Electron Spin Resonance Studies. Part XXXII.[1] Information from Hyperfine Splittings for Aliphatic Radicals about Shape and Conformation

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A previous study of the relationship between the hyperfine splitting parameters of an aliphatic radical and the geometry at its tervalent carbon atom has been extended to a wider range of radicals. In particular, the significance of $a(^{13}C)$ is discussed, data for some simple ketyls $\cdot CR^1R^2\cdot O^-$ are reported and interpreted, and it is suggested that useful information is available from the ratio a(Me) : a(H) both for radicals $\cdot$CHMe$\cdot$X and for the pairs of radicals $\cdot$CMeXY and $\cdot$CHXY. It is noted that, in radicals of the type $\cdot CHY\cdot CH_2X$ (X = an electronegative substituent, Y = OH or OR), $a(CH_2)$ is unusually low; it is argued that this is a manifestation of an interaction which is associated with an eclipsed conformation of the C–X bond and the half-filled orbital and also with less deformation from coplanarity at the tervalent carbon atom than in the absence of X. Finally, INDO calculations for some small cyclic radicals support the conclusion from the experimental data that the species are not coplanar at the tervalent carbon atom.

We have previously presented evidence that, in organic radicals in which the tervalent carbon atom is attached to at least one hydroxy- or alkoxy-substituent, the three bonds to that carbon atom are not coplanar.[2] (For simplicity, we refer to such species as 'bent'.) The degree of bending increases with the number of such substituents and is also dependent, for cyclic radicals, on the size of the ring. It was suggested that the capacity of the oxygen-containing substituents to induce bending is related to their $+M$ effects; thus, $p\pi$-conjugation leads to an increase in the electron density at the tervalent carbon atom, and bending occurs to reduce the resulting inter-electronic repulsions. The dependence of bending on ring size was attributed to increase in the $p:s$ ratio of the ring bonds involving the tervalent carbon atom as the strain in the ring is increased. The results of INDO calculations for two of the simpler radicals were in reasonable agreement with the conclusions from the experimental data.

We have now extended our study of radical geometry to a much wider range of substituted alkyl radicals. In particular, first, we have examined the significance of $a(\alpha\text{-}^{13}C)$ in the light of data for a more extensive list of radicals than was available before. Secondly, we have explored in greater detail the possibility, previously hinted at,[2] that for radicals of the type $\cdot$CHMe$\cdot$X the ratio of the hyperfine splitting constants for the (β) methyl protons and the single (α) proton can give information about the hybridisation of the tervalent carbon atom; † we have concluded that it can do so, and this in turn has enabled us to discuss further the factors that determine the hybridisation of this carbon atom, and hence the shape of the radical, and to attempt to separate the dependence of proton-splitting constants on delocalisation within the radical from their dependence on the shapes of the species. Thirdly, we have noted the unusually low splittings for the methylene protons in radicals of the type $\cdot CHY\cdot CH_2X$ (Y = OH or OR, X = an electronegative group) and have discussed their origin. Finally, we have carried out INDO calculations for several of the radicals for which we have discussed the experimental data; in the case of some simple cyclic radicals, the results reinforce our inferences about the bent nature of these species from the experimental data.

The Interpretation of $a(\alpha\text{-}^{13}C)$.—The use of the titanium(III) ion–hydrogen peroxide system in conjunction with spectrometer conditions described before [2] enabled us to determine $a(\alpha\text{-}^{13}C)$ for the radicals $\cdot CH_2\cdot OMe$ and $\cdot$CHMe$\cdot$OH from the satellite lines due to ^{13}C in natural abundance; the values are in Table 1, together with those for $\cdot CH_2\cdot OH$ and $\cdot CMe_2\cdot OH$ determined previously.[2] (The value for the latter radical previously reported was wrongly transcribed; the correct value, 6·50 mT, is in agreement with the result from a photolytic study.[3]) We first consider the possibility that these data can be accounted for, in terms of the radicals' being planar, by means of Karplus–Fraenkel theory for $a(^{13}C)$, which takes into consideration the spin densities on atoms attached to the tervalent carbon.[4] According to this treatment, $a(\alpha\text{-}^{13}C)$ is given for the radicals $\cdot CH_2\cdot OH$ and $\cdot CH_2\cdot OMe$ by equation (i), where $S^C =$

$$a(\alpha\text{-}^{13}C) = (S^C + 2Q_{CH}^C + Q_{CO}^C)\rho_\alpha + Q_{OC}^C\rho_O \quad \text{(i)}$$

$-1·27$ mT and $Q_{CH}^C = 1·95$ mT. There are several empirically derived sets of σ–π parameters for C–O bonds, including $Q_{CO}^C = 3·60$, $Q_{OC}^C = -2·43$ mT (from studies of various radicals including quinones, some ketyls and phenoxyls, and a semidione [5]), 1·77 and $-2·71$ mT (from semiquinones [6]) (very similar to those employed by other authors [7]), and, as found for the hydroquinone radical cation,[7] 3·21 and $-4·64$ mT (the

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† α, β, γ Refer respectively to the tervalent carbon atom and successive atoms or to protons attached to these carbon atoms.

[1] Part XXXI, R. O. C. Norman and P. M. Storey, *J. Chem. Soc.* (*B*), 1971, 1009.

[2] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

[3] R. Livingston, J. K. Dohrmann, and H. Zeldes, *J. Chem. Phys.*, 1970, **53**, 2448.

[4] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

[5] M. Broze and Z. Luz, *J. Chem. Phys.*, 1969, **51**, 749.

[6] M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 1350.

[7] P. D. Sullivan, J. R. Bolton, and W. E. Geiger, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 4176.

results based on these sets of values are designated, respectively, *A*, *B*, and *C* in Table 1). Customary procedure is now to derive ρ_α by means of the McConnell relationship[8] (we took $Q_H^{CH} = -2{\cdot}3$ mT for this purpose). For the species ·CHMe·OH and $\cdot CMe_2 \cdot OH$, equation (i) requires modification to include Q_{CMe}^C and possibly, Q_{MeC}^C and ρ_{Me}^π. For Q_{CMe}^C we have employed the value (1·6 mT) which has been suggested as appropriate for an sp^2–sp^3 C–C bond,[5] rather than the value of 1·44 mT used by Karplus and Fraenkel.[4] We have derived ρ_α for ·CHMe·OH and $\cdot CMe_2 \cdot OH$ from *a*(Me),[9] with $Q_H^{Me} = 2{\cdot}93$ mT, as well as (for ·CHMe·OH) from *a*(α-H). The spin density on oxygen has been derived assuming that the methyl groups each withdraw 8% of the spin density at an α-carbon.[9] In calculating $a(\alpha\text{-}^{13}C)$ values (see Table 1), we have chosen to ignore the contribution from spin density on the methyl group (*i.e.* the contribution $\rho_{Me}^\pi Q_{MeC}^C$) because it is not clear how much of the spin density is in a π orbital nor which is the appropriate value of *Q*; in any case, its inclusion should lead to *lower* calculated values of $a(\alpha\text{-}^{13}C)$ since Q_{MeC}^C is probably negative.

