Investigations of Structure and Conformation. Part IV.[1] An Electron Spin Resonance and INDO Molecular Orbital Study of the Influence of Electronic Interactions upon Radical Geometry

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INDO MO Calculations provide support for conclusions based on e.s.r. hyperfine splittings that α-hydroxyalkyl radicals are bent at the radical centre and that α,β-dihydroxy- and α-hydroxy-β-ammonio-ethyl radicals preferentially adopt an almost eclipsing conformation: evidence is also obtained that in this conformation there is distortion from tetrahedral geometry at the β-carbon (this explains the unusually low β-hydrogen splittings observed). In contrast, the radical $\cdot CH_2 \cdot CH_2OH$ is planar at the radical centre and prefers a conformation in which the β-C–O bond subtends an angle of 90° with the orbital of the unpaired electron.

ISOTROPIC e.s.r. hyperfine splittings for the radical $\cdot CH(OH) \cdot CH_2OH$ have been interpreted[2] in terms of a specific interaction between the radical centre (rendered carbanion-like by the $+M$ effect of the α-hydroxy-group) and the β-C–O bond. It has been suggested[2] that there is a highly preferred, eclipsing conformation with distortion from tetrahedral geometry at the β-carbon [this would account for the anomalously low a(β-H), 0·926 mT at 8°], and also that the geometry about the tervalent carbon is more nearly planar than is that in the radical

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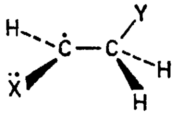
[1] Part III, B. C. Gilbert, R. O. C. Norman, and M. Trenwith, *J.C.S. Perkin II*, 1974, 1033.

[2] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 786.

$\cdot$CH(OH)Me [$\cdot$CH(OH)$\cdot$CH$_2$OH has $a(\alpha\text{-}^{13}C)$ 4·47 mT (at 7°) and $a(\alpha\text{-H})$ 1·789 mT (at 29°); *cf.* 5·41 and 1·50 mT, respectively, for $\cdot$CH(OH)Me]. The interaction appears to be typical [3,4] for ethyl radicals having both a $+M$ α-substituent (*e.g.* hydroxy, alkoxy, acetoxy, halogeno, alkylthio) and a β-substituent with an electron-withdrawing $-I$ effect (*e.g.* hydroxy, alkoxy, acetoxy, quaternary ammonium), to an extent which is dependent on the combined effects of both. Evidently the phenomenon is analogous to that thought [5] to account for the preferred conformations of ionic species ($^+$CH$_2\cdot$CH$_2$Y, $^-$CH$_2\cdot$CH$_2$Y) and can be represented as in (1) and (2).



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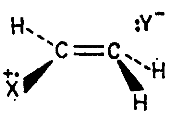

(2)

We note, further, an estimate for the barrier to rotation about the C_α–C_β bond in $\cdot$CH(OAc)$\cdot$CH$_2$OH, obtained [6] from an analysis of the temperature dependence of $a(\beta\text{-H})$, of 6·3—8·4 kJ mol^{-1}. It has also been pointed out [3] that those radicals of the type $\cdot$CH(X)$\cdot$CH$_2$Y which undergo subsequent fragmentation reactions are just those for which an eclipsing conformation is apparently favoured.

In order to derive more extensive evidence for the determination of radical structure and conformation by electronic interactions we have extended earlier variable temperature e.s.r. studies [2] to include both a wider range of radical type and an investigation of the dependence of hyperfine splittings in some radicals on solvent composition. Furthermore, INDO (Intermediate Neglect of Differential Overlap) MO calculations [7] have been performed for the species $\cdot$CH(OH)$\cdot$CH$_2$OH, $\cdot$CH(OH)$\cdot$CH$_2\overset{+}{N}$H$_3$, $\cdot$CH(OH)Me, and $\cdot$CH$_2\cdot$CH$_2$OH. It was hoped that preference for an eclipsing conformation might be demonstrable for the first two radicals, and that the geometrical consequences of the electronic interaction involving distortion at the β-carbon [and consequently a lower $a(\beta\text{-H})$] and flattening at the α-carbon [higher $a(\alpha\text{-H})$, lower $a(\alpha\text{-}^{13}C)$] would be detectable. Particular consideration was also paid to the angular dependences of calculated β-splittings for all species.

