# A Study of Bonding in Some Organoaluminium Compounds by $^{27}Al$ Nuclear Quadrupole Resonance Spectroscopy

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$^{27}Al$ N.q.r. spectra have been measured for a wide range of monomeric and dimeric aluminium complexes of the type $Me_3AlX$ and $(R^1R^2AlX)_2$. Measurements are also reported for $Bu^t_3Al$, $(Me_2AlOMe)_3$, and $(Me_2AlSMe)_n$ and for $^{69}Ga$ in trimethylgallium. The results are interpreted in terms of the simple treatment of Townes and Dailey which is shown to account well for all the observed trends. $^{35}Cl$, $^{75}As$, $^{121}Sb$, and $^{123}Sb$ n.q.r. spectra for the appropriate complexes are also reported. The potential of n.q.r. spectroscopy as a tool in structure determination is stressed.

NUCLEAR quadrupole resonance (n.q.r.) spectroscopy[1] provides a uniquely useful procedure for studying chemical bonding since the frequencies observed for covalent compounds of non-transition elements depend entirely on the distribution of *p*-electrons in the valence shell of the atom in question. Measurements of this kind are of especial value in the study of chemical bonding in molecules and much useful information has been obtained in this way.[1]

Aluminium is an almost ideal subject for three reasons. First, naturally occurring aluminium consists of a single isotope, $^{27}Al$. Secondly, this isotope has a high nuclear spin ($\frac{5}{2}$) allowing two independent transitions ($\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2}$ and $\pm\frac{3}{2} \longleftrightarrow \pm\frac{5}{2}$) to be observed;† from these one can calculate[3] not only the nuclear quadrupole coupling constant[1] ($e^2Qq/h$) but also the asymmetry parameter[1] ($\eta$). Thirdly, aluminium is a very versatile element, occurring in a variety of different bonding situations. It forms salts and it also occurs in a variety of covalent compounds including some (*e.g.*, $Al_2Me_6$) that are 'electron deficient' and contain three-centre bonds.[4]

Preliminary studies[5,6] of a variety of organoaluminium compounds had established the potentialities of such an approach. We were able to show[5] that the original formulation of hexamethyldialuminium by Longuet-Higgins[4] is correct‡ in contrast to an alternative recently suggested by Nyburg *et al.*[7] and the structures of several mixed alkylaluminium halides were established[6] in this way. Here we report a detailed study of a number of organoaluminium compounds of various kinds.

## EXPERIMENTAL

All the compounds studied were highly sensitive both to air and moisture. They were handled under nitrogen in a dry box (protected with sodium–potassium alloy), glove bags, Schlenk-type glassware, and standard vacuum techniques. Liquids and low-melting solids were finally purified by degassing in a vacuum followed by vacuum transfer to ampoules which were sealed and used without opening in the n.q.r. studies. The remaining solids were sublimed or recrystallized as recommended in the literature (Table 1) and then sealed in ampoules.

TABLE 1

Preparation of materials

| Compound | Literature ref. |
|---|---|
| (1b) | C. A. Smith and M. G. H. Wallbridge, *J. Chem. Soc. (A)*, 1970, 2675. |
| (1c—e), (1g), (8) | N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316. |
| (1f) | C. H. Hendrickson and D. P. Eyman, *Inorg. Chem.*, 1967, **6**, 1461. |
| (1h) | S. Takeda and R. Tarao, *J. Chem. Soc. Japan*, 1965, **38**, 1567. |
| (1i) | J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1967, **89**, 5362. |
| (2) | H. Lehmkuhl, *Ann. Chem.*, 1968, **719**, 40. |
| (4a), (5a) | A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, 1940, **5**, 106. |
| (7) | E. G. Hoffmann, *Ann. Chem.*, 1960, **629**, 104. |
| (10a) | T. Mole and J. R. Surtees, *Austral. J. Chem.*, 1964, **17**, 310. |
| (10b) | W. C. Kaska, Ph.D. Thesis, University of Michigan, 1963. |
| (11) | T. Mole and J. R. Surtees, *Chem. and Ind.*, 1963, 1727. |
| (12) | T. Mole, *Austral. J. Chem.*, 1966, **19**, 373. |
| (13) | D. G. Brauer and G. D. Stucky, *J. Amer. Chem. Soc.*, 1969, **91**, 5462. |

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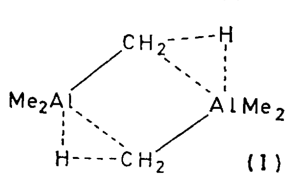
† In certain circumstances[2] the transition $\pm\frac{1}{2} \longleftrightarrow \pm\frac{5}{2}$ can also be observed. However the corresponding frequency is necessarily the sum of those for the other two transitions.

‡ In view of an apparent misunderstanding[8] of our previous communication[6] we point out that the diagram reproduced there was intended to imply only the type of bonding suggested by Nyburg *et al.*,[7] not the precise molecular geometry. Perhaps a better representation would have been (I). This bears the same relation to the Longuet-Higgins[4] structure that edge-protonated cyclopropane does to corner-protonated cyclopropane. Recent work[9] has further confirmed the correctness of the Longuet-Higgins structure.



[1] See E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants,' Academic Press, New York, 1969.

[2] M. H. Cohen, *Phys. Rev.*, 1954, **96**, 1278.

[3] R. Livingston and H. Zeldes, 'Table of Eigenvalues for Pure Quadrupole Spectra, Spin $\frac{5}{2}$,' Oak Ridge National Laboratory, No. 1913, 1955.

[4] H. C. Longuet-Higgins, *J. Chem. Soc.*, 1946, 139.

[5] M. J. S. Dewar and D. B. Patterson, *Chem. Comm.*, 1970, 544.

[6] M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, *J. Amer. Chem. Soc.*, 1971, **93**, 1030.

[7] S. K. Byram, J. K. Fawcett, S. C. Nyburg, and R. J. O'Brien, *Chem. Comm.*, 1970, 16.

[8] F. A. Cotton, *Inorg. Chem.*, 1970, **12**, 2804.

[9] J. C. Huffman and W. E. Streib, *Chem. Comm.*, 1971, 911.

The simple complexes (1) of trimethylaluminium were made by adding a slight excess of the ligand to trimethylaluminium (Alfa Inorganics), mixing thoroughly, and removing excess of ligand by vacuum distillation. Complex (1a) does not seem to have been reported. The structure follows from analogy and from its n.q.r. spectrum which showed it to contain both aluminium and antimony.

The remaining compounds (4b—f), (5b), (5c), (6), (9b), and (9c) were donated by Texas Alkyls, Pasadena, Texas, in 25 mm o.d. septum-sealed ampoules and were used without purification except for (6) which was distilled on the vacuum line.