TABLE 1

Observed and calculated values of $a(\alpha\text{-}^{13}C)$ for some oxygen-conjugated radicals

Radical	$a(\alpha\text{-}^{13}C)$/mT (observed)	ρ_α	$a(\alpha\text{-}^{13}C)$/mT (calculated) *A* [a]	*B* [a]	*C* [a]
$\cdot CH_2 \cdot OMe$	4·72 ± 0·03	0·730 [b]	3·89	2·48	3·01
$\cdot CH_2 \cdot OH$	4·74 ± 0·03	0·756 [b]	4·12	2·65	3·28
·CHMe·OH	5·41 ± 0·05	0·652 [b]	3·11	1·84	2·21
		0·764 [c]	4·07	2·62	3·39
$\cdot CMe_2 \cdot OH$	6·50 ± 0·05	0·675 [c]	3·21	1·91	2·47

[a] For parameters employed, see text. [b] From the McConnell equation (with $Q_H^{CH} = -2{\cdot}3$ mT). [c] From *a*(Me) (with $Q_H^{Me} = 2{\cdot}93$ mT).

The calculated values are in each case significantly lower than the observed values. Now, the McConnell treatment may not give a reliable estimate of ρ_α, and even the method based on *a*(Me) may have limitations.[2] However, the crucial points are, first, that only if ρ_α is given an unrealistically high value (essentially unity) can a value as high as 6 mT for $a(\alpha\text{-}^{13}C)$ be reproduced, and then only by the first set of σ–π parameters we have used; and secondly, for any given method of evaluating ρ_α, $a(\alpha\text{-}^{13}C)$ is predicted to decrease when a methyl substituent is introduced in place of hydrogen, whereas in practice it increases. We believe that these discrepancies arise because the hydroxy-group induces bending at the α-carbon atom, and that the degree of bending increases on the introduction of a methyl substituent;[2] in this context, it is notable that Karplus–Fraenkel treatment for the radical $\cdot CH_2 \cdot CO_2^-$, which we should expect to be planar,[2] gives calculated values for $a(\alpha\text{-}^{13}C)$ and $a(\beta\text{-}^{13}C)$ in close agreement with the experimental data.[3]

E.s.r. Spectra of Some Aliphatic Ketyls.—In order to examine further the importance of the electronic effects of oxygen substituents in determining the geometry of oxygen-conjugated alkyl radicals, we wished to compare the hyperfine splitting constants for some simple aliphatic ketyls, $\cdot CR^1R^2 \cdot O^-$, with those for their conjugate acids, $\cdot CR^1R^2 \cdot OH$. Data are available for the latter, but when this work began data for the former were limited to some radicals studied in the solid state[10] (this method not allowing measurements to be made with the precision we desired) and, in solution, to some highly hindered structures (*e.g.*,[11] $\cdot CBu^t_2 \cdot O^-$); subsequently, data were reported for two of the radicals which we have studied.[12]

We developed the titanium(III) ion–hydrogen peroxide system for the generation of three simple ketyls by oxidation of the corresponding alcohols in basic solution; with the use of tartaric acid as a sequestering agent, it was possible to make observations up to *ca.* pH 13, which was in excess of the pK_a of each of the alcohol-derived radicals.[13] When methanol was oxidised, the spectrum at pH 8·5 was essentially that of the radical $\cdot CH_2 \cdot OH$ [$a_H(2)$ 1·74 mT]; as the pH was raised, the lines of the triplet became broader (with Δ*H* decreasing in the order $\tilde{M}_s = +1 > \tilde{M}_s = -1 > \tilde{M}_s = 0$) and the splitting constant changed progressively (Table 2). The data are consistent with the view that the spectrum at pH 12·9 is essentially that of the radical anion $\cdot CH_2 \cdot O^-$ (which, as estimated from the pK_a of 10·7 for $\cdot CH_2 \cdot OH$,[13] comprises more than 99% of the equilibrium mixture of the two species at this pH) and that this and its conjugate acid undergo rapid proton exchange with each other when both are present; the asymmetric broadening results because $\cdot CH_2 \cdot O^-$ has a higher *g*-factor and a lower splitting constant than its conjugate acid. In addition, we infer that the splitting constants for the two species are of the same sign (negative), for on this assumption the calculated (averaged) splitting constants for the pH range 9·4—12·3 are in reasonable agreement with experiment whereas, on the assumption of opposite signs, they are not. Finally, it is notable that the lines in the spectrum remained relatively broad (Δ*H*, 0·1 mT) even at pH 12·9, when essentially only the radical anion is present; thus, the species $\cdot CH_2 \cdot O^-$ probably represents another example of the growing list of species with linear heavy-atom frameworks in which the line-width appears to be associated with a spin-rotation interaction arising from the highly anisotropic molecular motion of such radicals.[14,15]

Spectra from the oxidation of ethanol and isopropyl

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[8] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

[9] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[10] J. E. Bennett, *Nature*, 1964, **203**, 514.

[11] N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, 1960, **82**, 4424.

[12] K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 1186.

[13] K.-D. Asmus, A. Henglein, A. Wigger, and G. Beck, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 756.

[14] R. Livingston and H. Zeldes, *J. Magnetic Resonance*, 1969, **1**, 169.

[15] H. G. Benson, A. J. Bowles, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1971, **20**, 713.

alcohol were obtained at pH 8·0 and 13·2 (Table 2); the same spectrum as from the oxidation of isopropyl alcohol at pH 13·2 was obtained from the reduction of acetone at this pH by the titanium(III)–hydrogen peroxide–formate ion system, in which the reducing agent is [16] $\cdot\mathrm{CO_2^-}$. At pH 8·0 the splitting constants are the same as in acid solution and are those of the radicals $\cdot\mathrm{CHMe{\cdot}OH}$ and $\cdot\mathrm{CMe_2{\cdot}OH}$, respectively. By analogy with the behaviour of methanol, we infer that the splitting constants at pH 13·2 are the weighted average values for mixtures of these radicals and their respective conjugate bases; from the $\mathrm{p}K_\mathrm{a}$ values [13] ($\cdot\mathrm{CHMe{\cdot}OH}$, 11·6; $\cdot\mathrm{CMe_2{\cdot}OH}$, 12·2), the conjugate bases represent 97·5 and 91% of the equilibrium mixtures from ethanol and isopropyl alcohol, respectively, from which their calculated splitting constants are: $\cdot\mathrm{CHMe{\cdot}O^-}$, $a(\alpha\text{-H})$ 1·09 and $a(\mathrm{Me})$ 2·01 mT; $\cdot\mathrm{CMe_2{\cdot}O^-}$, $a(\mathrm{Me})$ 1·69 mT. These results are in reasonable agreement with those from solid-state studies [10] [$\cdot\mathrm{CH_2{\cdot}O^-}$, $a_\mathrm{H}(2)$ 1·5 mT; $\cdot\mathrm{CHMe{\cdot}O^-}$, $a(\alpha\text{-H})$ 1·3 and $a(\mathrm{Me})$ 1·92 mT; $\cdot\mathrm{CMe_2{\cdot}O^-}$, $a(\mathrm{Me})$ 1·61mT]; as expected, the values for $\cdot\mathrm{CH_2{\cdot}O^-}$ and $\cdot\mathrm{CMe_2{\cdot}O^-}$ are slightly lower than those reported for a solution study at pH 11—12 (when significant proportions of the conjugate acids are present) [$\cdot\mathrm{CH_2{\cdot}O^-}$, $a(\alpha\text{-H})$ 1·434 mT; $\cdot\mathrm{CMe_2{\cdot}O^-}$, $a(\mathrm{Me})$ 1·731 mT].[12]

