The Crystal Structure of Triphenylaluminium

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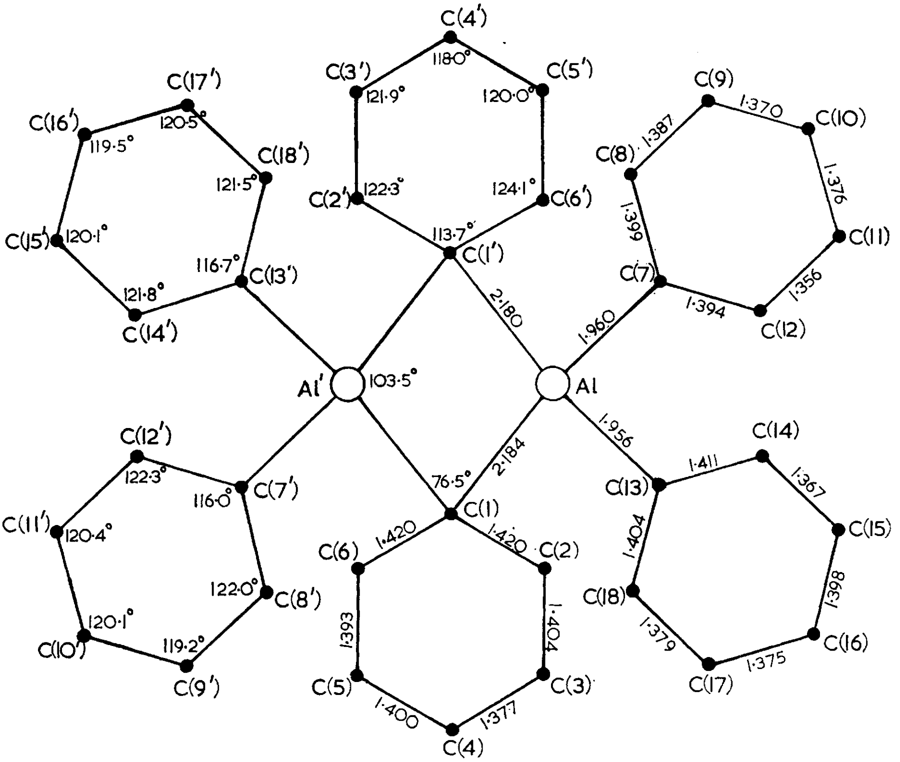
THE crystal structure of trimethylaluminium was determined by Lewis and Rundle,[1] and was further refined by Vranka and Amma.[2] The electron-deficient dimeric structure is considered to have three-centre Al–C–Al bonds. Trimethylaluminium is also dimeric in solution, and is associated in the vapour. Triarylaluminiums have been shown[3,4] to be associated in solution, the degree of association varying with concentration. In order to establish the mode of association in the solid state, and to examine the rôle of an unsaturated group in a three-centre bond, we have completed an X-ray crystal-structure analysis of triphenylaluminium.

Triphenylaluminium crystallises in the triclinic system with eight molecules of $AlPh_3$ in a cell of dimensions: $a = 20{\cdot}89_0$, $b = 17{\cdot}80_6$, $c = 8{\cdot}32_8$ Å, $\alpha = 94{\cdot}0°$, $\beta = 96{\cdot}3°$, $\gamma = 110{\cdot}1°$, space group $F\bar{1}$. The choice of a face-centred cell, rather than the conventional $P\bar{1}$ with $Z = 2$, gives a less oblique cell and facilitated indexing of the Weissenberg photographs. The structure was determined from 1636 independent non-zero reflections, obtained by visual estimation of equi-inclination Weissenberg photographs. The positions of the 19 non-hydrogen atoms of the asymmetric unit were obtained from a sharpened 3-dimensional Patterson synthesis. After least-squares refinement of co-ordinates and anisotropic temperature factors, the 15 hydrogen atoms were located from a difference synthesis. The R factor is 9·2%.

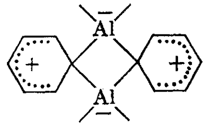
The crystal contains centro-symmetric dimeric molecules, with symmetrically bridging phenyl groups. The principal molecular dimensions are shown in the Figure. Standard deviations, estimated by inversion of the block-diagonal least-squares matrix, are 0·005 Å for the Al–C distances, 0·008 Å for the C–C distances, and 0·5° for the angles.

The central aluminium–carbon ring has dimensions similar to those found[2] for the trimethyl compound (Al–C = 2·16 Å, Al–C–Al = 74·4°). The dihedral angle between planes C(1)–Al–C(1′)–Al′ and C(1) to C(6) is 84·4°. This departure from 90° is consistent with a reduction in intramolecular non-bonded repulsions between hydrogen atoms.

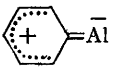
The bridging phenyl group is considerably distorted from a regular hexagon. The angle C(2)–C(1)–C(6) is 113·7°, and the C(1)–C(2) and C(1)–C(6) bonds are each 0·02 Å longer than the mean for the ring. Although these bonds are not



individually of significantly greater length than the mean for the ring, the fact that both show an increased length results in a highly significant reduction in the inter-bond angle. Smaller distortions of the same kind occur in the terminal phenyl groups.



(I)



(II)

These distortions suggest that π-electrons from each of the benzene rings are partially localised in the Al–C bonds, with a resultant lengthening of the adjacent C–C bonds. Thus small contributions from structures (I) and (II) provide some reduction in the electron-deficiency of the aluminium atom.

(*Received, March 20th*, 1967; *Com.* 270.)

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