The Bis(trimethylamine)—Alanyl Radical, $(Me_3N)_2\dot{A}lH_2$

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The e.s.r. spectrum of the title aluminium-centred radical, both in fluid solution and trapped in polycrystalline $(Me_3N)_2AlH_3$, is in accord with a quasi-trigonal bipyramidal structure; the reactions of this radical with alkyl halides and with alkenes are described.

Very few aluminium-centred radicals are known and the best characterised is the alane radical anion $H_3Al^{\cdot -}$, which we have generated in solution by hydrogen abstraction from H_4Al^- and studied using e.s.r. spectroscopy.[1] The same species is also formed during γ-radiolysis of solid tetrahydroaluminates.[2,3]

Alane (H_3Al) forms a bis(trimethylamine) complex (**1**) which is monomeric in both non-polar solvents and in the crystalline state where it adopts the trigonal bipyramidal (TBP) structure (**2**).[4] Here we report an e.s.r. study of the analogous bis(trimethylamine) complex of the alanyl radical ($H_2Al\cdot$) in hydrocarbon solvents and matrix-isolated in polycrystalline (**1**).

An anisotropic e.s.r. spectrum characteristic of axial symmetry was observed between 77 and 277 K from a powdered sample of (**1**) which had been exposed to γ-rays (^{60}Co source, dose *ca.* 1 Mrad) at 77 K. The spectrum obtained at 138 K is reproduced in Figure 1a and shows a large hyperfine splitting from ^{27}Al (I 5/2, 100% natural abundance); analysis (correct to second-order[5]) gives $a_{\parallel}(^{27}Al)$ 282.9, $a_{\perp}(^{27}Al)$ 234.3 G (1 G = 10^{-4} T), $g_{\parallel}$ 2.0012, and $g_{\perp}$ 2.0019. Values of a_{iso} (250.5 G), b (16.2 G), and g_{iso} (2.0017) may be derived from these anisotropic data. At higher temperatures, further hyperfine structure was resolvable and, because of the fortuitous coincidence of the parallel and perpendicular features when $m_I(^{27}Al)$ is +1/2, a remarkably isotropic splitting pattern was obtained for this transition (see Figure 1b). Similar additional splitting was resolvable for the other five ^{27}Al hyperfine components, but appreciable residual anisotropy was also present. The fine structure on the $m_I(^{27}Al)$ + 1/2 component is readily interpreted in terms of coupling to equivalent pairs of protons [a(2H) 9.9 G] and of nitrogen nuclei [$a(2^{14}N)$ 5.7 G] (see Figure 1c). We therefore assign this spectrum to the bis(trimethylamine)–alanyl radical (**3**).

Radical (**3**) was also generated as a transient species in solution by hydrogen-atom abstraction from (**1**) [equations (1) and (2)]. Thus, during continuous u.v. irradiation of di-t-butyl peroxide (*ca.* 15% v/v) and (**1**) (*ca.* 1 M) in cyclopropane–toluene (30 : 1—1 : 1 v/v) at 199—211 K, an isotropic spectrum composed of six equally intense broad lines was observed under conditions of low resolution (see Figure 2a). With lower modulation amplitude and microwave power, each of these six peaks was resolvable into the same nine-line pattern obtained from the matrix-isolated radical (see Figure 2b). Least-squares fitting of the line positions to the isotropic Hamiltonian[6] yielded $a(^{27}Al)$ 255.6, a(2H) 9.9, and $a(2^{14}N)$ 5.7 G, g 2.0018 at 201 K.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2\,Bu^tO\cdot \qquad (1)$$

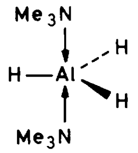
$$Bu^tO\cdot + (Me_3N)_2AlH_3 \longrightarrow (Me_3N)_2\dot{A}lH_2 + Bu^tOH \qquad (2)$$