The n.q.r. frequencies were measured with a coherency-controlled super-regenerative spectrometer following the design of Peterson and Bridenbaugh[10] but modified to operate with maximum sensitivity over the range 3—50 MHz. Switches allow the selection of six cathode chokes and five cathode resistors and a choice of feedback capacitors so that the lowest possible value can be used in each frequency range. These modifications distorted the shape of the signal but greatly improved the sensitivity. For the lowest frequency range the time constant was increased to 100 s and the plate voltage raised. Frequencies were measured with a model 5245 L Hewlett-Packard Electronic Counter. Since a super-regenerative receiver was used, the signals were accompanied by side-bands. The central peak was determined in the usual way by varying the quench frequency. In the case of compound (10a), the $^{27}$Al signal was so weak that it is possible that the wrong peak may have been selected. The accuracy of the other $^{27}$Al frequencies was limited by the difficulty of determining the centre of the peak because of the long time constant that had to be used. Similar difficulties also arose in the case of $Me_3As$ and $Me_3Sb$. The signals were in all cases reproducible within the limits of error of the recorder.

A check on the reliability of our assignments was provided in several cases by observation of the $\pm\frac{1}{2} \longleftrightarrow \pm\frac{5}{2}$ transitions. The frequencies for these were in each case the sum of those already estimated for the $\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2}$ and $\pm\frac{3}{2} \longleftrightarrow \pm\frac{5}{2}$ transitions.

*Interpretation of N.q.r. Spectra.*—Theoretical interpretations of n.q.r. spectra can be carried out at various levels of sophistication[1] ranging from *ab initio* calculations to an interpretation based on simple-minded MO theory. If we are concerned with the possible practical value of n.q.r. spectroscopy as an aid to the understanding of structure and reactivity in organic molecules, the latter is clearly the more valuable since it ties in with the conventional representation of molecules in terms of a simple MO approach. We will therefore discuss our results in terms of the treatment suggested by Townes and Dailey[1,11] in which the net electric field gradient at the nucleus is attributed entirely to unequal distribution of the $p$-electrons in the valence shell, the populations of the corresponding $p$-AOs being estimated by simple arguments. In the present connection we need the results[1] for molecules of the type $MX_3Y$, where the central atom (M) forms identical bonds to three groups X and where the MY bond lies on a threefold axis of symmetry (*e.g.*, $CHCl_3$), and for molecules of the type $MX_2Y_2$ with tetrahedral geometries, the groups $MX_2$ and $MY_2$ lying in orthogonal planes (Figure).

In the first case the asymmetry parameter is zero while the coupling constant ($e^2Qq$) is given in terms of that ($e^2Qq_0$) for a single $p$-electron by equation (1) where $\alpha$ is the

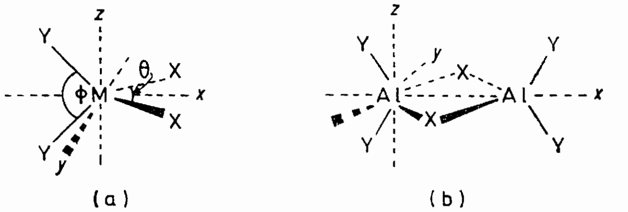
$$\frac{e^2Qq}{(e^2Qq_0)} = -\frac{3\cos\alpha}{1-\cos\alpha}(a-b) \qquad (1)$$

XMX bond angle, $a$ is the population of an AO of M used to form an MX bond, and $b$ the population of the AO of M used to form the MY bond.

In the second case, *i.e.*, tetrahedral molecules of the type $MX_2Y_2$ (Figure), the usual assumptions concerning hybridization and orthogonality lead to the relation (2) where $\theta$ and

$$\cot^2\frac{\theta}{2} + \cot^2\frac{\phi}{2} = 1 \qquad (2)$$

$\phi$ are the XMX and YMY angles respectively (Figure). It can be shown that one of the three principal axes of the field gradient tensor lies along the intersection of the $MX_2$ and $MY_2$ planes while the other two lie at right angles to it, in the $MX_2$ and $MY_2$ planes respectively. If $\theta < \phi$, the axis of maximum field gradient ($z$) lies in the $MY_2$ plane and that ($y$) of minimum field gradient in the $MX_2$ plane. The third axis, defined by the intersection of the planes, is the axis ($x$) of intermediate field gradient [Figure, (a)].



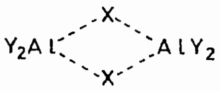
(a) Principal axes for $MX_2Y_2$; (b) relation to a bimolecular aluminium complex

The coupling constant and asymmetry parameter ($\eta$) are given by equations (3) and (4) where $c$ and $d$ are the populations of the MX and MY AOs of M respectively. Note that $\eta = 1$ when the central atom (M) is tetrahedral.

$$\left|\frac{e^2Qq}{(e^2Qq_0)}\right|\left(1+\frac{\eta}{3}\right) = |c-d| \qquad (3)$$

$$\eta = -3\cos\theta \qquad (4)$$

In the case of bimolecular aluminium complexes of the type (II) the principal axes are as indicated in the Figure, (b).



(II)

Note that equations (1), (3), and (4) are derived on the assumption that hybrid orbitals ' follow ' the corresponding bonds. In the case of bent (' banana ') bonds, the angles in equations (1), (3), and (4) refer to angles between the corresponding AOs of M.

In order to apply these relations, it is necessary to know ($e^2Qq_0$). The ground state of the aluminium atom has the configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)$ with a single $3p$-electron. It therefore seems natural to equate the ob-

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[10] G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instr.*, 1964, **35**, 698; 1965, **36**, 702.

[11] See T. P. Das and E. L. Hahn, ' Nuclear Quadrupole Resonance Spectroscopy,' 'Solid State Physics,' eds. F. Seitz and D. Turnbull, suppl. no. 1, Academic Press, New York, 1958.

served [12] quadrupole coupling constant for free aluminium atoms to $(e^2Qq_0)$, as in equation (5). This value rests of

$$(e^2Qq_0)(^{27}\text{Al}) = 37{\cdot}52\ \text{MHz} \qquad (5)$$

course on the assumption that the value for a free atom can also be used for molecules (see below).

## RESULTS AND DISCUSSION

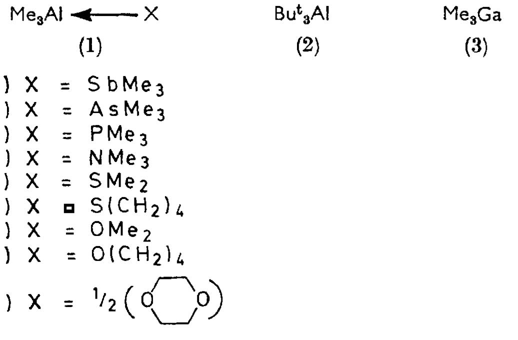
*Coupling Constants for Monomeric Complexes.*—The first series of compounds to be considered contain a single aluminium atom, being complexes (1) of trimethylaluminium with various donors. The results are in Table 2. Values are also included for tri-t-butylaluminium (2) and trimethylgallium (3), both of which are monomeric.[13] Apart from minor differences between Al–$CH_3$ and Al–$CMe_3$ bonds, (2) can be regarded as the limit of (1) in which the donor (X) vanishes.

