^{27}Al Nuclear Quadrupole Resonance Spectrum of Hexamethyldialuminium

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Summary The ^{27}Al nuclear quadrupole resonance (n.q.r.) spectrum of Al_2Me_6 indicates a very high asymmetry parameter, supporting the Longuet-Higgins structure.

RECENTLY, Nyburg *et al.*[1] have claimed that the dimer of trimethylaluminium has a structure in which the two $AlMe_3$ units are linked by hydrogen bonds, rather than by three-centre Al–C–Al bonds as originally suggested by Longuet-Higgins.[2] We report further evidence concerning the structure of the dimer, based on its ^{27}Al n.q.r. spectrum. To our knowledge, this is the first measurement of this kind that has been reported for an aluminium-alkyl.†

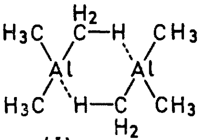
A sample of the dimer (*ca.* 6 g) was examined at dry ice–acetone temperature (−77°) with a super-regenerative spectrometer similar to that described by Peterson and Bridenbaugh.[4] Since ^{27}Al has a nuclear spin of 5/2, two fundamental (and one combination) resonances were observed, *i.e.*:

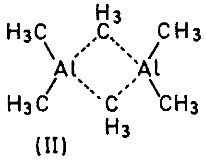
$$\begin{aligned} \nu(1/2\text{–}3/2) &\quad 5{\cdot}372\ \text{MHz} \\ \nu(3/2\text{–}5/2) &\quad 6{\cdot}454\ \text{MHz} \\ \nu(1/2\text{–}5/2) &\quad 11{\cdot}826\ \text{MHz} \end{aligned} \tag{1}$$

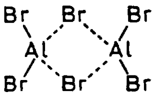
From these one can calculate[5] the following value for the coupling constant (e^2qQ/h) and asymmetry parameter (η):

$$\begin{aligned} e^2qQ/h &= 23{\cdot}546\ \text{MHz} \\ \eta &= 0{\cdot}784 \end{aligned} \tag{2}$$

The high value of η accounts for the strength of the (1/2–5/2) transition which would be forbidden if $\eta = 0$.[6] Relatively few cases have been reported where such high-order transitions are detectable.


(I)


(II)


(III)

Such a high asymmetry parameter seems to rule out the hydrogen bonded structure[1] (I), since in it the Al–C bonds would all be similar and the asymmetry parameter consequently small. The Longuet-Higgins structure (II) would on the other hand be closely analogous to the dimer of aluminium bromide (III) for which a very similar asymmetry parameter has been reported.[7]

Further support for this intuitive argument comes from an analysis[7,8] of the n.q.r. parameters for bridged dimers of tervalent compounds MX_3 of Group III elements (M). This leads to the following predictions:

$$\eta = -3\cos\alpha \tag{3}$$

$$(e^2qQ/e^2qQ_0) \times (1 + \eta/3) = |b - a| \tag{4}$$

Here α is the interorbital angle of the two orbitals of M used in bridging, b is the electron population of each of the orbitals of M used in the terminal (unbridged) bonds, a that of each of the orbitals of M used in the bridged bonds, e^2qQ_0 is a constant which for aluminium has the value 37·52 MHz,[9] and e^2qQ is derived from the measured coupling constant [Equation (2)].‡

Equations (2) and (3) lead to a value of α (105·8°) in excellent agreement with experiment[10] (105·3 ± 0·4°), suggesting that this treatment is valid for trimethylaluminium dimer. In that case, from equations (2) and (4), $|b - a| = 0{\cdot}791$.

The aluminium orbitals used for the bridge bonds must therefore be very electron-deficient. This would be expected for (II), because a simple MO treatment implies that the bridge bonds should be effectively covalent bonds between methyl and the Al_2 unit. The two electrons in each three-centre bond should therefore be distributed over carbon, aluminium, and aluminium roughly in the ratio 1 : 1/2 : 1/2.

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† The ^{27}Al n.m.r. spectrum of triethylaluminium dimer has been measured in solution, leading to an estimate of *ca.* 10 MHz for the quadrupole coupling constant (ref. 3).

‡ We omit the small correction factor (ref. 7) for nonelectroneutrality of aluminium.

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