EXPERIMENTAL

E.s.r. spectra were recorded on Varian V4502 and E3 spectrometers, each equipped with 100 kHz modulation and an X-band klystron. The procedure for measuring hyperfine splittings, the errors in which are reported when appropriate, has been described; [8,9] spectrum simulation was effected with a program kindly supplied by Dr. M. F. Chiu. Apart from 1-[*N*-methyl-*N*-(2-hydroxypropyl)-amino]propan-2-ol, which was prepared by the method of Foster and West,[10] all materials were commercial samples and were used directly, with the exception of di-t-butyl peroxide which was purified on a basic alumina column. Measurements of pH were made to within ±0·1 unit using a Beckman model 72 pH meter and a phthalate buffer as standard.

INDO MO Calculations were executed, using the program described in ref. 9, on the Elliot 4130 computer at the University of York.

Radicals were generated in the cavities of the e.s.r. spectrometers by hydrogen abstraction from parent compounds with $\cdot$OH, from the reaction in a flow system of H$_2$O$_2$ and Ti^{III}, or with $\cdot$OBu^t, generated photolytically. Two- and three-way, single-stage mixing flow systems with gravity feed and flow rates of *ca.* 100 ml min^{-1} for each stream were employed; all solutions were deoxygenated with a nitrogen purge. Temperature variation was achieved using iced or hot water, and the mean values quoted (±2°) were measured with thermometers placed in each stream just before entry of the solutions into the cavity. Reactants for experiments (with compounds other than ethane-1,2-diol and amino-derivatives) which were conducted in the two-way system at pH 1—2 were typically as follows. One solution contained 12·5% (w/v) titanium(III) chloride solution (10 ml l^{-1}), concentrated sulphuric acid (*ca.* 5 ml l^{-1}), and the organic substrate (*ca.* 10 ml l^{-1}); the other solution contained 100-volume hydrogen peroxide solution (3 ml l^{-1}) and similar concentrations of acid and organic compound. Flow experiments with ethane-1,2-diol were conducted at pH *ca.* 5 [where dehydration of $\cdot$CH(OH)$\cdot$CH$_2$OH to $\cdot$CH$_2$CHO does not occur [3]], in which case sulphuric acid was omitted from both streams, the former containing disodium ethylenediaminetetra-acetate (6 g l^{-1}) and sufficient ammonia (*d* 0·880) to adjust to the appropriate effluent pH. Amino-compounds were investigated with the three-way flow system, the substrate being separated from the Ti^{III} stream (to avoid complexation) and the peroxide solution (to avoid nitroxide formation). Typical conditions for reaction at pH 1—2 are those described in ref. 1. For non-aqueous studies a flow system comprising a special small-scale apparatus having an integral glass mixing chamber and sample cell was employed. Reactant concentrations and other conditions were similar to those described above, although the attainment of sufficiently high flow rates often necessitated application of water-pump suction to the outlet tube of the system.

The photolytic generation of radicals employed continuous irradiation from a 2 kW Thorn xenon lamp focused on the spectrometer cavity with a quartz optical system incorporating a water filter. The organic substrate was mixed with either acetone or di-t-butyl peroxide in which latter case a solvent was admixed; all solutions were degassed on a vacuum line using a freeze–thaw technique. A V4540 variable temperature accessory was employed to control the temperature of each sample, which was measured to within ±2° with a thermocouple.

RESULTS AND DISCUSSION

E.s.r. Spectroscopy.—Splitting constants in aqueous solution as a function of temperature (in the range 7—46°)

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[3] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

[4] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Magnetic Resonance*, 1973, **11**, 100.

[5] R. Hoffmann, L. Radom, J. A. Pople, P. von R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, 1972, **94**, 6221.

[6] R. Gablick and J. Hellebrand, Magnetic Resonance Related Phenomena, Proceedings Congress AMPERE, 1970, p. 1184.

[7] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[8] B. C. Gilbert and M. Trenwith, *J.C.S. Perkin II*, 1973, 1834.

[9] B. C. Gilbert and M. Trenwith, *J.C.S. Perkin II*, 1973, 2010.

[10] T. Foster and P. R. West, *Canad. J. Chem.*, 1973, **51**. 4009.