TABLE 2

N.q.r. parameters ($^{27}$Al) for trimethylaluminium complexes and tri-t-butylaluminium and ($^{69}$Ga) for trimethylgallium

| Compound | Observed frequency/MHz[a] $(\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2})$ | Observed frequency/MHz[a] $(\pm\frac{3}{2} \longleftrightarrow \pm\frac{5}{2})$ | Estimated possible error (±MHz) | $e^2Qq$ (MHz) | $\eta$ | $\Delta H_c$[b] kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|
| (1a) | 4·84 | 9·63 | 0·025 | 32·13 | 0·062 | |
| (1b) | 4·29 | 8·525 | 0·01 | 28·45 | 0·071 | |
| (1c) | 3·57 | 7·08 | 0·01 | 23·60 | 0·074 | 21·02 ± 0·28[c] |
| (1d) | — | 3·46 | 0·05 | 11·52 | (0)[d] | 29·96 ± 0·19[c] |
| (1e) | 4·48 | 8·91 | 0·025 | 29·75 | 0·061 | 16·69 ± 0·18[e] |
| (1f) | 4·56 | 9·03 | 0·01 | 30·12 | 0·093 | 16·95 ± 0·18[e] |
| (1g) | 4·25 | 8·45 | 0·01 | 28·18 | 0·068 | 20·29 ± 0·20[e] |
| (1h) | 4·06 | 8·03 | 0·01 | 26·82 | 0·086 | 22·90 ± 0·19[e] |
| (1i) | 4·63 | 9·25 | 0·01 | 30·83 | 0·026 | — |
| (2) | 6·85 | 13·61 | 0·01 | 45·41 | 0·071 | — |
| (3) | 81·05 | — | 0·05 | 162·10 | (0)[f] | |

[a] At 77 K. Errors are estimated maximum errors. [b] Heat of formation of the complex $Me_3Al$–X from $Me_3Al$ + X in hexane. [c] Ref. 16*c*. [d] Assumed since second signal outside the range of spectrometer. [e] Ref. 16*d*. [f] Assumed since $I = \frac{3}{2}$; $^{71}$Ga signal observed at correct ratio.



$Me_3Al \longleftarrow X$ (1) $\quad Bu^t_3Al$ (2) $\quad Me_3Ga$ (3)

(a) X = $SbMe_3$
(b) X = $AsMe_3$
(c) X = $PMe_3$
(d) X = $NMe_3$
(e) X = $SMe_2$
(f) X = $S(CH_2)_4$
(g) X = $OMe_2$
(h) X = $O(CH_2)_4$
(i) X = ½(O O)

All these compounds conform to the conditions assumed in deriving equation (1) since any differences between the three Al–$CH_3$ bonds, due to asymmetry of the ligand, must be small. The measured asymmetry parameters do admittedly differ from zero; this, however, can be attributed [1] to crystal-field effects, particularly since the values of $\eta$ are much the same in all cases including some (*e.g.*, X = $AsMe_3$) where the ligand is symmetrical.

*The Value of* $e^2Qq_0$.—The limiting member (2) of the series is certainly planar. If hyperconjugation is neglected, $\alpha = 120°$ and $b = 0$ in equation (1). Substituting the observed values for $e^2Qq$ [45·51 MHz; Table 2] and $(e^2Qq_0)$ [37·52 MHz; equation (5)] we find equation (6). This result is not reasonable. It implies that the Al–C bonds are polarized in the sense $Al^{\delta-}$–$C^{\delta+}$.

$$a = 1{\cdot}21 \qquad (6)$$

A similar anomaly is seen in trimethylgallium (3) where the observed coupling constant (162·10 MHz) is again much greater than the value for the free atom (125·04 MHz [14]). The situation is indeed even worse because hyperconjugation must be important [15a,b] in (2), leading to a transfer of electrons into the 'empty' 3*p*-AO of aluminium and so making $b > 0$. Thus either the MO treatment used here is incorrect or the value for $(e^2Qq_0)$ is not the same for a free atom as for an atom in a molecule.

There are in fact good reasons for believing that the 'free atom' value for $(e^2Qq_0)$ must be too small. Detailed *ab initio* SCF calculations have shown that in an LCAO treatment of molecules one must use AOs that are smaller than those appropriate to free atoms.[15c] Since the field gradient at the nucleus varies as the inverse cube of the linear dimensions of an AO and so as the cube of the effective nuclear charge, the value of $(e^2Qq_0)$ to be used in equations (1) and (3) must be much larger than the 'free atom' value [*cf.* equation (5)].

If the orbital populations in compound (2) were known, $(e^2Qq_0)$ could then be found from the measured coupling constant by using equation (1). Unfortunately there seem to be neither reliable theoretical estimates of the orbital populations nor values for the dipole moment of the C–Al bond or the electronegativity of aluminium.

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[12] H. Law and G. Wessel, *Phys. Rev.*, 1953, **90**, 1.

[13] For evidence that compound (2) is monomeric, see H. Lehmkuhl, *Ann. Chem.*, 1968, **719**, 40.

[14] R. T. Daly, jun., and J. H. Holloway, *Phys. Rev.*, 1954, **96**, 539.

[15] (*a*) K. A. Levison and P. G. Perkins, *Discuss. Faraday Soc.*, 1969, 183; (*b*) K. A. Levison and P. G. Perkins, *Theoret. Chim. Acta*, 1970, **17**, 15; (*c*) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 2191.

However attempts to use equation (1) in a quantitative sense would probably in any case be a waste of time since the treatment on which it is based is so approximate and since the sizes of AOs are further affected by the formal charge at the atom in question [so that ($e^2Qq_0$) varies correspondingly]. One can, therefore, use equation (1) only in a qualitative way to interpret trends in observed coupling constants.

*Effect of the Ligand.*—On passing from compound (2) to (1), the $^{27}$Al coupling constant should decrease for two reasons. First, the inter-bond angle $\alpha$ decreases with formation of a bond between aluminium and the donor; secondly, formation of this bond raises the population [$b$ in equation (1)] of the fourth aluminium AO. Both effects should be greater, the stronger the bond between Al and X in (1), *i.e.*, the better the group X is as a donor.

In the formation of (1a—d) the donor has only a single pair of unshared valence electrons. The Al–X bonds in these compounds are therefore $\sigma$-bonds, analogous to the H–X bond in the conjugate acid $HX^+$. The strength of the Al–X bond in compounds (1a—d) should therefore be greater, and the $^{27}$Al coupling constant correspondingly less, the greater the basicity of X. There is in fact a large and progressive decrease in coupling constant in the series (2) > (1a) > (1b) > (1c) > (1d), corresponding to the observed order of basicity in the series $SbMe_3 > AsMe_3 > PMe_3 > NMe_3$. The increasing degree of binding is also reflected by the thermodynamic stabilities of the complexes from $AlMe_3$ and X. This is known [16] to increase in the series (1b) < (1c) < (1d) and the antimony derivative (1a) is unlikely to be out of step.

