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# THE MOLECULAR STRUCTURE OF THE COMPLEX TRIMETHYLALUMINIUM TRIMETHYLPHOSPHANE, $(CH_3)_3AlP(CH_3)_3$, DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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## Summary

The molecular structure of $(CH_3)_3AlP(CH_3)_3$ has been determined by gas phase electron diffraction. The main molecular parameters are Al-C = 1.973(3) Å, Al-P = 2.53(4) Å, P-C = 1.822(3) Å, $\angle$P-Al-C = 100.0(1.3)°, and $\angle$Al-P-C = 115.0(0.7)°. The Al-C bond distance in the complex is significantly longer, and the C-Al-C valence angle significantly smaller than in free monomeric $(CH_3)_3Al$. The P-C bond distance in the complex is significantly shorter and the $\angle$C-P-C valence angle significantly larger than in free $P(CH_3)_3$. All these changes are in the direction predicted by the valence shell electron pair repulsion model.

## Introduction

Trimethylaluminium, $Me_3Al$, forms stable complexes with amines, ethers and phosphanes [1]. The enthalpy of formation of the complex

$$Me_3Al+D = Me_3AlD$$

in normal hexane solution is

$\Delta H_f = -29.96\pm0.19$ kcal $mol^{-1}$ when $D = NMe_3$,

$\Delta H_f = -20.29\pm0.20$ kcal $mol^{-1}$ when $D = OMe_2$,

and $\Delta H_f = -21.08\pm0.28$ kcal $mol^{-1}$ when $D = PMe_3$ [2].

We have previously determined the molecular structures of $Me_3AlNMe_3$ [3] and $Me_3AlOMe_2$ [4] and compared the structures of the complexes with the structures of the free acceptor and the free donor. We now report the result of a similar study of $Me_3AlPMe_3$.

## Experimental and calculation procedure

$Me_3AlPMe_3$ was synthesized by direct combination of $Al_2Me_6$ and $PMe_3$ [1] and purified by distillation. The electron scattering pattern was recorded on the Oslo electron diffraction unit [5] with a reservoir temperature of about 85 °C (corresponding to a vapor pressure of about 20 mm Hg [1]) and a nozzle temperature of about 90 °C. Vapor pressure measurements show that the complex is not measurably dissociated at 135 °C and 94 mm Hg [1]. Exposures were made with nozzle-to-photographic-plate distances of about 48 and 20 cm. The optical densities of six plates from the first set and four from the second were processed using the programs described by Andersen *et al.* [6]. The modified molecular intensity points obtained by averaging the intensity values for each nozzle-to-plate distance are shown in Fig. 1.

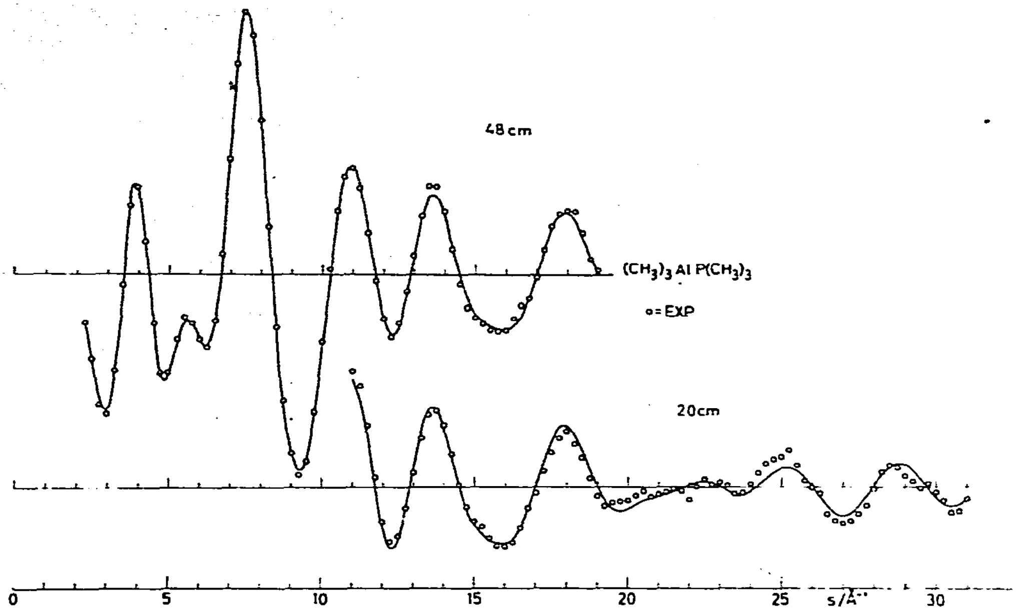

Fig. 1. Experimental modified molecular intensity points for $Me_3AlPMe_3$ from s = 2.25 to 19.00 Å$^{-1}$ (upper curve) and from s = 11.00 to 31.00 Å$^{-1}$ (lower curve). In the upper curve only every second experimental point is shown. Full lines: theoretical intensity curves calculated for best model.

