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CONFORMATION AND HYPERCONJUGATION IN β-SUBSTITUTED ALKYL RADICALS

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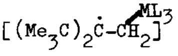
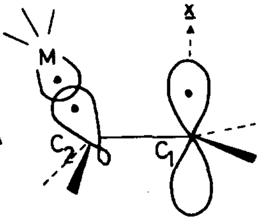
New experimental results pertaining to β-group (ML_3) interaction in radicals of type $R_2\dot{C}-CH_2ML_3$ have led Griller and Ingold(1) to conclude that the theory involving σ-π hyperconjugation, invoked by Lyons and Symons(2) to explain the conformation exhibited by certain radicals of this type, must be rejected. Since I have been responsible, not only for this recent suggestion(2), but also for the original hypothesis that β-proton hyperfine coupling arises as a result of hyperconjugation(3), it seems appropriate that I should attempt to explain why this conclusion(1) seems to me to be less than compelling. Indeed, I will try to show that the new results actually accord well with predictions based on this theory. The present situation is as follows:

(i) Krusic and Kochi(4) first established that there is a preference for conformation A for radicals of the type $R_2\dot{C}-CH_2ML_3$ (when R is H or alkyl, and M is a "heavy" atom such as Si, Sn, P or As). This was explained in terms of p(π)-d(π) homoconjugation.

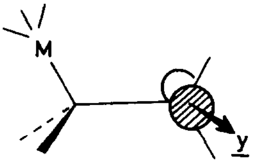
(ii) Independently, we established(2) that β-atoms (M) in such groups can exhibit unexpectedly large hyperfine coupling constants, the explanation offered being a π-σ hyperconjugation. The effect was compared with that postulated for comparable carbonium-ion systems(5,6). Subsequently, the initial theory has received support(7), but, in the present author's view, there are very firm arguments against this hypothesis(8). (However, a reverse donation involving lone-pair electrons on M is supported by both groups(7,8).)

An extremely interesting situation, nicely exploited by Griller and Ingold(1), arises when two t-butyl groups are incorporated  $[(Me_3C)_2\dot{C}-\overset{ML_3}{C}H_2]$ since these bulky groups appear to constrain group ML_3 into conformation A for purely steric reasons. This makes it possible to compare the ability of such groups to delocalise the unpaired electron with their tendency to adopt the out-of-plane configuration(A) in the absence of steric strain. The results show that $A_{iso}(^{13}C)$ for $^{13}CF_3$ or $^{13}CCl_3$ groups is considerably greater than that for $^{13}CH_3$, and indeed that the s-orbital spin-density on M, deduced from A_{iso} in the usual manner(9), is about the same for ^{29}Si in $^{29}SiMe_3$ as for ^{13}C in $^{13}CF_3$ or $^{13}CCl_3$. It is this near equality that has led to the apparently definitive dismissal of the 'hyperconjugation' theory, since β-CF_3 clearly does not adopt conformation A in the absence of steric effects(1).

A



B



I find this conclusion less than compelling for two reasons: (a) the extent of spin-polarisation and electron delocalisation arising from hyperconjugation(10) is only partially measured by the magnitude of $A_{iso}(M)$ since spin-density is also to be found in the $p(\sigma)$ orbital of M. Hence, for a given degree of delocalisation (or polarisation) A_{iso} will vary with the extent of s-p hybridisation at M in the (β) σ-bond. The way in which this varies is generally thought to be reflected in the spin-spin coupling constants, J_{H-M}, for H-ML_3 molecules. If this is accepted, then the data show that on going from H-CMe_3 to H-CF_3 or H-CCl_3, there is a large increase in J_{H-M}, thus indicating an increase in 2s-character for carbon in the H-C bond. This could at least partially account for the increase in $A_{iso}(^{13}C)$ on going from -CH_3 to -CF_3 or -CCl_3, and must similarly contribute to the far larger increase in $A_{iso}(^{29}Si)$ on going from $R_2\dot{C}CH_2SiMe_3$ to $R_2\dot{C}CH_2SiCl_3$(1). (b) Although this factor must surely be taken into account, there is another factor that needs to be considered. The problem should be viewed, at least, in terms of three electrons rather than one. Thus we need to consider the role of the C-M σ-bonding electrons as well as that of the unpaired electron in the stabilisation process. The significance of this aspect is readily seen by reference to the two-electron, carbonium ion system(11). Here, empty $d(\pi)$-orbitals on M are insignificant, but large kinetic and spectroscopic effects are found(5,6). We treat the effect as a minor perturbation on the classical structure (A). We consider the three electron system and the three component orbitals, (i) $2p_x$ on C_1, (ii) the sp^n σ-orbital on C_2 and(iii)the sp^m σ orbital on M. These combine to give M.O.(i), resembling the σ-orbital, which contains two electrons and is stabilised by the interaction which causes slight delocalisation onto C_1.

