

ON THE STRUCTURE OF TERTIARY ALKYL RADICALS

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E.s.r. evidence has been presented which, it is claimed, establishes that the t-butyl radical is non-planar.¹ The data were used to calculate a C-C-C angle of ca. 117°, and theoretical results supported this value. The essence of these results is that the ¹³C coupling for the central carbon atom is 45.9 G, rather than 36.7 to 40.7 G as previously supposed.² This coupling arises from (a) spin-polarisation, which occurs in planar systems (ca. 27 G, based on ¹³CH₃ at low temperatures), and (b) admixture of 2s-character into the wave function which occurs only when there is deviation from planarity. (b) can be used as a rough measure of deviations from planarity. The extent of 2s admixture is given by dividing 19 G by 1130 G, the calculated value for 100% 2s orbital occupancy.³ This gives 1.7% 2s-character. This corresponds, using Coulson's relationship,⁴ to a bond angle of ca. 119.5°, rather than the value of 117° derived previously.¹ Is this small deviation real, or is there simply a change in the extent of spin-polarisation?

An argument for bending on going from $\dot{C}H_3$ to $\dot{C}Me_3$ is based upon electronegativity differences.^{1,5} As the electronegativity difference ($X_B - X_A$) for AB₃ increases, so the tendency to become pyramidal increases. Changes in ΔX need not lead to changes in bond angle, since once planarity is achieved, all that will result as ΔX decreases is a greater resistance to bending. Now, BH₃⁻ radicals are planar, on the criterion of the isotropic coupling to boron.⁶ Since ΔX for CMe₃ falls between that for BH₃⁻ and $\dot{C}H_3$, this would imply that $\dot{C}Me_3$ radicals should certainly be planar. Also, the ¹⁴N isotropic coupling constants for NH₃⁺ and NMe₃⁺ are

almost equal. Since there is evidence for real delocalisation of the unpaired electron onto the methyl groups for NMe_3^+ radicals,⁷ spin polarisation on nitrogen has really increased. Hyperconjugative delocalisation for OMe_3 is less than that for NMe_3^+ ,⁷ so that a similar increase in spin-polarisation should show up as an increase in $A_{\text{iso}}(^{13}\text{C})$. Again, all the AB_3 radicals, AlH_3^- , SiH_3 and PH_3^+ , together with AlR_3^- , SiR_3 and PR_3^+ , (R = alkyl), show large increases in $A_{\text{iso}}(\text{A})$ compared with the values expected for planar radicals, and are surely pyramidal.⁸ The major trend on going from Al to P is a flattening, as predicted,⁵ but on going from AlH_3^- to AlR_3^- there was an increase in $A_{\text{iso}}(^{27}\text{Al})$, whilst on going from PH_3^+ to PR_3^+ there was a comparable decrease. These changes were very large compared with that presently under consideration. I conclude that no general statement regarding the expected effect on bond angle on replacing -H by -CH₃ can be made for such radicals.

The results for temperature changes on $A_{\text{iso}}(^{13}\text{C})$ and $A_{\text{iso}}(^1\text{H})$ for Me_3C radicals,¹ showed no change in the -25 to + 50°C range but below this the ^{13}C coupling increased slightly, whilst the ^1H coupling fell, the total observed changes being ca. 0.2 G. This behaviour is not indicative of non-planarity, since one would have expected any trend to be small at low temperature and to increase on heating. One might conclude that the parameters are temperature insensitive (as would be expected for planar radicals at these temperatures) and that the small changes observed in the -75°C region are caused either by a medium effect or, more likely, by restricted rotation. I conclude that deviations from planarity are much less than those suggested,¹ and that evidence cannot be taken as clear proof of non-planarity.

References

1. D.E. Wood, L.F. Williams, R.F. Sprecher, J. Amer. Chem. Soc., **94**, 6241 (1972).
2. C. Hesse and J. Roncin, Molec. Phys., **19**, 803 (1970).
3. P.W. Atkins and M.C.R. Symons, The Structure of Inorganic Radicals, Elsevier, Amsterdam (1967).
4. C.A. Coulson, Volume Commemoratif Victor Henri, Contributions à l'Etude de la Structure Moléculaire, p. 15 (1948).
5. L. Pauling, J. Chem. Phys., **51**, 2767 (1969).
6. R.C. Catton and M.C.R. Symons, J. Chem. Soc. (A), 2622 (1969).
7. J.A. Brivati, K.D.J. Root, M.C.R. Symons and D.J.A. Tinling, J. Chem. Soc. (A), 1942 (1969).
8. A. Begum, A.R. Lyons and M.C.R. Symons, J. Chem. Soc. (A), 2290 (1971).