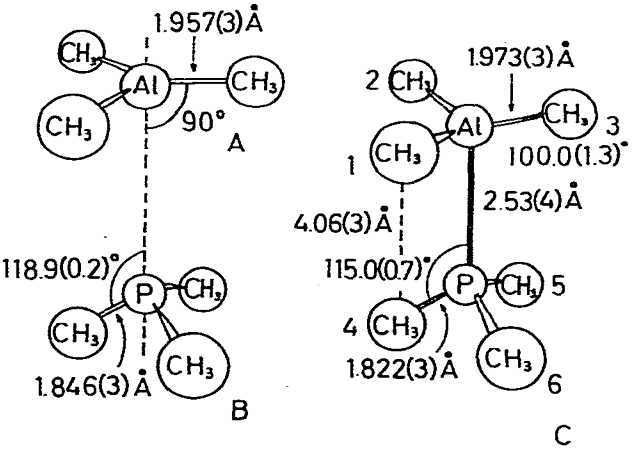

Fig. 2. Molecular structures of free monomeric $Me_3Al$ [3] (A), free $PMe_3$ [20] (B) and the complex $Me_3AlPMe_3$. (The $r_g$ P-C bond distance listed in ref. 20 has been converted to $r_a$).

A molecular model of $Me_3AlPMe_3$ is shown in Fig. 2. It was assumed that: (i) $Me_3AlPMe_3$ has $\underline{C}_{3v}$ symmetry, (ii) The C atoms of donor and acceptor are staggered with respect to rotation about the Al-P bond. (iii) All Me groups have $\underline{C}_{3v}$ symmetry with the threefold axes coinciding with the Al-C or P-C bonds. (iv) The H-C(Al) and H-C(P) bond distances are equal. (v) The angle of rotation of the Me groups about the C-Al or C-P bonds is such that the C-H bonds are staggered with respect to the bonds radiating from the Al or P atom.

The molecular structure is then determined by eight independent parameters, e.g. the C-H (mean), Al-C, Al-P and P-C bond distances and the Al-C-H, P-Al-C, Al-P-C and P-C-H valence angles.

The molecular structure was refined by least squares calculations on the intensity data under the constraints of a geometrically consistent $r_a$ structure using programs written by Seip [7]. Since large amplitude libration about the Al-P bond could lead to average values for the distances $C_1 \cdots C_4$ and $C_1 \cdots C_5$ (see Fig. 2) that are significantly different from those calculated from the equilibrium geometry, these distances were refined as independent parameters. The final refinements were carried out with a non-diagonal weight matrix and a separately refined scale factor for each nozzle-to-plate distance. The molecular parameters obtained and their estimated standard deviations are listed in Table 1. The standard deviations have been expanded to take into account an estimated uncertainty of 0.1 % in the electron wavelength.

Modified molecular intensity curves calculated for the best model are shown in Fig. 1. An experimental radial distribution curve and the difference between this curve and one calculated for the best model is shown in Fig. 3.

Table 1. Bond distances, valence angles, and root mean square vibrational amplitudes of $Me_3AlPMe_3$. (Estimated standard deviations in parentheses)[a]

| | $R_a$/A | $\ell$/A |
|---|---|---|
| Al-P | 2.53(4) | 0.116(20) |
| Al-C | 1.973(3) | 0.067(3) |
| P-C | 1.822(3) | 0.058(3) |
| C-H (mean) | 1.119(3) | 0.079(3) |
| $Al\cdots C_4$ | 3.69(3) | 0.17(2) [d] |
| $P\cdots C_1$ | 3.46(3) | 0.17(2) [d] |
| $Al\cdots H_1$ | 2.61(6) | 0.22(7) |
| $P\cdots H_4$ | 2.46(3) | 0.12(4) |
| $C_1\cdots C_2$ | 3.37(1) | 0.133 [e] |
| $C_4\cdots C_5$ | 2.86(2) | 0.103(12) |
| $C_1\cdots C_4$ [b] | 4.31(3) | 0.29(2) |
| $C_1\cdots C_5$ [b] | 5.04(4) | 0.22(2) |
| $C_1\cdots C_4$ [c] | 4.06(3) | |
| $C_1\cdots C_5$ [c] | 5.11(2) | |
| $\angle$P-Al-C | 100.0(1.3)° | |
| $\angle$C-Al-C | 117.1(0.8)° | |
| $\angle$Al-P-C | 115.0(0.7)° | |
| $\angle$C-P-C | 103.4(0.8)° | |
| $\angle$Al-C-H | 111.9(4.5)° | |
| $\angle$P-C-H | 111.4(1.9)° | |