The sulphur complexes (1e and 1f) also seem to fit the same pattern, judged by the correspondence between coupling constant and heat of complex formation shown by the data in Table 2. Thus the differences between the coupling constants and heats of complex formation for the trimethylamine (1d) and trimethylphosphine (1c) derivatives corresponds to a change in coupling constant of 1·37 MHz per kcal change in the heat of complex formation while the corresponding ratio for the trimethylamine (1d) and dimethyl sulphide (1e) complexes is 1·41 MHz kcal$^{-1}$. Dimethyl sulphide is of course an extremely weak base.

*The* Al–O *Bond.*—The results for the ether complexes (1q—1i) are out of step with those for the other ligands. Thus although ethers are far stronger bases than are the corresponding sulphides, the coupling constants for the ether complexes are only slightly less. Thus the heat of formation of (1q) is similar to that for the trimethylphosphine complex (1c) but the coupling constant is almost the same as for (1b).

This discrepancy is presumably due to the same factors that make Al–O bonds in general anomalously strong. Our results indicate that the additional strength is not due to strong $\sigma$-bonding. It seems likely that the additional pair of unshared oxygen electrons may play a role, leading to $p_\pi$–$d_\pi$ bonding. The transfer of charge from oxygen to aluminium by $\pi$-bonding would of course tend to reduce the corresponding transfer by $\sigma$ bonding. Since only the latter contributes to changes in the $^{27}$Al coupling constant, $\pi$-bonding should tend to increase both the heat of complex formation and the coupling constant.

This interpretation seems to be supported by the behaviour of gallium where the bond to oxygen is not abnormally strong. Tong [17] has found a fairly good linear correlation between the heats of complex formation and n.q.r. coupling constants for a series of complexes formed by gallium trichloride with nitrogen, oxygen, and sulphur bases. Further support also seems to be provided by the crystal structure [18] of the dioxan complex (1i). Normally one might expect the oxygen atom in such a complex to have pyramidal geometry but $\pi$-bonding to the acceptor should tend to make the oxygen atom planar. Although the oxygen atoms in (1i) are not planar, the Al–O–C bond angles are large (122°). Indeed, the departure from planarity may well be due to the constraints imposed by the ring, the COC angles being only 108°. A determination of the structure of the acyclic complex (1g) would be of interest in this connection.

*The High Basicity of Tetrahydrofuran.*—The tetrahydrofuran complex (1h) is more stable than the dimethyl ether complex (1g) and the $^{27}$Al coupling constant is correspondingly less (by 1·3 MHz). These results would be expected since tetrahydrofuran is known to be a stronger base than dimethyl ether. On the other hand the coupling constants of the sulphur analogues (1e) and (1f) differ by an amount (0·3 MHz) comparable with the ' noise ' due to crystal-field effects. The heats of complex formation for (1e) and (1f) are also the same within the limits of experimental error. These results support the current view that the high basicity of (1h) is steric in origin, the increase in steric repulsion on salt formation being less for (1h) than for other ethers. Such steric effects should be less in the case of sulphides both because the sulphur atom is bigger than oxygen and because the CSC bond angles in sulphides are less than the COC bond angles in ethers.

Note that the coupling constant for the dioxan complex (1i) is higher than that for (1g) by 2·65 MHz. Presumably (1i), in which both oxygen atoms are attached to trimethylaluminium residues, is weakened by the resulting dipole–dipole repulsion.

*Hybridization of Aluminium and Ligand* AOs.—We have also measured the $^{75}$As, $^{121}$Sb, and $^{123}$Sb n.q.r. spectra of compounds (1a) and (1b), together with those of trimethylarsine and trimethylstilbine for comparison. The results are shown in Table 3 together with the derived coupling constants. The observed frequencies correspond to values of the asymmetry parameter close

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[16] N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316; C. A. Smith and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1970, 2675; C. H. Hendrickson and D. P. Eyman, *Inorg. Chem.*, 1967, **6**, 1461; C. H. Hendrickson, D. Duffy, and D. P. Eyman, *Inorg. Chem.*, 1968, **7**, 1047.

[17] D. A. Tong, *Chem. Comm.*, 1969, 790.

[18] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1967, **89**, 5362.

to zero (0·036 for $SbMe_3$). In the case of (1b) only the two lowest signals could be detected, those being weak.

TABLE 3

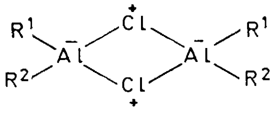
$^{75}As$, $^{121}Sb$, and $^{123}Sb$ parameters for $AsMe_3$, $SbMe_3$, and their $AlMe_3$ complexes at 77 K

| Compound | Frequencies of transitions/MHz [b] | | | Coupling constant/MHz |
|---|---|---|---|---|
| | $\frac{1}{2} \longleftrightarrow \frac{3}{2}$ | $\frac{3}{2} \longleftrightarrow \frac{5}{2}$ | $\frac{5}{2} \longleftrightarrow \frac{7}{2}$ | |
| $AsMe_3$ | 96·7 | — | — | 193·4 |
| (1a) | 82·4 | — | — | 164·8 |
| $SbMe_3$ $^{121}Sb$ | 74·3 | 148·3 | — | 494·6 |
| $^{123}Sb$ | 45·2 | 89·9 | 135·1 | 630·3 |
| (1b) $^{121}Sb$ | 66·4 | (—) [a] | — | 442·0 |
| $^{123}Sb$ | 40·4 | (—) [a] | (—) [a] | 563·4 |

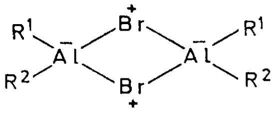
[a] Signals not observed; see text. [b] Estimated maximum possible error, ± 0·1 MHz.

The n.q.r. frequency of monomeric trimethylaluminium is not of course known but it is unlikely that it can differ much from that of tri(t-butyl)aluminium. On this basis one can see that the percentage change in the $^{27}Al$ coupling constant on formation of (1a) or (1b) (37 and 29% respectively) is very much greater than the corresponding changes (15 and 11% respectively) in the Sb or As n.q.r. frequencies. While no quantitative conclusion can be drawn from these results, it seems clear that the AO used by aluminium in the Al–As or Al–Sb bonds must have much greater *p*-character than the As or Sb AOs. This in turn suggests that the MeAlMe bond angles in (1a) and (1b) should be considerably larger than the tetrahedral value while the MeAsMe and MeSbMe angles should be correspondingly smaller. It is interesting that the MeAlMe bond angle in (1d) is larger (114·8°) than the tetrahedral value.[19]

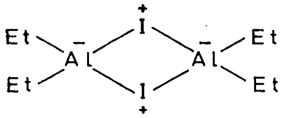
*Coupling Constants for Dimeric Complexes.*—All but two of the remaining compounds studied were derivatives of dialane[6] including compounds with bridging chlorine (4), bromine (5), iodine (6), oxygen (7), nitrogen (8), alkyl (9), phenyl (10), and phenylethynyl (11). We also studied the trimer (12) of dimethylaluminium methoxide and the polymer (13) of the corresponding sulphur compound. The results for compounds (4—8), (12), and (13) are in Table 4 and those for (9)—(11) in Table 5.