TABLE 1

Hyperfine splitting constants (mT) for some radicals of the type $\cdot CH(X)\cdot CH_2Y$ in aqueous solution at various temperatures

Radical	T/°C (±2°)	a(α-H)	a(β-H)	a(Other H, N) [a]	
$\cdot CH(OH)\cdot CH_2OH$ [b]	9	1·811	0·926	0·106 (α-OH)	[c]
	22	1·794	0·948	0·094 (α-OH)	0·020 (β-OH)
	32	1·786	0·966	0·084 (α-OH)	0·020 (β-OH)
	40	1·780	0·977	0·079 (α-OH)	0·021 (β-OH)
	46	1·759	0·975	0·071 (α-OH)	0·022 (β-OH)
$\cdot CH(OMe)\cdot CH_2OMe$ [d,e]	9	1·778	0·875	0·192 (α-OMe)	
	19	1·766	0·873	0·190 (α-OMe)	
	27	1·763	0·878	0·190 (α-OMe)	
$\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ [d]	9	1·834	1·163	0·113 (α-OH)	1·059 (β-N)
	22	1·813	1·169	0·103 (α-OH)	1·050 (β-N)
	30	1·806	1·172	0·096 (α-OH)	1·042 (β-N)
$\cdot CH(OH)Me$ [b]	8	1·515	2·263		
	23	1·497	2·253		
	33	1·496	2·259		
	45	1·491	2·253		
$\cdot CH_2\cdot CH_2OH$ [d]	7	2·193	2·780		
	18	2·184	2·769		
	32	2·183	2·768		
	44	2·178	2·753		

[a] Assignment in parentheses. [b] Splittings ±0·003 mT. [c] Expected β-OH splitting incompletely resolved [see Figure 1(a)]; see text for assignment. [d] Splittings ±0·006 mT. [e] Spectra above *ca.* 30° dominated by $\cdot CH_2O\cdot CH_2\cdot CH_2OMe$.

for the radical $\cdot CH(OH)\cdot CH_2OH$ from ethane-1,2-diol (at pH 5·3), $\cdot CH(OMe)\cdot CH_2OMe$ from 1,2-dimethoxyethane (pH 1·9), $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ from ethanolamine (pH 1·4) and both $\cdot CH(OH)Me$ and $\cdot CH_2\cdot CH_2OH$ from ethanol (pH 1·9) are presented in Table 1; they are generally in accordance with those reported previously for these species (see, *e.g.*, refs. 2, 3, and 10).

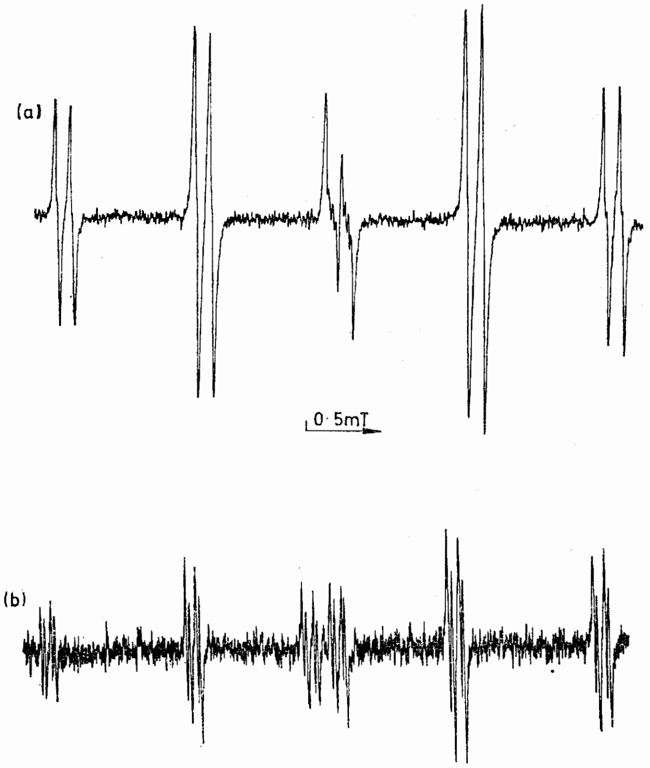
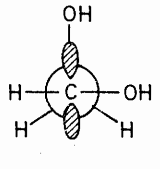


FIGURE 1 E.s.r. spectrum of the radical $\cdot CH(OH)\cdot CH_2OH$ from ethane-1,2-diol at (a) 9 ± 2° and (b) 46 ± 2°

In an earlier investigation we demonstrated that for $\cdot CH(OH)\cdot CH_2OH$ a(β-H) increases while a(α-H) decreases with increasing temperature, consistent with thermal depopulation of the eclipsing conformation (3) [see also (1) and (2)]. In confirming this we have now been able to achieve complete resolution of the hydrogen splitting from the β hydroxy-group * (except at 9°); Figure 1 shows the spectra recorded at 9 and 46°. Similar, though less marked trends are noted for the radicals from 1,2-dimethoxyethane and ethanolamine. Moreover, the observation for the latter species that a(β-N) *increases* with decreasing temperature also suggests [if we assume [3] that a(β-N) arises through a hyperconjugative interaction and therefore depends on $\cos^2 \theta_N$] that a conformation akin to (3) is favoured.