The bis(trimethylamine)–alanyl radical (**3**) is isolectronic with the phosphoranyl radical $(Me_3C)_2\dot{P}H_2$. Phosphoranyl radicals having pairs of equivalent ligands usually adopt quasi-TBP structures of local C_{2v} symmetry in which the unpaired electron may be considered to occupy the vacant equatorial site,[7,8] as shown in (**4**),[9a] (**5**),[9b] and (**6**)[9c] for which the isotropic hyperfine splittings (in G) are given alongside the relevant nuclei. The ^{31}P hyperfine splittings for TBP phosphoranyl radicals depend very much on the electronegativities of the ligands and for (**4**)—(**6**) correspond[10] to unpaired electron populations (ρ) of 0.11—0.20 in the P-3s atomic orbital; the hybridisation ratio (ρ_{3p}/ρ_{3s}), derived from the phosphorus hyperfine anisotropy, is typically 2—2.5.[11] The isotropic splitting from a leading magnetic nucleus of an apical ligand is always much greater than that when the same ligand occupies an equatorial site.[7]

Our e.s.r. data for (**3**) indicate[10] that $\rho_{3s}(^{27}Al)$ is *ca.* 0.18 and (ρ_{3p}/ρ_{3s}) is *ca.* 3.0, and comparison of the ligand splittings with those for the phosphoranyl radicals (**4**)—(**6**) suggests that

$(Me_3N)_2AlH_3$

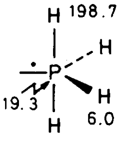
(1)



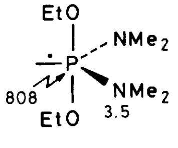
(2)

$(Me_3N)_2\dot{A}lH_2$

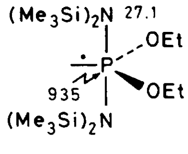
(3)



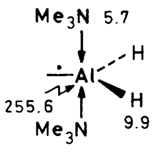
(4)



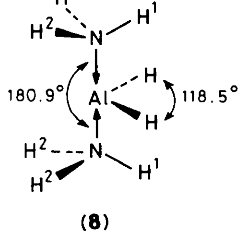
(5)



(6)



(7)



(8)

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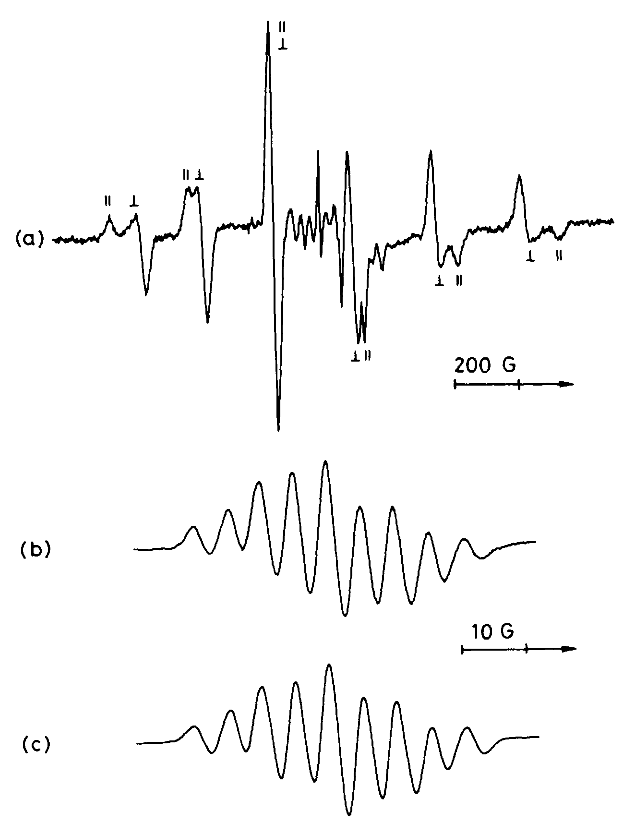

Figure 1. (a) Anisotropic e.s.r. spectrum of (**3**) in polycrystalline $(Me_3N)_2AlH_3$ at 138 K; the microwave frequency was 9051.28 MHz. Some unassigned lines are present in the central region of the spectrum. (b) Expansion of the $m_I(^{27}Al)$ +1/2 component at 276 K. (c) Computer simulation of (b) using a(2H) 9.9 and a(2N) 5.7 G; the linewidth is 3.0 G and the lineshape is 75% Lorentzian (25% Gaussian).