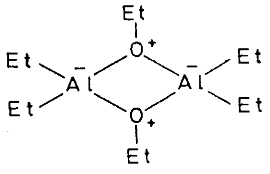
(4)
(a) $R^1 = R^2 = Me$
(b) $R^1 = R^2 = Et$
(c) $R^1 = R^2 = Pr^n$
(d) $R^1 = R^2 = Bu^i$
(e) $R^1 = Et$; $R^2 = Cl$
(f) $R^1 = Bu^i$; $R^2 = Cl$
(g) $R^1 = Ph$; $R^2 = Cl$



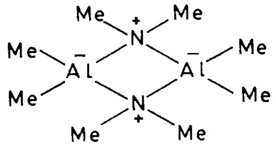
(5)
(a) $R^1 = R^2 = Me$
(b) $R^1 = R^2 = Et$
(c) $R^1 = R^2 = Br$



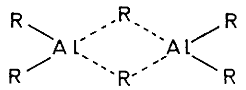
(6)



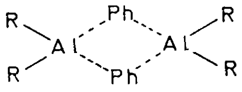
(7)



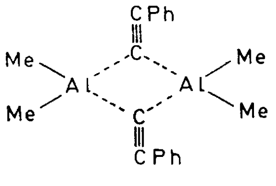
(8)



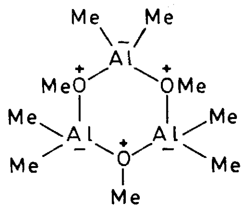
(9)
(a) R = Me
(b) R = Et
(c) $R = Bu^i$



(10)
(a) R = Me
(b) R = Ph



(11)



(12)

The symmetrical compounds in the series, with formulae of the type $(R_2AlX)_2$ where X is the bridging group, conform to the conditions assumed in deriving equation (3). Since the XAlX angle is less than the RAlR one, the principal axes should be as indicated in the Figure (b). This assignment has been confirmed by

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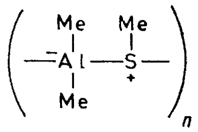
[19] G. A. Anderson, F. R. Forgaard, and A. Haaland, *Acta Chem. Scand.*, 1972, **26**, 1947.

Peterson and Bridenbaugh[20] for the analogous dimer of gallium chloride ($Ga_2Cl_6$) by a study of the n.q.r. Zeeman effect in a single crystal.



(13)

*Asymmetry Parameters: ' Banana ' Bonding.*—The asymmetry parameters in Tables 4 and 5 are remarkably large. Indeed compounds (7), (8), (11), and (13) seem to be the first non-ionic compounds for which $\eta$ has been found to have the maximum possible value of unity. The corresponding interorbital angles, calculated from equation (4), are much larger (109·5°) than the XAlX angles in the four-membered rings which must of course be close to 90° (for which $\eta = 0$). Evidently the Al AOs do not follow the bonds, the latter being bent ' banana ' bonds like those in cyclopropane.[21]

TABLE 4

$^{27}$Al N.q.r. parameters for polymeric aluminium complexes

| Compound | $T$/K | Observed frequency/MHz<br>($\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2}$) | <br>($\pm\frac{3}{2} \longleftrightarrow \pm\frac{5}{2}$) | Estimated possible error (±MHz) | $\frac{e^2Qq}{\text{MHz}}$ | $\eta$ |
|---|---|---|---|---|---|---|
| (4a) | 77 | 6·57 | 10·54 | 0·025 | 36·44 | 0·45 |
| (4b) | 77 | 6·68 | 11·03 | 0·025 | 37·82 | 0·42 |
| (4c) | 77 | 6·59 | 10·79 | 0·025 | 37·18 | 0·43 |
| (4d) | 77 | 6·67 | 10·56 | 0·025 | 36·60 | 0·47 |
|  | 196 | 6·57 | 10·44 | 0·025 | 36·15 | 0·47 |
| (4e) | 77 | 4·74 | 7·20 | 0·025 | 25·60 | 0·51 |
|  |  | 4·81 [a] | 7·43 [a] | 0·025 |  |  |
| (4f) | 77 | 4·83 | 7·70 | 0·05 | 26·66 | 0·46 |
| (4g) | 196 | 4·66 | 7·00 | 0·05 | 24·48 | 0·53 |
|  | Room | 4·66 | 6·94 | 0·05 | 24·32 | 0·54 |
| (5a) | 77 | 6·46 | 10·65 | 0·025 | 36·66 | 0·42 |
|  | 196 | 6·42 | 10·58 | 0·025 | 36·41 | 0·42 |
| (5b) | 77 | 6·525 | 10·96 | 0·025 | 38·15 | 0·37 |
|  |  |  | 11·35 [a] | 0·025 |  |  |
| (5c) | 77 | 3·034 | 3·83 | 0·01 | 13·86 [c] | 0·73 |
| (6) | 77 | 6·39 | 11·16 | 0·05 | 38·02 | 0·34 |
| (7) | 77 | 6·01 | 6·01 [b] | 0·01 | 22·71 | 1·00 |
| (8) | 77 | 4·225 | 4·336 [b] | 0·01 | 16·43 | 0·957 |
|  | Room | 4·18 | 4·18 | 0·01 | 15·77 | 1·00 |
| (12) | 77 | 4·25 | 5·89 | 0·025 | 20·91 | 0·62 |
|  |  | 4·56 | 5·76 | 0·025 | 20·81 | 0·73 |
| (13) | 77 |  | 4·90 | 0·05 | 18·52 | (1·00) [d] |
|  | Room |  | 4·80 | 0·01 | 18·41 | (1·00) [d] |

[a] Crystal-field splitting; mean value used in calculating $e^2Qq$ and $\eta$. [b] ($\pm\frac{1}{2} \longleftrightarrow \pm\frac{5}{2}$) transition also observed at expected frequency. [c] P. A. Casabella, P. J. Bray, and R. G. Barnes, *J. Chem. Phys.*, 1959, **30**, 1393. [d] Assumed; signal not resolved.

