cell of dimensions $a = 12{\cdot}31$, $b = 12{\cdot}76$, $c = 9{\cdot}35$ Å, $\alpha = 102{\cdot}8°$, $\beta = 91{\cdot}6°$, $\gamma = 61{\cdot}3°$, space group $P\bar{1}$. The structure was determined from 3126 visually determined structure amplitudes, and refined by isotropic least squares to $R = 16{\cdot}0\%$. Anisotropic refinement is continuing.

One molecule in each cell occupies a centre of symmetry, and the other two are mutually related by a centre of symmetry. In both types of molecule the phenyl groups are in bridging positions, with their planes almost perpendicular to the Al–Al direction.

Averaged dimensions and their e.s.d.'s are given in the Table. No individual value differs significantly from the corresponding mean value quoted. It is seen that in the phenyl groups the C–C bonds of the type marked (a) in the figure are longer than normal, whilst the ring angle adjacent to aluminium (d in the Figure) is considerably less than 120°. Similar distortions were found in triphenylaluminium.



FIGURE

Average bond lengths (Å) *and angles, with e.s.d.'s*

Al–Al	mean of 2	2·683 (3)
Al–C (phenyl) ..	„ „ 6	2·134 (5)
Al–C (methyl)	„ „ 6	1·979 (6)
Al–C–Al ..	„ „ 3	77·8° (0·3°)
C–C (a in Figure)	„ „ 6	1·424 (6)
C–C (b) ..	„ „ 6	1·410 (8)
C–C (c) ..	„ „ 6	1·377 (8)
C–C–C (d) ..	„ „ 3	115·9° (0·6°)
C–C–C (e) ..	„ „ 6	121·6° (0·4°)
C–C–C (f) ..	„ „ 6	120·0° (0·5°)
C–C–C (g) ..	„ „ 3	120·8° (0·8°)

Although the two types of molecule do not differ significantly in the dimensions given in the Table, they do differ markedly in a surprising way. The centrosymmetric molecule necessarily has a planar central ring, but the other molecule, which has no crystallographic symmetry, is far from planar. This molecule is shown in the Figure. It is clear from the orientation of the phenyl groups that the molecule is to be regarded as folded about the Al–Al line, and the dihedral angle is 14·0°. The Al–Al distance is unchanged, 2·685 (4) Å in the planar molecule, 2·680 (4) in the folded molecule. Accompanying the folding of the molecule is a rotation of all four methyl groups away from the phenyl groups, each by an angle of 8°, with close retention of C_{2v} symmetry. Since corresponding atoms in the two kinds of molecule have very similar (and normal) vibration parameters, the differences between them are real and not a result of crystal disorder. It seems likely either that the folding of the molecule involves a broad, flat potential well so that crystal packing forces are able to produce the difference in conformation, or that, as a result of non-bonded interactions between the methyl and phenyl groups, two different stable molecular conformations exist.

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[1] J. F. Malone and W. S. McDonald, *Chem. Comm.*, 1967, 444.

[2] E. A. Jeffery, T. Mole and J. K. Saunders, *Chem. Comm.*, 1967, 696.