(**3**) also adopts a quasi-TBP structure (**7**). The unpaired electron in (**7**) would be distributed mainly between the aluminium and the apical nitrogen atoms in a SOMO of composition similar to that established for TBP phosphoranyl radicals.[7,8] The SOMO in such species is calculated to be antibonding between the central atom and the apical ligands, accounting for the reduction in a(2N) on going from (**6**) to (**7**), since the electronegativity of Al is much less than that of P.

Further support for the structure (**7**) was obtained from *ab initio* m.o. calculations for the bis(ammonia)–alanyl radical $(H_3N)_2\dot{A}lH_2$ at the UHF/6-31G** level using the GAUSSIAN 82 program.[12] Optimisation of the geometry within C_{2v} symmetry led to the structure (**8**)‡ for which the computed hyperfine splittings are +220.7 (^{27}Al), +6.4 (2N), and +0.04 G ($2H_{eq}$). An INDO I calculation[13] for (**8**) gave a(2N) +11.0 G and $a(2H_{eq})$ +12.2 G, although the computed Al-3s spin population (0.36) is much too large.

The chemical reactivity of (**3**) in cyclopropane–toluene solution appears to be similar to that of $H_3Al^{\bullet -}$.[1] Thus, in the presence of n-propyl bromide or chloride (1 M) at 200 K, the spectrum of (**3**) was replaced by that of $Pr^{n\bullet}$, showing that halogen atom abstraction takes place readily from both alkyl halides. In the presence of 1,1-di-t-butylethylene, (**3**) reacts to afford a spectrum which we assign to the very persistent adduct $Bu^t_2\dot{C}CH_2Al(NMe_3)_2H_2$[$a(^{27}Al)$ 49.3, $a(2H_\beta)$ 16.4 G,

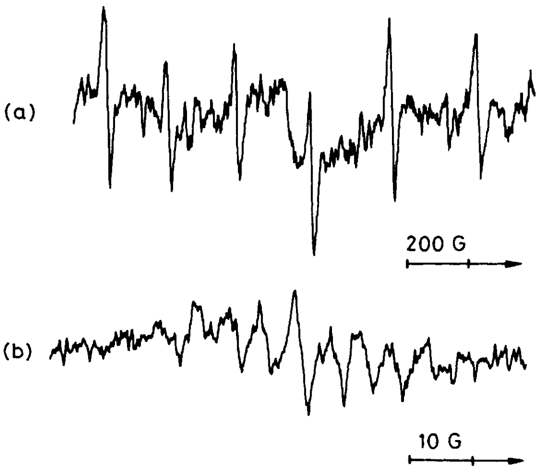

Figure 2. (a) Isotropic e.s.r. spectrum of (**3**) in cyclopropane–toluene (30 : 1 v/v) at 201 K. (b) Expansion of the $m_I(^{27}Al)$ −5/2 component at 208 K.

g 2.0024 at 235 K]. The Al–C bond must eclipse the semi-occupied C_α-$2p_\pi$ orbital in the preferred conformation of this radical.

With ethylene itself (4 M), the spectrum of a transient adduct is observed [$a(^{27}Al)$ 55.9, a(4H) 19.0 G, g 2.0025 at 197 K] although the splittings from the four protons originating from the alkene are the same within the linewidth (*ca.* 3 G) in the temperature range 197—233 K. Under forcing instrumental conditions, a further splitting (apparently a 1 : 2 : 1 triplet) of 2.7 G was poorly resolvable for the stronger lines; this splitting presumably arises from the two γ-protons attached to aluminium. The adduct could possess a symmetrically bridged equilibrium structure or a 1,2-shift of the $(Me_3N)_2AlH_2$ group might be taking place rapidly on the e.s.r. time-scale. Alternatively, and probably most likely, the difference between $a(2H_\alpha)$ and $a(2H_\beta)$ may be unresolvable within the linewidth for an unsymmetrically 'bridged' structure in which there is a large hyperconjugative interaction between the semi-occupied C_α-$2p_\pi$ orbital and the Al-C_β bond which eclipses it.

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‡ Bond lengths (Å) and bond angles (°) for (**8**) are Al–H 1.619, Al–N 2.248, N–H^1 1.002, N–H^2 1.002; AlNH^1 108.6, AlNH^2 111.2, H^{1}NH^2 108.5, and H^{2}NH^2 108.7.