[a] For numbering of the atoms consult Fig. 2. The distances are given as $r_a$. The angles have not been corrected for shrinkage. [b] Refined as independent parameter. [c] Calculated for rigid model of $C_{3v}$ symmetry. [d] These amplitudes were assumed equal. [e] Assumed equal to the corresponding amplitude in $Me_3Al$ [18].

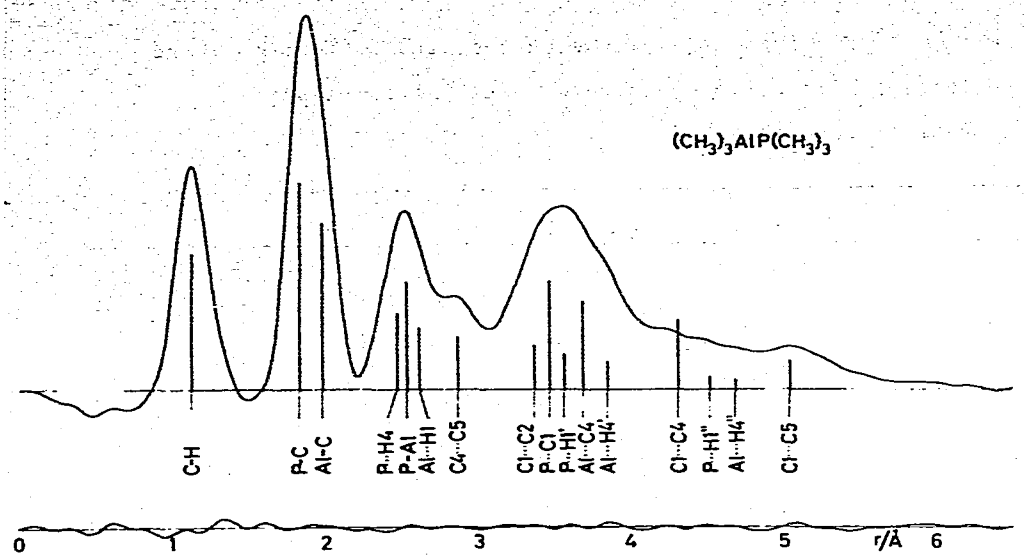

Fig. 3. Upper curve: experimental radial distribution curve. Lower curve: difference between the experimental curve and a theoretical curve calculated for the best model. Artificial damping constant k = 0.002 Å$^2$.

## Discussion

The Al-P bond distance. Though very inaccurately determined, the Al-P bond distance in $Me_3AlPMe_3$, 2.53(4) A, is significantly larger than in aluminium phosphide, 2.367 A, where each Al atom is surrounded by four P at the corners of a regular tetrahedron [8]. A difference of this magnitude is not unexpected since the bond in $Me_3AlPMe_3$ is a pure dative bond, while the bond in $(AlP)_x$ may be regarded as a resonance hybrid between a single covalent bond and a dative bond where the contribution from the latter is 25 %. In Table 2 we have collected representative bond distances between fourcoordinate Al and N ranging from 1.78 to 2.10 A. Inspection of the table shows that the bond distance between fourcoordinate Al and N increases monotonically with per cent dative character. Though the shortest Al-N bond distances might be rationalized as an effect of dative π-bonding [9],we prefer to regard the variation as due to an inherent difference between the lengths of covalent and dative Al-N bonds. Before going on we should point out that since electronegative substituents like Cl on Al are known to have a large inductive effect on the length of dative Al-N bonds [2,16,17], the entries in Table 2 have been limited to compounds where Al is bonded to N,H and C only.