TABLE 5

$^{27}$Al N.q.r. parameters for alkyl-, phenyl-, and phenylethynyl-bridged dimers

| Compound | $T$/K | Observed frequency/MHz [a]<br>($\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2}$) | <br>($\pm\frac{3}{2} \longleftrightarrow \pm\frac{5}{2}$) | $e^2Qq$ | $\eta$ |
|---|---|---|---|---|---|
| (9a) | 77 | 5·38 | 6·51 [b] | 23·71 | 0·78 |
|  | 196 | 5·37 | 6·45 [b] | 23·55 | 0·79 |
| (9b) | 196 | 5·62 | 6·2 | 23·23 | 0·87 |
| (9c) | 77 | 6·15 | 6·87 | 25·42 | 0·87 |
| (10a) | 77 |  | 6·78 | 24·27 | (0·67) [c] |
|  | Room | 4·93 | 6·54 [d] | 23·41 | 0·67 |
| (10b) | Room | 4·53 | 5·39 | 19·71 | 0·79 |
| (11) | Room | 6·74 | 6·74 [d] | 25·49 | 1·00 |

[a] Estimated possible error, ±0·05 MHz, except for (10a) where the error could be as much as 0·1 MHz. [b] ($\pm\frac{1}{2} \longleftrightarrow \pm\frac{5}{2}$) transition also observed. [c] Assumed. [d] Two unresolved signals of unequal intensity, in accordance with the crystal structure (ref. 28*a*).

The asymmetry parameter of (8) changed slightly between 77 K and room temperature. This change is probably a crystal-field effect, due to anisotropic thermal expansion of the crystals.

The external bond angles in compound (8) raise a further point. The observed[22] value (115·9°) is considerably greater than that (109·5°) corresponding to the asymmetry parameter. If this discrepancy is taken seriously it would imply that the external bonds in (8) are also ' bent.' It seems more likely that, in orbital

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[20] G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.*, 1969, **51**, 238.

[21] C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, 1947, **15**, 151.

[22] V. H. Hess, H. Hinderer, and S. Steinhauser, *Z. anorg. Chem.*, 1970, **377**, 1.

terms, the AOs themselves are bent. The greater interelectronic repulsions near the nucleus should tend to enforce a more nearly tetrahedral geometry in that region than in parts of the AO more distant from the nucleus. The n.q.r. frequency is determined mainly by the form of AOs near the nucleus while chemical bonding depends on the outer parts of AOs. One should not therefore expect any quantitative correspondence between bond angles and interorbital angles deduced from n.q.r., even in cases where strain is absent.

*Effect of the Bridging Groups.*—The dimers $(R_2AlX)_2$ fall into three categories. First, there are those [(4)—(8)] where X has an unshared pair of electrons so that X and Al are linked by normal covalent bonds. Secondly, there are compounds (9) with bridging alkyl groups which are linked to Al–X–Al bonds. Thirdly, there are compounds [(10) and (22)] with unsaturated bridging groups where the $\pi$-electrons may participate in bridging. It is easily seen that in all cases the populations of the aluminium AOs used in bridging should be less than those used in the terminal bonds. In compounds (4)—(8) the bridging atom carries a formal positive charge and is therefore more electronegative than the terminal atoms or groups while in (9) the bridging bonds involve sharing of pairs of electrons between three atoms instead of two. Moreover the bent ' banana ' bonds in the bridge must be weaker and so more polarizable than the terminal bonds; the electronegative bridging atom should be correspondingly more successful in attracting electrons from aluminium.

The compounds in Table 4 can be regarded as chelated co-ordination complexes derived from the ion $R_2Al^+$ which would be linear, corresponding to equations (3) and (4) with $\theta = 90^\circ$, $\phi = 180^\circ$, $d = 0$. Co-ordination with the donor X introduces electrons into the previously empty aluminium AOs. The repulsion between these electrons should lead to an increase in $\theta$ and a corresponding decrease in $\phi$ [Figure and equation (2)]. The net effect [see equations (3) and (4)] in complexes of a given type will be a decrease in the coupling constant and an increase in the asymmetry parameter, these changes being greater, the greater the donor activity of X. The results in Table 4 are in agreement with this prediction, the coupling constants decreasing in the order (X =): $Cl > RO > R_2N$. The asymmetry parameter also increases, being in the range 0·4—0·5 for most of the compounds with halogen bridges but unity, or close to unity, for those with bridging oxygen or nitrogen. A value of unity for $\eta$ implies $sp^3$ hybridization of aluminium, $\theta$ and $\phi$ having the tetrahedral value (109·5°).

*Univalent and Bivalent Bridging Groups.*—In compounds (4)—(8) the bridging atom has two AOs and four electrons for bonding to aluminium. The Al–X bonds are therefore normal two-centre covalent bonds. In the case of (9), however, the bridging group has one AO only and is therefore linked to the aluminium atoms by a two-electron three-centre bond. Other things being equal, one would then expect the electron densities in the aluminium AOs to be lower, and the coupling constant correspondingly greater, in the latter case. The coupling constants for (7) and (8) are indeed less than that for (9) but those for (4a), (5a), and (6) are much greater. Evidently the polarization of the Al–halogen bonds is so extreme that it outweighs the presence of four electrons rather than two. The Al–Cl bond is certainly highly polar, as is shown by the very low $^{35}Cl$ n.q.r. frequencies[6] (Table 6) in the corresponding complexes.

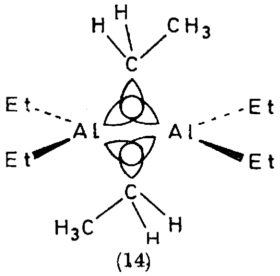
TABLE 6

$^{35}Cl$ N.q.r. frequencies for alkylaluminium and phenylaluminium chlorides

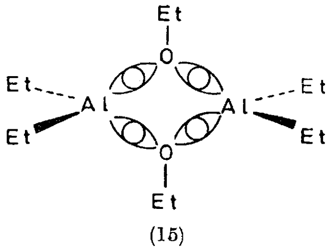
| Compound | (4b) | (4c) | (4d) | (4e) | (4f) | (4g) |
|---|---|---|---|---|---|---|
| Observed frequency[a]/MHz | 9·89 | 9·97 | 10·18 | 10·46<br>11·35[b]<br>11·50[b] | 10·82<br>11·72 | 10·48[c]<br>11·47[c] |

[a] At 77 K unless otherwise stated. Estimated maximum possible error, ±0·025 MHz. [b] Crystal-field splitting. [c] At 196 K.

The results for compounds (7) and (9b) seem to contradict the conclusions reached above concerning the relation between coupling constants and asymmetry parameters. Thus since the coupling constant for (7) is similar to that for (9b), one would expect the asymmetry parameters to be comparable. This is not the case, the values of $\eta$ for (7) and (9b) being 1·00 and 0·87, respectively. Yet even this small discrepancy can be reasonably explained in terms of the simple MO treatment. The interorbital angle near the nucleus depends on two factors; the angle between the orbitals as a whole, and the enhanced correlation effects near the nucleus. Bending a bond should therefore lead to corresponding changes in the interorbital angle near the nucleus. It is immediately obvious that the bending of the aluminium orbitals in this way should be greater in (9b) with its ' dimethylated double bond ' than in (7) where the bridging atom contributes two AOs. This is seen clearly from the orbital diagrams in (14) and (15).