TABLE 2

Hyperfine splitting constants (mT) for radicals derived from alcohols by oxidation in basic solution

Alcohol	pH (±0·05)	$a(\alpha\text{-H})$	$a(\mathrm{Me})$
MeOH	8·5	1·74	
	9·4	1·70	
	9·8	1·65	
	10·7	1·45	
	11·8	1·43	
	12·3	1·42	
	12·9	1·41	
EtOH	8·0	1·50	2·24
	13·2	1·10	2·02
$\mathrm{Me_2CHOH}$	8·0		1·98
	13·2		1·72

The reduction in both α- and β-proton splittings when the OH substituent is replaced by $\mathrm{O^-}$ in these radicals could be associated with an increase in the degree of bending,[2] an increase in the proportion of the spin removed on to the oxygen substituent (delocalisation),[17] or a combination of the two.

Evidence that at least the first factor is important is derived both from the ratio $a(\mathrm{Me}) : a(\alpha\text{-H})$ for the radical $\cdot\mathrm{CHMe{\cdot}O^-}$ and from INDO calculations, and each of these approaches is discussed later in detail.

We were unable to obtain $a(\alpha\text{-}^{13}\mathrm{C})$ for the radical anions in Table 2. It is notable that, for the species $\cdot\mathrm{CBu^t_2{\cdot}O^-}$, $a(\alpha\text{-}^{13}\mathrm{C})$ has the relatively high value of [11] 4·96 mT, which has been taken as evidence that the species is bent.[18] On the other hand, the alternative suggestion has been made that the high value reflects a large spin density at the α-carbon atom and also a large value of $Q_{\mathrm{CC'}}{}^{\mathrm{C}}$ (C′ = the unique carbon of $\mathrm{Bu^t}$).[5,19] However, even with $\rho_\alpha = 0{\cdot}9$ and $Q_{\mathrm{CC'}}{}^{\mathrm{C}} = 2{\cdot}1$ (a much larger value than customary), the calculated value for $a(\alpha\text{-}^{13}\mathrm{C})$ is still only 4·2 mT and, in the light of our earlier discussion, we believe that the observed value reflects a significant degree of bending. Finally, it is of interest that $a(\alpha\text{-}^{13}\mathrm{C})$ for the species $\mathrm{Bu^t{\cdot}\dot{C}(O^-){\cdot}CHBu^t_2}$ has the comparatively low value of 3·4 mT.[19] It is improbable that the replacement of one t-butyl group in the radical $\cdot\mathrm{CBu^t_2{\cdot}O^-}$ by the substituent $\mathrm{CHBu^t_2}$ could cause large enough changes in ρ_α and/or $Q_{\mathrm{CC'}}{}^{\mathrm{C}}$ to account for the marked reduction in $a(\alpha\text{-}^{13}\mathrm{C})$. We suggest instead that steric factors are responsible; thus, a bent configuration for the species $\mathrm{Bu^t{\cdot}\dot{C}(O^-){\cdot}CHBu^t_2}$ involves significantly more steric compression than a planar one, so that the species adopts a less bent configuration than other, less highly substituted, members of the series.

The Ratio $a(\mathrm{Me}) : a(\alpha\text{-H})$ *in Radicals of the Type* $\cdot\mathrm{CHMe{\cdot}X}$.—We have previously pointed out that the ratio $a(\mathrm{Me}) : a(\alpha\text{-H})$ for radicals having the general structure $\cdot\mathrm{CHMe{\cdot}X}$ lies close to $|1{\cdot}2|$ * for X = methyl, ethyl, substituted alkyl (*e.g.* $\mathrm{CH_2OH}$), cyano, or a carbonyl-containing substituent but is appreciably larger for X = OH or OEt.[2] We inferred that the value of 1·2 is typical of radicals which are coplanar at the tervalent carbon atom and that larger values reflect deformation from coplanarity and occur because, as the degree of bending increases, $a(\alpha\text{-H})$ decreases in magnitude proportionately more rapidly than does $a(\mathrm{Me})$.

We have now extended our examination of the significance of this ratio, principally with the aid of recently reported data from elsewhere and also with the use of the results we obtained for the radical $\cdot\mathrm{CHMe{\cdot}O^-}$. In addition, we examined the effect of some other oxygen-containing substituents, generating the radicals by oxidation of the appropriate parent compound $\mathrm{MeCH_2X}$ ($\mathrm{X = OMe, OPr^i, OCH(OEt)_2, OCHMeOEt}$) with the titanium(III)–peroxide system; assignments of spectra were unambiguous and details are in the Experimental section. Finally, since we wished to ascertain the effect produced by conjugation of the tervalent carbon atom with an aromatic ring, we measured the spectrum of the radical $\cdot\mathrm{CHMe{\cdot}Ph}$; the species was successfully generated by oxidative decarboxylation of α-phenylpropionic acid by the titanium(III)–peroxide system at pH 1 (*cf.* formation of the benzyl radical [20]) and its hyperfine splitting constants, assigned by analogy to those for the benzyl radical, are: 1·63 (α-H), 1·79 (Me), 0·49 (*o*-H), 0·17 (*m*-H), and 0·61 mT (*p*-H). The relevant data and ratios, *R*, of $a(\mathrm{Me}) : a(\alpha\text{-H})$ are in

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* The sign is presumably negative, but is omitted in our discussion here and in Table 3; see also the discussion of Table 4.

[16] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 400.

[17] D. R. G. Brimage, J. D. P. Cassell, J. H. Sharp, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2619.

[18] E. T. Strom, *J. Phys. Chem.*, 1968, **72**, 4715.

[19] G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, 1971, **54**, 2164.

[20] R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1967, 926.

Table 3 except for the majority of the values we have tabulated before [2] and shall not discuss here.