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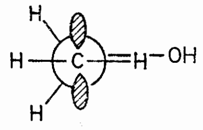

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The much larger value of a(β-H) for $\cdot CH_2\cdot CH_2OH$ than for $\cdot CH(OH)\cdot CH_2OH$ and related radicals suggests that for this species conformation (4) is favoured; the *decrease* in a(β-H) with increasing temperature is consistent with depopulation of this conformation. Because the β-H splitting for $\cdot CH_2\cdot CH_2OH$ is much closer to that expected for free rotation about the C_α–C_β bond [*ca.* 2·7 mT (from $\cdot CH_2CH_3$); see *e.g.* ref. 2] than are the values for $\cdot CH(OH)\cdot CH_2OH$, $\cdot CH(OMe)\cdot CH_2OMe$, and $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$, we conclude also that the restriction to rotation is much smaller for $\cdot CH_2\cdot CH_2OH$ than for the other radicals.

All radicals listed in Table 1 show a decrease in a(α-H) with increasing temperature; presumably this reflects the

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* The larger of the two small splittings is tentatively assigned to the hydrogen atom of the α- rather than the β-hydroxy-group on the basis of the e.s.r. results for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ (see Table 1).

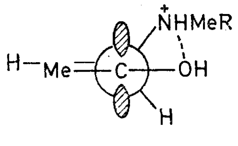
increase in positive contributions to the (negative) α-H splitting which arise from vibrationally excited modes with increased deviation from planarity. The slight decrease in a(β-H) for ·CH(OH)Me probably arises in a related fashion [increasing out-of-plane bending leads to increasing (negative) contributions to a(β-H) *via* spin polarisation in opposition to the dominant (positive) contribution from hyperconjugation]. It is interesting to note that the gradient of the temperature dependence of a(α-H) for ·CH(OH)Me is considerably larger (−0·65 μT K^{-1} over the limited range available; *cf.* the value of −0·29 μT K^{-1} obtained from results[11] over the range −33 to 57°) than that observed for the methyl radical (−0·13 μT K^{-1} at 245 K;[12] *cf.* also −0·19 μT K^{-1} for norborn-7-yl[13] at 130 K); this may well be typical of radicals which are non-planar at the tervalent carbon [*cf.* +0·63 μT K^{-1} for norbornen-7-yl[13] at 173 K, the positive sign in this case indicating the increase in a(α-H) for a positive splitting]. The particularly large temperature gradients for a(α-H) in ·CH(OH)·CH$_2$OH and ·CH(OH)·CH$_2\overset{+}{N}$H$_3$ (−1·41 and −1·33 μT K^{-1}, respectively, over the ranges 9—46° and 9—30°) are consistent with the decrease in the influence of the extra radical-flattening effect of the electronic interaction previously discussed [see (1) and (2)] as the temperature is raised.

Investigation of the α- and β-hydrogen splittings for the radicals ·CH(OH)·CH$_2$OH and ·CH(OH)Me as a function of solvent composition was also undertaken. For ·CH(OH)·CH$_2$OH, generated at ambient temperature (*ca.* 20°) with the flow system and Ti^{III}–H$_2$O$_2$ reaction, there is a 2·1% decrease in a(α-H) and a 3·9% increase in a(β-H) on increasing the concentration of ethane-1,2-diol in water from 2 to 91% (v/v); for 91% CH$_2$(OH)·CH$_2$OH, the radical ·CH(OH)·CH$_2$OH has a(α-H) 1·790, a(β-H) 1·014, a(α-OH) 0·102 mT (splittings ±0·006 mT), *cf.* results in Table 1. These trends are as expected if structure (2) contributes to the resonance hybrid, since, with decreasing medium polarity, the charge separation involved should become increasingly disfavoured. In contrast, for ·CH(OH)Me, a(α-H) increases (by 2·0%) and a(β-H) decreases (by 0·9%) as the concentration of ethanol in water is increased from 3 to 94% (v/v).