The barrier to internal rotation about the Al-P bond. The average values obtained for the $C_1 \cdots C_4$ and $C_1 \cdots C_5$ distances when these are refined as independent parameters, 4.31(3) Å and 5.04(4) Å, are larger, respectively shorter than the distances calculated for a rigid model of $C_{3v}$ symmetry,4.06 and 5.11 Å. At the same time the root mean square vibrational

Table 2. The Al-N bond distance as function of per cent dative character [a)]

| Compound | Reference | Al-N/Å | Dative character/% |
|---|---|---|---|
| $Li[Al(NCBu^t_2)_4]$ | 9 | 1.78(1) [b)] | 0 |
| $(AlN)_x$ | 10 | 1.893 [c)] | 25 |
| $(C_6H_5AlNC_6H_5)_4$ | 11 | 1.914(5) | 33 |
| $(HAlNC_3H_8)_4$ | 12 | 1.913(2) | " |
| $(CH_3AlNC_3H_8)_4$ | 12 | 1.923(1) | " |
| $[(CH_3)_2AlN(CH_3)_2]_2$ | 13 | 1.963 [c)] | 50 |
| - " - | 14 | 1.964 [c)] | " |
| cis$[(CH_3)_2AlNHCH_3]_3$ | 14 | 1.940 [c)] | " |
| $[(CH_3)_2AlN(CH_2)_2]_3$ | 15 | 1.93 [c)] | " |
| $H_3AlN(CH_3)_3$ | 16 | 2.063(8) | 100 |
| $(CH_3)_3AlN(CH_3)_3$ | 3 | 2.099(10) | " |

[a)] Note that Al is fourcoordinate in all the compounds and that the entries have been selected so that Al is bonded only to N,C or H.

[b)] The bond distance listed is for the terminal Al-N bond.

[c)] Average value calculated from the bond distances listed in the reference.

amplitude of these distances, 0.29(2) A and 0.22(2) A respectively, are very large, suggesting that the barrier to internal rotation is very low. The impression is enforced by inspection of the radial distribution curve which shows no isolated peaks for the $C_1\cdots C_4$ and $C_1\cdots C_5$ distances. We therefore conclude that the barrier to internal rotation in $Me_3AlPMe_3$ is of the order of 0.5 kcal $mol^{-1}$ or less.

It is of interest to compare the barrier in $Me_3AlPMe_3$ with that in $Me_3AlNMe_3$. In the radial distribution curve of the latter complex the peaks corresponding to the $C_1\cdots C_4$ and $C_1\cdots C_5$ distances are separated by a distinct minimum, and the vibrational amplitudes are determined as 0.176(15) A and 0.130(13) A, respectively. That the rotational barrier in $Me_3AlNMe_3$ is higher than in $Me_3AlPMe_3$ is not surprising since the much shorter Al-donor bond leads to a much shorter $C_1\cdots C_4$ distance, 3.475(20) A calculated for a rigid model of $\underline{C}_{3v}$ symmetry, and hence increased van der Waals repulsion between the Me groups in donor and acceptor.

The structure of the acceptor. Comparison of the structures of $Me_3AlPMe_3$ and free monomeric $Me_3Al$ [18] (see Fig. 2) show that the length of the Al-C bonds increases significantly on formation of the complex and that the Al-C bonds are folded back from the incoming donor atom. Similar significant changes in the structure of the acceptor has previously been found in $Me_3AlNMe_3$ and $Me_3AlOMe_2$. Both changes are in the direction predicted on the basis of the valence shell electron pair repulsion (VSEPR) model [19].

The structure of the donor. Comparison of the structure of the complex with that of free $PMe_3$ [20] (see Fig. 2), show that the length of the P-C bonds decreases significantly on formation of the complex and that the C-P-C valence angle increases significantly. Again both changes are in the direction predicted by the VSEPR model. Similar significant changes in the structure of the donor have previously been found in $H_3BPMe_3$ [21] and have been indicated in the case of $Me_3GaPMe_3$ [22]. It seems reasonable to assume that all trialkylphosphanes will be similarly deformed in all complexes with main group elements, unless the alkyl groups on P or the substituents on the acceptor atom are particularly bulky.

For complexes with transition elements the picture is made more complex by the possibility of back donation. Within the framework of the VSEPR model such back donation would be expected to decrease the C-P-C angle and increase the P-C bond distance. The compounds $Me_3PS$ and $Me_3PO$ have recently been reinvestigated by gas phase electron diffraction [23] and vibrational spectroscopy [24]. The short P-S and P-O bond distances and high force constants indicate considerable multiple bond character. If this is assumed to be due to $p\pi$-$d\pi$ back donation, these compounds may serve as models for transition metal complexes. The electron diffraction investigation show that in these compounds too the C-P-C angle is significantly greater and the P-C bond significantly shorter than in free $PMe_3$.

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