We cannot offer proof that the difference between the value of *R* and the value of *ca.* 1·2, which applies to species believed to be planar, increases with the degree of bending of the radical and is thus a measure of bending. Nevertheless, the assumption that this is so enables the effects of a wide variety of groups to be rationalised in a simple manner, with recourse only to other characteristics of those groups for which there is independent evidence. We note the following.

TABLE 3

Hyperfine splitting constants (mT) for β-Me and α-H in radicals of the type ·CHMeX, and their ratio

X	*a*(Me)	*a*(α-H)	*a*(Me)/*a*(α-H)	Ref.
Ph	1·79	1·63	1·10	*a*
Pr^n	2·480	2·188	1·13	*b*
CHO	2·15	1·81	1·19	*c*
CEt_3	2·49	2·17	1·15	*d*
$SiEt_3$	2·515	2·022	1·24	*e*
$GeEt_3$	2·572	2·065	1·25	*e*
$SnEt_3$	2·589	2·041	1·27	*e*
SEt	1·98	1·68	1·18	*f*
SSEt	2·06	1·68	1·23	*f*
SPh	2·076	1·680	1·24	*g*
NH_3^+	2·67	2·27	1·18	*h*
NH_2	2·02	1·53	1·32	*i*
NHEt	2·00	1·46	1·37	*j*
NEt_2	1·96	1·37	1·43	*j*
$NHCONH_2$	2·19	1·69	1·30	*k*
OH	2·24	1·50	1·49	*a*
OMe	2·20	1·37	1·60	*a*
OEt	2·228	1·396	1·60	*l*
OPr^i	2·20	1·38	1·59	*a*
OPh	2·237	1·421	1·57	*g*
$OCONH_2$	2·32	1·73	1·34	*k*
$OCH(OEt)_2$	2·30	1·51	1·52	*a*
OCHMeOEt	2·27	1·45	1·57	*a*
$OB(OEt)_2$	2·352	1·855	1·27	*m*
OPH(O)OEt	2·46	1·77	1·39	*n*
OPMe(O)OEt	2·45	1·80	1·36	*n*
$OP(O)(OEt)_2$	2·46	1·81	1·36	*n*
O^-	2·01	1·09	1·84	*a*

[a] This work. [b] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 7155. [c] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, following paper. [d] Ref. 9. [e] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 6161. [f] J. Q. Adams, *J. Amer. Chem. Soc.*, 1970, **92**, 4535. [g] A. Hudson and K. D. J. Root, *J. Chem. Soc.* (*B*), 1970, 656. [h] N. H. Anderson and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1971, 993. [i] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **53**, 3932. [j] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **52**, 3840. [k] H. Taniguchi, H. Hatano, H. Hasegawa, and T. Maruyama, *J. Phys. Chem.*, 1970, **74**, 3063. [l] H. Fischer, *Z. Naturforsch.*, 1965, **20a**, 428. [m] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 3942. [n] A. R. Metcalfe and W. A. Waters, *J. Chem. Soc.* (*B*), 1967, 340.

(i) For the first 11 entries in Table 3, *R* is close to 1·2. With the exception of the sulphur-containing substituents which we discuss below, none of the substituents is of the type which we expect to induce bending. Thus, the phenyl and formyl substituents would be expected to encourage coplanarity in order to maximise π-delocalisation (*cf.* the effects of COEt [2]), propyl would be expected to resemble methyl and ethyl,[2] the four substituents of the type MEt_3 do not have $+M$ effects, and this is true also of the substituent $-NH_3^+$ which, understandably, resembles [2] $-OH_2^+$.

(ii) The greater value of *R* for $-O^-$ than for $-OR$, indicating a greater degree of bending, can be correlated with the larger $+M$ effect of the former substituent. (It is notable that OAlkyl apparently induces a greater degree of bending than OH.)

(iii) Likewise, the greater value of *R* for OR than for $-OCONH_2$, $-OB(OEt)_2$, and the series of phosphorus-containing substituents can be related to a reduction of the $+M$ effect of oxygen in the latter group of substituents, as compared with OR, arising from the electron-withdrawing capacity of the second (formally doubly bound) oxygen atom in each member of that group.

(iv) The *R* values for the sulphur-containing substituents suggest that the radicals are not bent, in contrast to oxygen-conjugated radicals; this is in accord with a previous suggestion that sulphur groups induce smaller deviations from coplanarity than oxygen groups,[21] and it can be ascribed to the smaller $+M$ effect of sulphur than oxygen. In contrast, it can be inferred from the generally smaller values of *a*(Me) for the sulphur-containing as compared with the oxygen-containing radicals that the sulphur groups are more effective than the oxygen groups at delocalising the unpaired electron.

(v) As judged by *R* values, the four nitrogen substituents in which the nitrogen atom possesses an unshared pair of electrons all induce bending, reinforcing earlier suggestions, based on their relatively small *a*(α-H) values and supported by INDO calculations,[22] that α-aminoalkyl radicals of the types $\cdot CR_2NR_2$ (R = H or Alkyl) [22,23] and $\cdot CH(CO_2^-)NH_2$ [23,24] are bent. We further conclude that the degree of bending falls off in the orders $NEt_2 >$ NHEt $> NH_2$ (*cf.* ref. 23) and $NH_2 > NHCONH_2$, both of which mirror trends amongst the oxygen substituents.

The above approach is limited to examination of the effect of only one substituent X, in addition to H and Me, on the shape of a radical. It is desirable to extend it, if possible, so as to be able to study the effects of two other substituents. Now, from the foregoing discussion we should expect that, for planar radicals, the ratio (*R'*) of the splitting constants for the methyl-protons in a radical of the type ·CMeXY and the α-proton in one of the type ·CHXY should be approximately constant; further, since a methyl substituent removes about 8% of the spin from an adjacent tervalent carbon atom as inferred from data for the radicals $\cdot CH_2Me$, $\cdot CHMe_2$, and $\cdot CMe_3$,[9] we could anticipate that the value of *R'* for planar radicals would be about 8% less than the value of *R* for such radicals (1·2) in Table 3. This expectation was borne out in practice; as the data in Table 4 show, *R'* is close to 1·1 for those radicals which we should expect to be planar (first five entries; range 1·03—1·17).

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[23] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.

[24] H. Paul and H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 972.