This is the effect that contributes to the marked stabilisation of carbonium ions. As indicated in Fig. 1, this will decrease as the electronegativity of M in ML_3 increases. M.O.(ii), having a node close to C_2, involves interaction between $2\underline{p}_x$ on C_1 and both the σ and σ^* C-M orbitals. This contains the unpaired electron, partially delocalised into the σ^* orbital, but largely onto M rather than C_2. Since M.O.(i) involves two electrons, and M.O.(ii) only one, we suggest that overall stability for A will be controlled more by M.O.(i) than by M.O.(ii)(12), whilst spin-delocalisation onto M involves both M.O.(i) and M.O.(ii), with the latter probably the more important.

Hyperconjugative stabilisation via M.O.(i) is reduced by replacing $-CH_3$ by $-CF_3$ and hence $-CH_3$ will be favoured in the out-of-plane site in preference to delocalisation should be greater for $-CF_3$ than for $-CH_3$, as is observed. On replacing β-CH_3 or β-CF_3 by β-$SiMe_3$, M.O.(i) becomes more important and hence conformation A is stabilised. The spin delocalisation for $-SiMe_3$ remains about the same as for $-CF_3$, but via M.O.(i) for the former, and M.O.(ii) for the latter. Another factor to be considered is the σ-σ^* splitting, which is probably smaller for C-Si than for C-C or C-H bonds. The very large increase in delocalisation for β-$SiCl_3$(1), is not likely to reflect a further increase in stability for conformation A since it is probably a consequence of delocalisation via M.O.(ii)(13).

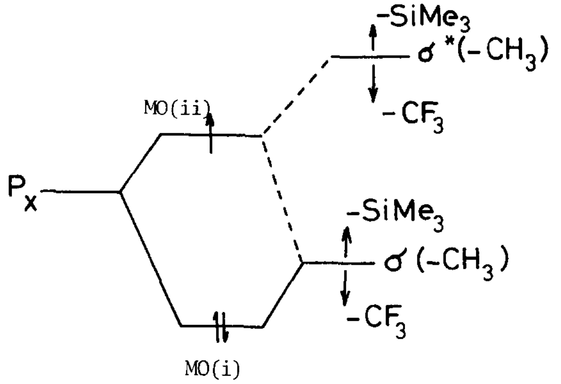


Fig. 1.

Energy level diagram depicting interaction between the $\underline{p}_x$ orbital containing the unpaired electron and the bonding and antibonding orbitals between C_2 and ML_3 in $R_2\dot{C}$-$CH_2(ML_3)$.

The extent to which factors (a) and (b) contribute to the final results is difficult to gauge. Since both must surely be involved we conclude that the results in Reference 1 in no sense eliminate π-σ hyperconjugation as a major contributing factor and indeed that they are nicely accommodated by this theory.

Finally, it is worth noting that a size effect may also contribute to stability caused by π-σ hyperconjugation. As the effective radius of M increases, so the size of the σ-orbitals in the vicinity of M also increases and the extent of overlap with the $2p_x$-orbital on C_1 increases. Since there are strong forces resisting deformation, the extent of such overlap is probably of great importance.

I thank Dr. K.U. Ingold for stimulating discussion.

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12. To assess the total barrrier to interchange between A and B, the structure of B should also be taken into account, as described in Reference (11).
13. It is significant that $A(^{29}Si)$ for R_4Si^- is likely to be ca. 50%, the value of $A(^{29}Si)$ for SiF_4^- (by analogy with comparable phosphorus radicals). This shows that delocalisation into the complete ML_3 unit should really be considered, and this will be larger for $-SiCl_3$ than for $-SiMe_3$.