A Two-electron Hydrogen Bridge Bond in Crystalline Trimethylaluminium Dimer

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Summary The *X*-ray crystal intensity data for $AlMe_3$ dimer obtained by Vranka and Amma have been subjected to further refinement and indicate the presence in the molecule of two-electron hydrogen bridge bonds Al–H–C.

As far as the aluminium and carbon atoms are concerned, there has been no doubt about the near-D_{2h} symmetry of the molecular framework of Al_2Me_6 in the solid state since its crystal structure was first subjected to *X*-ray analysis by Lewis and Rundle in 1953.[1] This *X*-ray analysis confirmed the interpretation of a number of earlier spectroscopic studies.[2] Before 1953 there were a number of speculations put forward for the positions of the hydrogen atoms. The papers of Burawoy[3] and of Pitzer and Gutowsky[4] raised the possibility of protons lying within the bridging Al–C bonds.

Lewis and Rundle did not attempt to locate the hydrogen atoms and they stated: "To have this (D_{2h}) symmetry all methyl groups would have to be rotating or statistically arranged so as to achieve this symmetry." The positions occupied by the hydrogen atoms were not examined until 1967 when Vranka and Amma[5] tried, without success, to refine the *X*-ray data of Lewis and Rundle. They obtained new three-dimensional *X*-ray data and showed that there is significant distortion of the molecular framework away from D_{2h} to the lower C_{2h}.

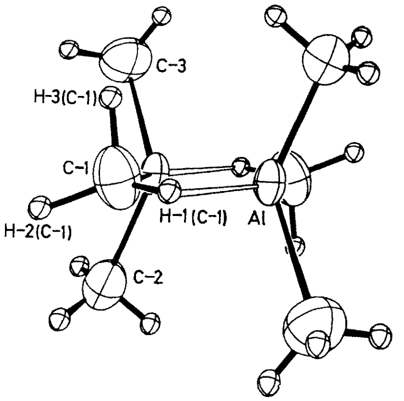
Vranka and Amma examined difference Fourier maps and from them listed the co-ordinates of all nine independent hydrogen atoms. From these they calculated all the bond lengths and interbond angles involving hydrogen and carbon atoms but, apart from listing them and noting that "... no physical significance should be attached to differences in C–H bond distances and H–C–H bond angles" made no further comment on the stereochemistry which their results implied, possibly because their attempts to refine the hydrogen positions were unsuccessful.

We re-examined the problem after a reported *X*-ray analysis[6] of Al_2Ph_6. In this dimer, the bridge angle Al–C–Al (76·5°) and Al–C bridge length, 2·18 Å, are remarkably similar to those in Al_2Me_6 (74·7° and 2·16 Å) However, the bridging carbon atoms in Al_2Ph_6 are clearly sp^3 hybridized and are likely to be similarly hybridized in Al_2Me_6. If this is so, one might expect one proton of each bridging methyl group to be involved in an Al–C bridge bond and this is exactly what the results of ref. 5 imply.

We used the 553 independent reflections and positional and anisotropic thermal parameters for Al and C atoms[5] in a least-squares refinement and obtained virtually no changes. (Conventional *R*, 12·1%, ref. 5, 12·8%.) The difference map phased on the Al and C atoms showed remarkably distinct peaks in the area close to the bridging carbon C-1; there were more diffuse peaks near C-2 and C-3. We began with hydrogen positions found from the difference map (these were all close to those of ref. 5) and allocated initial isotropic temperature factors 10% greater than the equivalent isotropic factors of the carbon atoms to which the hydrogen atoms were attached. Least-squares refinement for hydrogen positions and isotropic temperature factors was successful ending with $R = 10{\cdot}7\%$ compared with 11·7% (ref. 5). As far as the hydrogen atoms attached to the bridging carbons C-1 are concerned, we believe that these positions are close to the true ones. The distances from C-1 are all reasonable, being H-1, 1·08(12); H-2, 1·15(14); H-3, 1·15(8) Å, and the distance of H-1 (C-1) from Al is 1·78(13) Å which agrees well with the Al–H distance of 1·72 Å found in aluminium hydride.[7] All bond lengths and angles in which the terminal hydrogen atoms are involved are within 2σ of accepted values. The aluminium–carbon bond lengths are: Al–C-1, 2·143(13); Al–C-2, 1·958(14); Al–C-3, 1·972(12) Å.

The molecule is illustrated in the Figure.[8] Atom H-1(C-1) lies close to the central ring plane (0·10 Å). Hydrogen atoms H-2(C-1) and H-3(C-1) make, with C-1, a plane which is not at right angles to the central ring but at 78·7° to it. The plane C-2–Al–C-3 is, however, at 89·2° to the central ring.

Monomeric $AlMe_3$ is D_{3h} (planar) in the vapour state[9] whereas in the dimer the Al atom is 0·60 Å away from the C-1–C-2–C-3 plane. Possibly there is not a substantial change in the energy of the Al–C bonds when the dimer is formed. The Al–C bond energy term is about 65 kcal. mole^{-1} in the monomer[10] whereas the heat of dimerization[11] is about 20 kcal.mole^{-1}. These thermochemical results are readily explained by the structure, in which dimerization is brought about by H-1(C-1) forming a two-electron hydrogen bridge bond of strength about 10 kcal.mole^{-1}.



FIGURE

Although we believe the positions of the bridging hydrogen atoms derived from the data of ref. 5 are substantially correct, $AlMe_3$ dimer is clearly of sufficient importance to warrant further study by neutron diffraction. This type of bond may be present in other organo-aluminium compounds.

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