The situation for bent radicals is more complex. We know that, as the degree of bending increases, *a*(α-H) (which is of negative sign in planar radicals) decreases in magnitude, passes through zero, and then increases in magnitude as it becomes positive; at the same time, *a*(Me) decreases in (positive) magnitude.[2] Hence, *R′* should at first increase, reach (−) infinity, and then decrease from (+) infinity, corresponding to its changing from negative to positive. Again the data in Table 4 are in accord with these trends. First, for those acyclic radicals which contain one oxygen- or nitrogen-conjugated substituent, *R′* is significantly greater than 1·1 except for the case in which X = OH, Y = CO_2H (in which, possibly, the tendency of the former substituent to induce bending is outweighed by the tendency for the carboxy-group to induce coplanarity and thereby maximise delocalisation of the unpaired electron.*) Moreover, *R′* is greater for radicals containing the O^- substituent than for their conjugate acids, consistent with our view that O^- induces a greater degree of bending than OH. Secondly, the value of *R′* rises considerably for the radicals from 1,3-dioxan and its 2-methyl derivative, which have been inferred previously, from other evidence, to be more bent than the mono-oxygen-conjugated radicals.[2] Thirdly, for the radicals derived from 1,3-dioxolan and its 2-methyl derivative, the very small value of *R′* is compatible with our earlier arguments [2] that these five-membered cyclic radicals are more bent than their six-membered relatives of the 1,3-dioxan series so that *a*(α-H) is positive for the radical with Z = H and *R′* is now positive also. Likewise, the very small value of *R′* for the radicals from oxiran and 2-methyloxiran is consistent with our conclusion that *a*(α-H) in the former is positive.[2] Finally, it is improbable that *R′* for the radicals from 1,1-dimethoxy-methane and -ethane could be as small as 1·2 if *a*(α-H) for the former were negative, and we suggest that this radical is sufficiently strongly bent for *a*(α-H) to be positive.

TABLE 4

Hyperfine splitting constants (mT) for the proton(s) in the group *Z*, and their ratio for *Z* = Me and *Z* = H, in radicals of the type ·CXYZ

Radical		Splitting constants for protons in the group Z			
X	Y	Z = Me	Z = H	Ratio (*R′*)	Ref.
H	H	2·687	2·304	1·17	*d, e*
H	Me	2·468	2·238	1·10	*d*
Me	Me	2·272	2·211	1·03	*d*
H	CO_2H	2·48	2·12	1·17	*f*
Me	CO_2H	2·15	2·00	1·08	*f*
OH	CO_2H	1·67	1·71	0·98	*f*
Me	O^-	1·69	1·09	1·55	*g*
Me	OH	1·98	1·50	1·32	*g*
H	OH	2·24	1·74	1·29	*g*
H	O^-	2·01	1·41	1·42	*g*
Me	NH_2	1·827	1·53	1·19	*h*
H	NEt_2	1·958	1·290	1·52	*h*
O–$[CH_2]_3$–O [a]		1·41	0·02	70·5	*i*
OMe	OMe	1·46	1·19	1·23	*i*
CH_2–O [b]		1·486	2·33	0·64	*j, i*
O–$[CH_2]_2$–O [c]		1·29	2·15	0·60	*i*

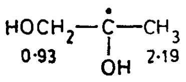
[a] 1,3-Dioxan-2-yl. [b] Oxiranyl. [c] 1,3-Dioxolan-2-yl. [d] Ref. 9. [e] R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74. [f] These radicals were obtained by oxidation of the appropriate acids under identical conditions; see Experimental. [g] Table 2; see text. [h] Ref. 22. [i] Ref. 2. [j] P. J. Krusic, personal communication.

α,β-*Disubstituted Radicals.*—We now discuss the effect which substitution in a methyl group attached to ter-

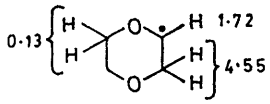
TABLE 5

Hyperfine splittings (mT) for some radicals of the type ·CHY·CH_2X [a]

Radical	Y	X	*a*(α-H)	*a*(β-H)	*a*(other)	Ref.
1	H	H	2·238	2·687		*b*
2	H	OH	2·20	2·80		*c*
3	OH	H	1·50	2·24		*d*
4	OH	OH	1·754	0·994	0·104 (OH), 0·032 (OH)	*e*
5	OMe	OH	1·70	0·86	0·18 (3H)	*f*
6	OEt	OH	1·66	0·88	0·18 (2H)	*f*
7	OBu^t	OH	1·73	0·86	0·16 (2H)	*f*
8	OH	OMe	1·823	0·884	0·179 (3H)	*g*
9	OMe	OMe	1·78	0·89	0·20 (3H)	*f*
10	OAc	OH	1·98	1·22	0·13 (3H)	*f*
11	OMe	OAc	1·76	0·80	0·20 (3H)	*h*
12	OMe	NH_3^+	1·71	1·12	0·19 (3H), 0·96 (1N)	*f*
13	OEt	NH_3^+	1·71	1·13	0·18 (2H), 0·98 (1N)	*f*
14	OBu^t	NH_3^+	1·70	1·15	0·18 (2H), 0·98 (1N)	*f*
15	OAc	NH_3^+	2·00	1·40	0·12 (3H), 0·70 (1N)	*f*
16	CO_2H	OH	2·045	2·758		*i*
17	CO_2H	NH_3^+	2·117	2·503	0·340 (1N)	*j*
18	CO_2H	Me	2·017	2·378		*k*
19	CO_2H	CO_2H	2·07	2·19		*l*
20	OH	Me	1·506	2·140		*e*
21	OMe	CO_2H	1·75	2·14	0·14 (3H)	*l*



(22)[h]



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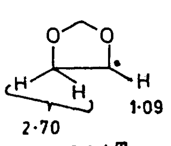

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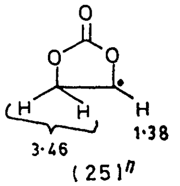

(25)[n]

[a] Splittings refer to room temperature in cases where more than one set of values exists. [b] Ref. 9. [c] Ref. 16. [d] This work. [e] Ref. 25. [f] D. J. Edge, B. C. Gilbert, R. O. C. Norman, and P. R. West, *J. Chem. Soc.* (*B*), 1971, 189. [g] A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **25**, 5311. [h] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, following paper. [i] H. Fischer, *Z. Naturforsch.*, 1964, **19a**, 866. [j] C. Corvaja, H. Fischer, and G. Giacometti, *Z. Phys. Chem.* (*Frankfurt*), 1965, **45**, 1. [k] H. Fischer and G. Giacometti, *J. Poly. Sci.*, Part C, 1967, **16**, 2763. [l] Unpublished work with Dr. D. J. Edge. [m] Ref. 2. For radical (23), *a*(β-H) is the sum of the values for axial and equatorial protons; see ref. 2. [n] C. Corvaja, M. Brustolon, and G. Giacometti, *Z. Phys. Chem.* (*Frankfurt*), 1969, **66**, 279.

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* We distinguish between radicals in which, formally, the tervalent carbon is adjacent to a π bond and those in which it is adjacent to an atom with an unshared pair of electrons; in the former, *e.g.* allyl, the unpaired spin is in a non-bonding π m.o. and the atoms concerned in π-bonding preferentially adopt a planar configuration, whereas in the latter the unpaired spin is in an antibonding π m.o. and bending is induced.

valent carbon can have on the splitting constants of the remaining two protons in the group; we shall show, in particular, that the introduction of certain electronegative substituents is associated with the occurrence of surprisingly low values of $a(\beta\text{-CH}_2)$ when the α-carbon atom is conjugated to an oxygen substituent. Some of the relevant data are in Table 5.