(14)



(15)

It is interesting that the external Me–Al–Me angle in (9a) (123°)[23] is considerably larger than that (115·9°)[20] in (8), as would be expected from the values for $\eta$ (0·87 and 1·00 respectively).

*Effect of the Terminal Group.*—Replacement of terminal alkyl groups by halogen lowers the coupling constant and raises the asymmetry parameter [*cf.* (4b) with (4e),

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[23] R. G. Vankra and E. L. Amma, *J. Amer. Chem. Soc.*, 1967, **89**, 3121.

(4d) with (4f), and (5a) with (5c)]. This would also be expected. An increase in the electronegativity of a *terminal group* increases the polarity of the bond linking it to aluminium and so lowers the population of the corresponding aluminium AO [$d$ in equation (3)]. Not only will this lower the coupling constant but it should also decrease the angle between the AOs used to form the terminal bonds. This angle is greater (*i.e.*, $\phi > \theta$) because the population of the terminal AOs is greater than that of the centre ones [$c > d$ in equation (3)] and the repulsion between the electrons is correspondingly greater. A reduction in the terminal populations should therefore allow $\theta$ to increase at the expense of a decrease in $\phi$. This in turn should lead to an increase in the asymmetry parameter [see equation (4)].

*Choice between Bridging and Terminal Positions.*—Ligands with two pairs of available electrons should be much more strongly bound to aluminium in bridging positions than in terminal ones. The difference should be less for alkyl groups which have only one AO available for bonding. Alkyl bridging groups should therefore be present only when no bivalent ligand is available, *i.e.*, in hexa-alkyl-dialanes. Thus OMe and $NMe_2$ certainly occupy bridging positions in (7) and (8) and the available evidence also indicates that halogen is also in all cases preferred over alkyl in the bridging positions. It has been shown that the bridging groups are chlorine by electron diffraction[24] in the case of (4a) and by *X*-ray crystallography[25] in the case of $(CH_3AlCl_2)_2$. The n.q.r. data very strongly suggest[6] that the same is generally true. Thus the fact that (4b) has a much larger coupling constant than (9b), and also than (4e), can be explained only if replacement of a bridging alkyl by chlorine raises the coupling constant whereas analogous replacement of a terminal alkyl lowers it. The data in Tables 4 and 5 indicate that replacement of a bridging alkyl by chlorine raises the coupling constant by 6—7 MHz while replacement of terminal alkyl lowers it by 5—6 MHz. As pointed out above, these changes are those to be expected on the basis of the Townes–Dailey theory and the changes in the asymmetry parameter are also in the expected direction.

Further confirmation is provided by the $^{35}Cl$ n.q.r. data[6] shown in Table 6. The fact that (4e) and (4f) gave two distinct * chlorine frequencies shows that the chlorine atoms in these occupy two chemically distinct locations. These can only be the terminal and bridging positions. The fact that only two distinct resonances were observed, and the fact that the intensities of the two signals were similar, indicates that both bridging positions must be occupied by chlorine. Similar remarks apply to (4g), showing that chlorine also takes precedence over phenyl in the bridging positions.

In each case the lower of the two observed frequencies can be assigned to the bridging chlorines. This would be expected both theoretically and from the analogy with gallium trichloride where the assignment of frequencies has been established unambiguously by studies[20] of the Zeeman effect.

Next we have to consider the distinction between phenyl and alkyl. Since $sp^2$-hybridized carbon is more electronegative than $sp^3$-hybridized carbon[26] an Al–Ph bond should be more polar in the sense $Al^{\delta+}–C^{\delta-}$ than Al–Alkyl. The arguments given above indicate that replacement of terminal alkyl by phenyl in a dimeric complex $(R_2AlX)_2$ should lower the $^{27}Al$ coupling constant. This effect is seen in the comparison between (4e), (4f), and (4g). Replacement of alkyl by phenyl lowers the coupling constant by 0·5—1 MHz per phenyl group.

The effect of replacing bridging alkyl by phenyl is harder to predict since the $\pi$-electrons of phenyl could conceivably be used for back-co-ordination.[27] Replacement of bridging alkyl by an equivalent but more electronegative group should raise the coupling constant by making the three-centre bonds more polar in the sense $Al_2^{\delta+}–C^{\delta-}$. Back-co-ordination will, however, lead to transfer of charge in the opposite direction and so to a decrease in the coupling constant. It is impossible to tell by qualitative arguments which of the two effects will predominate. Fortunately (10a) has a higher coupling constant than (9a). Since replacement of a terminal methyl in (9a) by phenyl should have lowered the coupling constant, this must imply that back-co-ordination is relatively unimportant. It has in fact been established by *X*-ray crystallography[28a] that the phenyl groups in (10a) occupy bridging positions.

These conclusions are confirmed by the difference in coupling constant between (10a) and (10b) (3·7 MHz) which is about four times the value deduced above for the difference between terminal methyl and terminal phenyl.

Similar arguments apply in the case of (11). Since $sp$-hybridized carbon is even more electronegative than $sp^2$-hybridized carbon, replacement of terminal methyl groups in (9a) by phenylethynyl should lead to a large decrease in the coupling constant. Since the coupling constant of (11) is in fact greater than that of (9a), the phenylethynyl groups must occupy the bridging positions. This has been shown to be so by $^1H$ n.m.r. spectroscopy.[28b] Here again back-co-ordination by the unsaturated bridging group appears to be unimportant.

*Monomeric and Dimeric Complexes.*—When $R_3Al$

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* *I.e.*, differing by more than the possible effects of crystal fields. One of the resonances in compound (4e) showed an additional small splitting, probably due to this.

[24] L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287; see also J. Weidlein, *J. Organometallic Chem.*, 213, **17**, 1969, and refs. therein.

[25] G. Allegra, G. Perego, and I. Immirzi, *Makromol. Chem.*, 1963, **61**, 69.

[26] See M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969, p. 147.

[27] M. J. S. Dewar, *Bull. Soc. chim. France*, 1952, **18**, C71; see M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, 1965, **16**, 321.

