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Electron Spin Resonance Evidence for Non-planarity in Some Oxygen-conjugated Carbon Radicals

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Summary E.s.r. parameters, especially $a(^{13}C)$, are consistent with the view that some oxygen-conjugated carbon radicals are not planar.

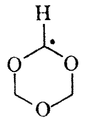
WE have been able to obtain information about the structure of some organic radicals in solution by observation of hyperfine splittings from ^{13}C in natural abundance in their e.s.r. spectra. The satellites were detected with a Varian E3 spectrometer under conditions of high gain, high modulation amplitude, very slow scan time, and high response time (up to 30 sec.); the radicals were generated with a flow technique described previously[1] with $[Ti^{III}] = [H_2O_2] = 0{\cdot}03M$ and concentrated or saturated aqueous solutions of the organic compound.

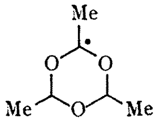
Radical (I) has $a(\alpha\text{-H}) = 0{\cdot}47 \pm 0{\cdot}02$ Oe (*cf.* ref. 2), $a(\alpha\text{-C}) = 98{\cdot}8 \pm 0{\cdot}5$ Oe, and $g = 2{\cdot}0028 \pm 0{\cdot}0001$; radical (II) has $a(\text{Me}) = 14{\cdot}85 \pm 0{\cdot}05$, $a(\alpha\text{-C}) = 107{\cdot}5 \pm 0{\cdot}3$ Oe, and $g = 2{\cdot}0029 \pm 0{\cdot}0001$. The $a(^{13}C)$-values for the tervalent carbon atoms are particularly large (*cf.*[3] 38 Oe for $\cdot CH_3$) and show that there is a significant degree of bending[4] at that atom and of *s*-character in the half-filled orbital; the bond angles apparently lie between those for $\cdot CH_2F[a(^{13}C) = 54{\cdot}8$ Oe] and $\cdot CHF_2$ $[a(^{13}C) = 148{\cdot}8$ Oe].[5]

This enables us to understand why the α-proton-splitting in the radical (I) is only 0·47 Oe. The introduction of *s*-character in the half-filled orbital should cause the splitting to change from a negative value for a planar π-radical (*e.g.*,[3] −23 Oe for $\cdot CH_3$) to a positive value for a σ-radical (*e.g.*,[6] +137 Oe for $\cdot CHO$); in (I), the degree of bending is evidently such that the splitting corresponds approximately to the point where the sign changes. The proton-splittings for $\cdot CH_2F$ and $\cdot CHF_2$ are 21·1 and 22·2 Oe, respectively,[5] and we infer, from the fact that the degree of bending in (I) is greater than that in $\cdot CH_2F$ but less than that in $\cdot CHF_2$, that the former value is negative and the latter positive, in accord with a recent calculation.[7]

We have determined $a(^{13}C)$ for $\cdot CH_2OH$ and $\cdot CMe_2OH$ as $47{\cdot}0 \pm 0{\cdot}5$ and $52{\cdot}8 \pm 0{\cdot}2$ Oe, respectively, from which we infer that these radicals are also non-planar though the degree of bending is smaller than in the bis-oxygen-substituted radicals (I) and (II).

For planar π-radicals, the successive substitution of hydrogen by an atom with an unshared pair of electrons, at positions where the spin density is appreciable, causes a progressive increase in the *g*-factor.[8] Although the *g*-factor increases when one oxygen substituent is introduced into the methyl radical[9] (*e.g.*, $g = 2{\cdot}00255$ for $\cdot CH_3$ and $2{\cdot}0033$ for $\cdot CH_2OH$), it decreases on introduction of a second oxygen substituent, as in the radicals (I) and (II), and decreases further when a third oxygen substituent is introduced $[g = 2{\cdot}0027 \pm 0{\cdot}0001$ for $\cdot C(OEt)_3]$. A tendency for *g* to decrease as the structure becomes more nearly tetrahedral is consistent with the low *g*-factors observed for carbon σ-radicals.[10]


(I)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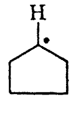
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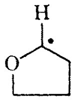
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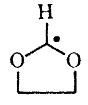
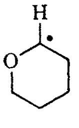

(V)


(VI)

Radical	(III)	(VI)	(IV)	(I)	(V)
$a(\alpha\text{-H})$ (Oe)	21·5	15·8	12·4	0·47	21·5
J (^{13}C–H) (Hz)	128	139	145	166	188

The values of $|a(\alpha\text{-H})|$ for the radicals (I) and (III)—(VI) are tabulated together with ^{13}C–H spin–spin coupling constants for the corresponding C–H bonds in the parent molecules. That $a(\alpha\text{-H})$ is less for (IV) than (III) is in accord with the effect of an oxygen substituent in acyclic radicals.[1] The value for (V) should not be as great as that for (III) if the signs of the two were the same, from which we infer that the sign for (V) is positive. Moreover, on the assumption that the sign for (V) is opposite to that for (III), (IV), and (VI), the values of $a(\alpha\text{-H})$ are linearly related with fair precision to the values of $J(^{13}C–H)$; such a correlation is to be expected because increase in the electronegativity of a group X should increase the *p*-character in the C–X bond,[11] and hence the *s*-character in the C–H bond of the fragment X–C–H and in the unfilled orbital of the fragment X–C•, thus affecting n.m.r. and e.s.r. couplings similarly. We conclude that the geometry at the tervalent carbon atom in the radical (V) is more nearly tetrahedral than that in (I), for a reason we shall discuss subsequently.

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