Our attention was first drawn to the fact that $a(\beta\text{-CH}_2)$ is far smaller for the radical $\cdot$CH(OH)$\cdot$CH$_2$OH (0·994 mT)[25] than for either $\cdot$CH$_2\cdot$CH$_2$OH (2·80 mT)[16] or $\cdot$CH(OH)$\cdot$Me (2·24 mT) (data for room temperature). Other low values of $a(\beta\text{-CH}_2)$ occur when a hydroxy- or alkoxy-group or, to a lesser extent, an acetoxy-group is attached to the α-carbon atom and a hydroxy-, alkoxy-, acetoxy-, or quaternary ammonium group is attached to the β-carbon atom; the values for these species can be compared with those for radicals with a carboxy-group at the α-carbon atom or a carboxy- or methyl group at the β-carbon atom. However, relatively large values occur when the α- and β-carbon atoms are both bonded to oxygen atoms which are part of a ring system [radicals (23)—(25)].

Now, $a(\beta\text{-H})$ is dependent upon the dihedral angle, θ, between the β-C–H bond and the singly occupied orbital, being generally given for π radicals by an expression of the form (ii) where B_0 and B are constants for a given value of ρ_α. The trends in Table 5 suggest that, in

$$a(\beta\text{-H}) = B_0 + B\cos^2\theta \qquad \text{(ii)}$$

certain structural situations, conformations in which θ is large are especially important; that is, there is a factor energetically favourable to conformations in which the β-C–X bond eclipses, or comes near to eclipsing, the half-filled orbital at C_α. Moreover, an explanation for the occurrence of low values of $a(\beta\text{-CH}_2)$ based on conformational preferences would be in accord with the fact that the values for the cyclic di-oxygen-substituted radicals (23)—(25), in which the β-C–O bond is structurally prevented from adopting such a position relative to the half-filled orbital, are not anomalously low.

However, a detailed examination of the results reveals that the situation has an added complexity. In the expression (ii) relating $a(\beta\text{-H})$ to θ, it has proved hard to ascertain the value of B_0, but although one calculation suggested a small negative value (—0·11 mT),[26] it is usually considered to be of positive sign[27] and a recent treatment, based on the temperature dependence of the splitting for the tertiary aliphatic protons in the tris-(*p*-isopropylphenyl)methyl radical points to a small positive value.[28] Consider the radical $\cdot$C(OH)Me$\cdot$CH$_2$OH, in which the methyl and hydroxymethyl substituents are influenced by the same ρ_α. Then, if B_0 were zero, B, as derived from a(Me) for which $\langle\cos^2\theta\rangle = \frac{1}{2}$, would be 4·38 mT; it would follow that the lowest possible value for $a(\beta\text{-CH}_2)$, which would only occur for a fixed conformation with $\theta = 60°$, would be $\frac{1}{4}B$, *i.e.* 1·09 mT, which is significantly greater than the observed value. Further, B_0 would need to have the improbably large negative value of —0·33 mT for the data for both a(Me) and $a(\beta\text{-CH}_2)$ to be fitted by the equation. In other words, even an essentially fixed conformation with $\theta = 60°$ for each β-C–H bond—corresponding to $\theta = 0°$ (complete eclipsing) for the β-C–O bond—would seem unlikely to give quite so low a value for $a(\beta\text{-CH}_2)$. [The same general considerations apply to other radicals in Table 5 in which $a(\beta\text{-CH}_2)$ is less than *ca.* 1 mT, but detailed treatment is less precise because comparisons have to be made with radicals in which ρ_α may differ slightly.]

It is also notable that the factor which establishes preferred conformations in which the values of θ for the β-C–H bonds are (approaching) 60° is not a simple bulk effect, for if it were we should expect low values of $a(\beta\text{-CH}_2)$ for the radicals (16)—(21). Instead, the effect appears to be a co-operative one involving specific pairings of α- and β-substituents.

We examined the phenomenon further by more detailed study of the radical (4) from ethylene glycol. With appropriate experimental conditions,[2] we were able to discern satellites from ^{13}C in natural abundance and thus to determine $a(\alpha\text{-}^{13}\text{C})$ as 4·47 ± 0·05 mT at 7 ± 3°. We also measured the hydrogen hyperfine splitting constants for this radical as a function of temperature; the data are in Table 6. Two features of the results are notable. First, $a(\alpha\text{-}^{13}\text{C})$ for the radical (4) is significantly smaller than that for the radical $\cdot$CHMe$\cdot$OH (5·41 mT), suggesting that the former radical is less bent than the latter; moreover, this view is in accord with the fact that $a(\alpha\text{-H})$ is larger for the radical (4) than for $\cdot$CHMe$\cdot$OH. Secondly, the increase with temperature of $a(\beta\text{-H})$ for the radical (4) is in contrast to the decrease for the radical $\cdot$CH$_2\cdot$CH$_2$OH [for which $a(\beta\text{-H})$ is 3·167 mT at[25] —71° and 2·80 mT at room temperature[16]]; while the latter trend suggests that preferred conformations for the radical $\cdot$CH$_2\cdot$CH$_2$OH are of the type (26), which become relatively less populated as the temperature is raised,[29] the former trend is consistent with our view that the preferred conformation for the radical (4) is (27). [Moreover, the temperature dependence of $a(\beta\text{-H})$ for radical (4) can be approximately fitted

TABLE 6

Hyperfine splitting constants (±0·005 mT) for the radical $\cdot$CH(OH)$\cdot$CH$_2$OH at various temperatures (±2°)[a]

Temp.	$a(\alpha\text{-H})$	$a(\beta\text{-H})$	a(O–H)
8°	1·811	0·926	0·106
29	1·789	0·955	0·084
43	1·780	0·976	0·069
53	1·764	0·992	0·069

[a] An incompletely resolved splitting of *ca.* 0·02 mT was also observed, evidently from the other OH proton.

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[25] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.

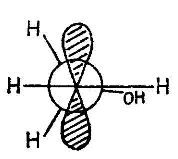
[26] J. P. Colpa and E. de Boer, *Phys. Letters*, 1963, **5**, 225; *Mol. Phys.*, 1964, **7**, 333.

[27] D. H. Geske, *Progress in Phys. Org. Chem.*, 1967, **4**, 125.

[28] N. L. Bauld, C. E. Hudson, and J. S. Hyde, *J. Chem. Phys.*, 1971, **54**, 1834.

[29] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

to a linear relationship, extrapolation of which gives the remarkably low value of *ca.* 0·5 mT at low temperature, presumably associated with conformation (27).] In addition, a(β-H) was found to increase with temperature for two other radicals containing α- and β-hydroxy-substituents; for the radicals ·CH(OH)·CH(OH)·CH$_2$OH and ·C(OH)(CH$_2$OH)$_2$, a(β-H) = 1·08 and 1·02 mT at 8°, and 1·13 and 1·06 mT at 43°.