[28] (*a*) J. F. Malone and W. S. McDonald, *Chem. Comm.*, 1970, 380; (*b*) E. A. Jeffery, T. Mole, and J. K. Saunders, *Austral. J. Chem.*, 1968, **21**, 137.

combines with a donor X, the strength of the resulting AlX dative bond is limited by the charge transfer produced in its formation ($R_3Al^{-}-X^{+}$). When, however, $R_2AlX$ dimerizes, the charges can be partly neutralized by polarization of the pre-existing AlX bonds. One would therefore expect the AlX bonds in $(R_2AlX)_2$ to be stronger than those in $R_3Al^{-}-X^{+}$. The population of the corresponding aluminium AOs [$d$ in equation (3)] should therefore be greater than that of the fourth aluminium AO in $R_3AlX$ [$b$ in equation (1)]. Since the RAl populations should be similar in both cases [$a \simeq c$ in equations (1) and (3)], the factor $|a - b|$ in equation (1) should be greater than $|c - d|$ in equation (3). If the aluminium atoms are in each case tetrahedral, $\cos \alpha = -\frac{1}{3}$ and $\eta = 1$ in equation (3). Both equations then reduce to the same form, *i.e.*, (7). The coupling

$$\frac{e^2Qq}{(e^2Qq_0)} = \tfrac{3}{4}|a - b| \text{ or } \tfrac{3}{4}|c - d| \qquad (7)$$

constant for $(R_2AlX)_2$ should therefore be lower than that of $R_3AlX$. This is true for the pair $Me_3Al\cdot OMe_2$ (28·18 MHz) and $(Et_2AlOEt)_2$ (22·71 MHz). The difference is far too great to be due to the substitution of ethyl for methyl. Indeed, the comparisons (4a)–(4b)–(4c)–(4d) and (9a)–(9b) suggest that changing alkyl groups has little effect on the coupling constant.

*Steric Effects: Dimer–Polymer Equilibria.*—Tervalent aluminium compounds $R_2AlX$ usually form cyclic dimers $(R_2AlX)_2$. In certain cases, however, trimers [*e.g.*, (12)] or polymers are formed. The bonding in such compounds is essentially similar to that in the dimer. The only difference is that they contain no strained rings. Conversion of the dimer into trimer or polymer must therefore be exothermic. However it also leads to a decrease in entropy, owing to the replacement of a larger number of small molecules by a smaller number of large ones. Since the entropy change will be much the same in all cases, being due mainly to changes in translational entropy, the equilibrium will be determined by the energy change on polymerization. This will depend on the strengths of the AlX bonds since the energy required to bend a bond in general varies with its strength. The bonds in turn are stronger for bivalent ligands than for univalent ones and are also stronger, the less electronegative the ligand. It is therefore easy to see why complexes with univalent bridging groups (*e.g.*, alkyl) or with bridging halogen are invariably dimeric whereas compound (12) and $(Me_2AlNHMe)_3$ are trimeric and (13) is polymeric.

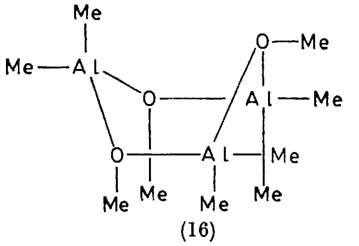
The difference in bonding between dimers and higher polymers is reflected in their n.q.r. spectra. As we have seen, the deformation of the AlX bonds in the dimer should reduce the populations of the corresponding aluminium AOs. The populations of these AOs in trimeric or polymers should therefore be greater and the $^{27}$Al coupling constants correspondingly smaller. This effect is seen in the comparison (8). Unfortunately no data are available for dimeric sulphur complexes.

$$(7)\ 22{\cdot}71\ \text{MHz} \quad (12)\ 20{\cdot}86\ \text{MHz} \qquad (8)$$

However the huge difference between the coupling constants for the linear polymer (13) (18·46 MHz) and the monomeric complex (1e) (29·75 MHz) shows that the value for an analogous dimeric complex would be much greater than that for (13).

The fact that (7) is dimeric [22] whereas (5) is trimeric [29] must be attributed to steric hindrance in the higher polymers derived from (7), owing to the greater bulk of the ethyl groups. The same factor could account for the fact that $Me_2AlNMe_2$ forms the dimer (8) whereas $Me_2AlNHMe$ forms the trimer $(Me_2AlNHMe)_3$. This interpretation is supported by the fact that the coupling constant for (8) is greater by nearly 5 MHz than the value for (1a), although normally (see section on uni- and bi-valent bridging groups) the coupling constants for dimeric complexes are lower than those for analogous monomeric ones. If steric effects are sufficient to prevent $Me_2AlNMe_2$ from forming higher polymers, they may well also destabilize the dimer, thus weakening the Al–N bonds and so raising the coupling constant. One would then expect a very considerable difference in coupling constant between (8) and the (presumably strain-free) trimer $(Me_2AlNHMe)_3$.[29] This could have been responsible for our failure to observe signals for the latter, the corresponding frequencies being below the lower limit of our spectrometer.

The splittings of the signals in compounds (4e) and (5b) are probably due to the crystal field. The intensities of both components were in each case similar. In compound (12) on the other hand the ratios of intensities were 2 : 1 for each pair of signals. Unless (12) has a rather strange crystal structure, this must imply that the aluminium atoms are not chemically equivalent, one of them differing from the other two. If so, (12) must exist as the boat conformer (16) rather than as the



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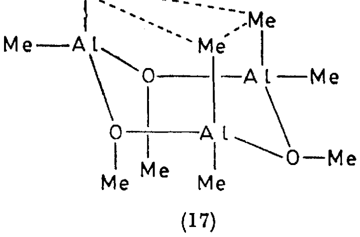

(17)

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[29] K. Gosling, G. M. McLaughlin, G. A. Sims, and J. O. Smith, *Chem. Comm.*, 1970, 1617.

chair (17), presumably to avoid steric interactions (· · ·) between axial methyl groups. A study of the crystal structure of (12) would clearly be of interest.

A further curious feature is the low asymmetry parameter of (12). One would certainly have expected this to be unity like that of the analogous dimer (7).

*Conclusions.*—Given the wide variety of compounds discussed in this paper, it is gratifying to find that the simple MO treatment of Townes and Dailey is so successful. Virtually all the observed trends can be explained in these terms, including the ' non-classical ' bonding present in electron-deficient molecules such as hexamethyldialane[6] (9a). These results not only help to justify the use of simple MO arguments in connections such as these but also indicate the potential of n.q.r. spectroscopy as a tool in the study of chemical bonding. Indeed, its success in this connection is such that it can also serve as an aid in determining structures of compounds containing ' n.q.r.-active ' elements.

In view of the growing importance of analogous organometallic compounds as catalysts in organic chemistry, studies of this kind may prove of practical importance for two reasons. First, n.q.r. measurements can be carried out much more easily and quickly than other methods of structure determination. Secondly, a knowledge of the electronic structures of such catalysts is clearly prerequisite to any interpretation of their reactivity.

The discussion given here is of course based on a very naïve MO approach. Measurements of this kind may prove still more significant in conjunction with more sophisticated theoretical treatments. We have recently shown[30] that the $^{35}$Cl n.q.r. coupling constants of a wide variety of aryl chlorides can be quantitatively interpreted in terms of semiempirical SCF MO calculations. If similar success attends calculations for other elements, this could not only provide even more detailed information concerning the electronic structure of molecules but could also prove of value in determining the parameters for elements (in particular metals) for whose compounds thermochemical data are lacking.

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