Molecular Structure of the Polymerization Catalyst, Dimeric Dimethylaluminiumoxybenzylideneaniline [$(AlMe_2{\cdot}O{\cdot}CPh{:}NPh)_2$]

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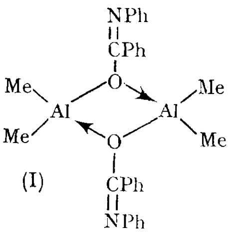
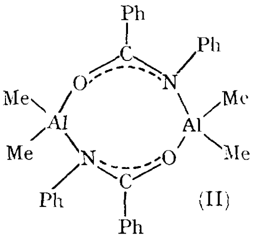
CERTAIN catalytic systems for stereospecific polymerization have recently been investigated by Tani and his co-workers.[1] They found that the reaction products of trialkylaluminiums and acid amides gave excellent results for polymerization of acetaldehyde and methyl methacrylate. Among them, $AlMe_2{\cdot}O{\cdot}CPh{:}NPh)_2$, prepared from $AlMe_3$ and PhCO·NHPh, is one of the most effective catalysts. From the studies of n.m.r. and i.r. spectra, the catalyst was found to have the structure $Me_2Al{-}O{-}CPh{=}NPh$, and cryoscopic measurement of its molecular weight in benzene showed it to be dimeric. Two plausible models were proposed for the structure of the catalyst.


(I)


(II)

To determine the exact structure, an X-ray structure analysis was undertaken. As the crystal is very unstable in air, it was sealed in a thin-walled glass capillary tube in argon.

Crystal data of $(AlMe_2{\cdot}O{\cdot}CPh{:}NPh)_2$: $a = 6{\cdot}64$ (needle axis), $b = 12{\cdot}05$, $c = 18{\cdot}28$ Å, $\beta = 94{\cdot}9°$, space group $P2_1/c$, $D_c = 1{\cdot}15$, $D_m = 1{\cdot}15$ g.cm.$^{-3}$, $Z = 2$ (as a dimer).

By use of Ni-filtered Cu-K_α radiation, intensity data were collected by multi-film equi-inclination Weissenberg photographs around the a axis. Crystals examined always had a twinned structure; the b^*–c^* plane was the twin plane. All the reflexion spots on the film were examined carefully and those from one component of the twinned crystal were identified and separated. Finally, 1437 independent reflexions were obtained from $0kl$ to $5kl$.

The initial co-ordinates of the aluminium atom were determined from the three-dimensional Patterson function. The other non-hydrogen atoms were then found from the minimum function and from the Fourier synthesis, both based on the location of the aluminium atom. The refinement was carried out by a block-diagonal least-squares method. For non-zero reflexions, $R = 0{\cdot}146$.

The molecular structure is shown in the Figure. The most remarkable feature is that the molecule is composed of a centro-symmetrical eight-membered ring, which corresponds to the model (II). The environment of the aluminium atom is a distorted tetrahedron; the bond angle C(1)–Al–C(2) (118°) is a little larger than that of O–Al–N (103°). The interatomic distances Al–C(1) and Al–C(2) are 1·97 and 2·01 Å respectively and these

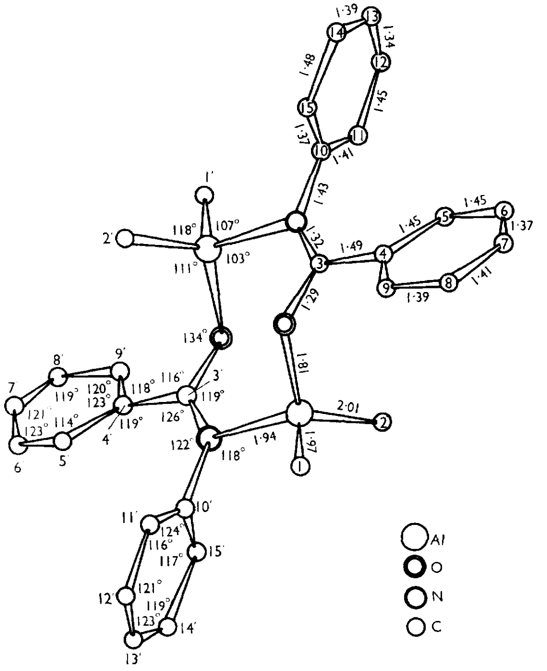


FIGURE. *Structure of* (AlMe$_2$·O·CPh : NPh)$_2$; *the estimated standard deviations in bond lengths and angles are less than* 0·02 *Å and* 1·5°, *respectively.*

are similar values to those of Al–C in (AlMe$_3$)$_2$,[2] and also in (AlMe$_3$)$_2$(dioxan).[3] The Al–N distance of 1·94 Å is nearly equal to the sum of the covalent radii of Al and N, 1·96 Å.

The Al–O distance of 1·81 Å is a normal value. The C(3)–O distance of 1·29 Å is a little larger than normal C–O distances in aldehydes and ketones, 1·23 Å. The environments of the N and C(3) atoms are nearly trigonal, and the interatomic distances and angles are mostly similar to those of acetanilide.[4] The configuration of the two adjacent benzene rings about the N–C(3) bond appears to be *cis*.

When this catalyst is treated with acetaldehyde at a temperature above the polymerization ceiling two molecules of acetaldehyde co-ordinate to one molecule of the dimeric catalyst; this is considered to be an intermediate complex in the polymerization of acetaldehyde. The crystal of this co-ordinated complex is more unstable than the catalyst itself.

Crystal data of (AlMe$_2$OCPhNPh)(MeCHO): a = 15·83, b = 12·61, c = 17·66 Å, space group *Pcca*, D_c = 1·12, D_m = 1·14 g.cm.$^{-3}$, Z = 8, M 297·3 (calcd. for one formula unit; cryoscopic measurement gave a value of 582, suggesting a dimer.)

(*Received, August* 6*th*, 1968; *Com.* 1059.)

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