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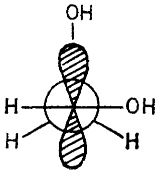
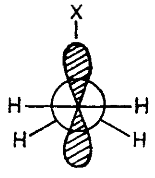
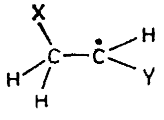


(27)



(28)

Finally, it should be noted that there are precedents for the occurrence of relatively low β-proton splittings, namely, in radicals of the type ·CH$_2$·CH$_2$X where X is Cl [for which a(β-CH$_2$) = 1·15 mT], SMe [a(β-CH$_2$) = 1·49 mT], or a silicon-, germanium-, or tin-containing substituent.[29-31] It has been suggested that these reflect the preferential population of conformations such as (28) in which the C–X bond eclipses the half-filled orbital, and that this in turn results from a stabilising 1,3-interaction for such conformations between the half-filled orbital and a suitable *d* orbital on the substituent.[29,30] However, such an interaction cannot be involved in our case because of the unavailability of *d* orbitals on oxygen; in any case, radicals of the type ·CH$_2$·CH$_2$OR do not have unusually low values of a(β-CH$_2$). Instead, we suggest the following rationalisation of the low values in the α,β-disubstituted radicals to which we have referred: in a radical of the type ·CHY·CH$_2$X, in which Y is a substituent with at least one unshared pair of electrons, the C–X bond tends to make a dihedral angle of 0° with the singly occupied orbital so as to maximise interactions of the type represented by the contribution of the structures (30) and (31). We justify this suggestion in the sequel.



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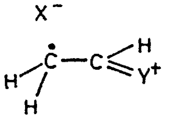

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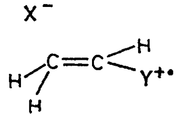

(31)

First, the contribution of the structures (30) and (31) should increase as the capacity of Y to release unshared electrons is increased (+*M* effect), in accord with the observation that a hydroxy- or alkoxy-group induces a larger effect than an acetoxy-group [*cf.* a(β-CH$_2$) for radicals (4)—(7) and (10)] and that substituents such as methyl and carboxy are ineffective. Likewise, the contribution of these structures should increase as the capacity of X to become associated with both electrons of the C–X bond is increased, in accord with the fact that acetoxy- and quaternary ammonium substituents, as well as hydroxy- and alkoxy-groups, are effective, whereas groups such as carboxy are not.

Secondly, the contribution of structures (30) and (31) should be associated with a tendency for the α-carbon atoms to form coplanar bonds, in accord with the inference from a(α-^{13}C) and a(α-H) data that the radical ·CH(OH)·CH$_2$OH is less bent than ·CH(OH)·Me. [We have previously discussed in a similar manner the evidence that ·CH(OH)·CF$_3$ is a less bent species than ·CH(OH)·Me.[2]]

Thirdly, the contribution of structures (30) and (31) is associated with deformation of the geometry of the β-carbon atom from tetrahedral towards coplanar insofar as bonding to the two hydrogen and one carbon atoms is concerned. This distortion could reduce hyperconjugative interaction between β-C–H and the half-filled orbital, as compared with that in a radical of the type ·CHY·Me for the same dihedral angle, and so could account for the fact that a(β-CH$_2$) can fall below the minimum value expected on the basis of equation (ii) and reference to a(Me) values. In support of this view, it is notable that INDO calculations for the ethyl radical show that, when one C–H bond is fixed with $\theta = 0°$ and then brought nearer the perpendicular with respect to C–C so as to deform the geometry at β-carbon in the way we have described, the splitting constants of the remaining two β-protons ($\theta = 60°$) are predicted to decrease.[29]

INDO Calculations.—We have carried out INDO m.o. calculations on some of the radicals discussed in this paper and on some of those discussed previously.[2]

The data in Table 7 were obtained by varying the geometry of each radical until its calculated energy was minimised. For the cyclic radicals, bond lengths and angles were taken from results of gas-phase electron-diffraction and microwave studies for the parent compounds,[32] ϕ was defined as the angle between the plane of the ring atoms and the α-C–H bond, and θ as the angle between this bond and the line from the α-carbon either bisecting the CH$_2$–CH$_2$ bond (cyclopropyl) or β-C–O bond (oxiranyl) or joining the γ-carbon atom (the four-membered cyclic species); a negative sign for θ indicates that the α-C–H bond is on the same side of this line as the ring oxygen. The values of θ and ϕ were varied alternately in an iterative procedure (θ in 2° steps and ϕ in 2·5° steps) until a minimum for the energy was found; the values of θ and ϕ so obtained are recorded in Table 7. (The previous calculation for oxiranyl employed a fixed value of θ.) For the radical anion ·CH$_2$·O$^-$, the C–H bond length was fixed at 1·08 Å with, initially, all the atoms coplanar and an $\angle$HCH of 120°. The C–O bond length was varied in 0·01 Å steps, giving an energy minimum at 1·31 Å, and this value was used while the $\angle$HCH was varied in 2·5° steps, giving an energy minimum at an angle of 112·5°. For these

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[30] J. K. Kochi and P. J. Krusic, *Chem. Soc. Special Publ.* **24**, 1970, ch. 7.

[31] A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Letters*, 1970, **5**, 552.

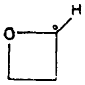
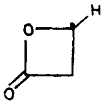
[32] 'Tables of Interatomic Distances,' *Chem. Soc. Special Publ.* 11, 1958.

values, the hydrogen and oxygen atoms were moved out of the initial plane and the angle ϕ, defined as that between the bonds and this plane, was varied in 1° steps, giving a minimum energy at $\phi = 11°$.

For the cyclic radicals, not only are bent structures predicted but also there is reasonably good agreement between the predicted splitting constants after annihilation and the observed values provided that the latter are positive for the α-protons (as we have previously argued that it is in the case of the oxiranyl radical [2]). Thus, the data are in accord with our earlier assertions that the introduction of oxygen at the tervalent carbon induces bending, that ring-strain can have the same effect, and that the two factors can be co-operative (compare the predicted value of ϕ for the oxiranyl radical with that for the cyclopropyl radical on the one hand and that for the oxetan-2-yl radical on the other). However, although the radical anion $\cdot CH_2\cdot O^-$ is predicted to be bent (*cf.* the calculated value of $\phi = 10°$ for its conjugate acid [2]), the predicted α-proton splitting is positive, contrary to the indications from experiment [for $\cdot CH_2\cdot OH$, also, the predicted $a(\alpha\text{-H})$ for the calculated configuration of minimum energy was in rather poor agreement with experiment [2]].

TABLE 7

INDO calculations for some small radicals

	Geometry [a]			Hyperfine splittings and $\langle S^2\rangle$		
				Calculated		
Radical	θ	ϕ		Before annihilation	After annihilation	Observed
	0°	35°	$a(\alpha\text{-H})$	−0·178	+0·884	0·65[b]
			$a(\beta\text{-H})$	+2·103[c]	+1·940[c]	2·34[b]
			$\langle S^2\rangle$	0·75421	0·75002	
	−16·6	40	$a(\alpha\text{-H})$	+1·728	+2·697	2·33[d]
			$a(\beta\text{-H})$	+1·049[c]	+1·068[c]	0·61[d]
			$\langle S^2\rangle$	0·75304	0·750006	
	−12·5	32·5	$a(\alpha\text{-H})$	−0·165	+0·838	0·81[d]
			$a(\beta\text{-H})$	+2·649[c]	+2·371[c]	2·83[d]
			$a(\gamma\text{-H})$	−0·071[c]	+0·011[c]	0·16[d]
			$\langle S^2\rangle$	0·75558	0·75002	
	−10	30	$a(\alpha\text{-H})$	−0·289	+0·690	0·65[e]
			$a(\beta\text{-H})$	+2·054[c]	+1·877[c]	1·79[e]
			$\langle S^2\rangle$	0·75427	0·75002	
$\cdot CH_2O^-$		11[b]	$a(\alpha\text{-H})$	+0·647	+1·267	1·42[e]
			$\langle S^2\rangle$	0·755071	0·750004	

[a] Defined in the text. [b] Ref. 9. [c] Average value of two non-equivalent splittings. [d] Ref. 2. [e] This work. [f] This value of ϕ is defined differently; see text.

EXPERIMENTAL

A Varian E-3 spectrometer, with **100 kHz** modulation and an *X*-band klystron, was employed. The magnetic field scan was calibrated with *p*-benzosemiquinone (a_H 0·237 mT) and Fremy's salt (a_N 1·30 mT); [33] splitting constants were measured to within 0·005 mT (except where stated otherwise) both directly and by comparison with an internal standard when one was present. We estimate the errors in the splittings reported for the high pH spectra from isopropyl alcohol and ethanol as ±0·01 mT. *g*-Factors were measured to within ±0·0001 by comparison with Fremy's salt (*g* 2·0055). With the exception of those mentioned below, all the materials were commercial samples and were used without further purification. Ethyl isopropyl ether was prepared from the reaction of sodium isopropoxide in isopropyl alcohol with diethyl sulphate and was collected as it distilled from the reaction mixture. Ethyl methyl ether was prepared by the reaction of diethyl sulphate with sodium methoxide in methanol, the ether being distilled off and bubbled directly into water to form one of the solutions used in the flow experiments.

INDO calculations [34] were carried out with a version of the INDO programme, kindly supplied by the Quantum Chemistry Programme Exchange, modified for compatibility with the Elliot 4130 computer; the annihilation routine [35] was kindly incorporated by Mr. M. F. Chiu, and utilised the appropriate parameters.[36]

Generation of Radicals.—A Varian mixing chamber coupled to an aqueous sample cell was used; each reactant was passed, with gravity feed, at a flow rate of *ca.* 180 ml min^{-1}. In most cases each solution was deoxygenated by passage of a stream of nitrogen. The variable-temperature studies were carried out by adjusting the temperature of the reactant solutions with the appropriate combination of ice or water heaters before the flow was connected. Thermometers placed near to the entry ports of the mixing chamber were used to monitor the temperature of both solutions immediately before mixing.

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For pH 1, the reactants were typically as follows. The first solution contained 12·5% (w/v) titanium(III) chloride solution (10 ml/l) and concentrated sulphuric acid (10 ml/l), and the second contained 100-volume hydrogen peroxide (3 ml/l) and the organic compound (*ca.* 10 ml/l or 10 g/l). Conditions for observations of ^{13}C satellites were as reported previously.[2] To achieve the high pH values required for obtaining ketyl radicals, reactant solutions were made up as follows: the first solution contained 12·5% (w/v) titanium(III) chloride (10 ml/l), tartaric acid (2·5 g/l), and the appropriate amount of either sodium hydroxide or potassium hydroxide, and the second solution contained 100-volume hydrogen peroxide (0·66 ml/l) and the appropriate alcohol (20 ml/l).

Radicals from various ethers, acids, and hydroxy-acids were studied in order to obtain a(α-H) and a(β-H) values for inclusion in Tables 3 and 4. In some cases extra splittings were detected and other radicals analysed: there follows a complete analysis of the e.s.r. spectra observed. Oxidation of triethyl orthoformate at neutral pH in the flow system, employing disodium ethylenediaminetetra-acetate,[2] gave a spectrum analysed in terms of a mixture of three radicals, $\cdot C(OEt)_3$ (*g* 2·0027), $\cdot CH_2CH_2OCH(OEt)_2$ [*g* 2·0025, a(α-H) 2·19, a(β-H) 2·72 mT], and $\cdot CHMe\cdot OCH(OEt)_2$ [*g* 2·0031, a(γ-H) 0·05 mT, α-H and β-H h.f.s. given in Table 3]. Oxidation of acetaldehyde diethyl acetal under similar conditions gave a mixture of radicals, assigned as follows: $\cdot CMe(OEt)_2$, reported previously;[2] $\cdot CHMe\cdot OCHMe\cdot OEt$ (*g* 2·0031, α-H and β-H splittings given in Table 3, with no further resolvable hyperfine structure); $\cdot CH_2CH_2\cdot OCHMe\cdot OEt$ [*g* 2·0026; a(α-H) 2·22, a(β-H) 2·75 mT] and $\cdot CH_2CH(OEt)_2$ [*g* 2·0027; a(α-H) 2·22, a(β-H) 2·70 mT]. Oxidation of ethyl methyl ether gave $\cdot CHMe\cdot OMe$ [with a(γ-H) 0·13 mT in addition to the splittings given in Table 3] and $\cdot CH_2OCH_2CH_3$ [a(α-H) 1·68, a(γ-H) 0·19 mT]. Ethyl isopropyl ether gave $\cdot CHMe\cdot OPr^i$ [with a(γ-H) 0·09 mT in addition to α- and β-splittings, Table 3] and $\cdot CMe_2\cdot OEt$ [a(β-H) 1·98, a(γ-H) 0·13 mT]. At pH 1, oxidation of lactic and glycollic acids, respectively, gave spectra assigned to the radicals $\cdot CMe(OH)\cdot CO_2H$ [*g* 2·0038; a(β-H) 1·67, a(OH) 0·19 mT] and $\cdot CH(OH)\cdot CO_2H$ [*g* 2·0038; a(α-H) 1·71, a(OH) 0·25 mT]. Oxidation of β-propiolactone gave mainly the radical described in Table 7 (*g* 2·0030) and a second species [$a_H(3)$ 1·64 mT, *g* 2·0031] which is presumably the radical formed by abstraction from the methylene group adjacent to carbonyl.

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