The radical ·CH(OH)·CH$_2$OH was also prepared by the photolysis of a mixture of ethane-1,2-diol, di-t-butyl peroxide, and t-butyl alcohol (1 : 8 : 4 v/v). Inclusion of the co-solvent was necessary to obviate problems of immiscibility, and it was also found that the best spectra are obtained at high peroxide concentrations. At 29°, the splittings (±0·006 mT) are: a(α-H) 1·752, a(β-H) 0·956, a(α-OH) 0·117, a(β-OH) 0·041 mT. The radical could also be generated by photolysis of solutions of ethane-1,2-diol and acetone (2 : 1 v/v) and has the following splittings (at 50°): a(α-H) 1·758, a(β-H) 0·953, a(α-OH) 0·138 mT. It was not possible, however, to extend these studies successfully to non-protic systems, principally because of solubility problems, and we feel that there is at present insufficient evidence for definite conclusions about solvent effects to be drawn.

Interest has been recently expressed[10] in the structure of radicals derived at low pH from β-amino-alcohols, including ·CMe(OH)·CH$_2\overset{+}{N}$HMe$_2$ from 1-(*NN*-dimethylamino)propan-2-ol and ·CMe(OH)·CH$_2\overset{+}{N}$H[CH$_2$·CH(OH)-Me]Me from 1-[*N*-methyl-*N*-(2-hydroxypropyl)amino]-propan-2-ol. For these radicals line broadening in the β-hydrogen hyperfine pattern was interpreted as evidence for restricted rotation caused by intramolecular hydrogen bonding. We have also examined these two amines at different temperatures in aqueous solution and confirm that the spectra of both radicals exhibit the previously reported line broadening; however, we have been unable to obtain sufficiently well resolved spectra at higher temperatures to allow quantitative conclusions to be drawn. We note for the latter species that the high temperature limit of the β-H resonance should be a 1 : 1 : 1 : 1 pattern as a result of the adjacent chiral centre (*cf.* ref. 8). At 19° and pH 1·4 the splittings (±0·01 mT) for the former radical are a(α-Me) 2·19, Σa(β-H) 2·01, a(N) 1·23, and a(H-NH) 0·14 mT (*cf.* ref. 10); for the latter species they are 2·17, 1·99, 1·24, and 0·14 mT, respectively.

We believe that the proposed[10] appreciable population of non-eclipsing, hydrogen-bonded rotamers such as (5) [*cf.* structure (24) of ref. 10] would produce β-hydrogen splittings considerably in excess of those observed; however, structures of the type (6) with θ_N *ca.* 10° could account for the low a(β-H) values as well as the large values of a(N). Thus, for conformation (5) we estimate that a(β-H) should equal *ca.* 1·7 mT {employing $B \cos^2 \theta$, with B 4·5 mT [from the β-H splitting for ·CH(OH)Me], and allowing interconversion to average the two splittings}; in contrast, for structures of the type (6) a(β-H) should equal *ca.* 1·2 mT (*cf.* observed average splittings of *ca.* 1·0 mT). We also feel that the increased bulk of an α-Me group over an α-H, coupled with an electronic interaction of the type discussed for ·CH(OH)·CH$_2$OH and ·CH(OH)·CH$_2\overset{+}{N}$H$_3$, is responsible for causing the restriction of rotation, between two preferred, eclipsing geometries [*e.g.* (6) and (7)]. We discuss such conformational effects below in the light of conclusions based on INDO calculations for ·CH(OH)·CH$_2\overset{+}{N}$H$_3$.



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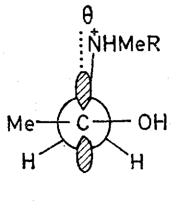

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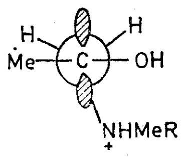

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INDO Calculations.—INDO MO Calculations[7] have been carried out for ·CH$_2$·CH$_2$OH, ·CH(OH)·CH$_2$OH, ·CH(OH)·CH$_2\overset{+}{N}$H$_3$, and ·CH(OH)CH$_3$ in order to seek

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

[12] H. Fischer and H. Hefter, *Z. Naturforsch.*, 1968, **23A**, 1763.

[13] J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Amer. Chem. Soc.*, 1973, **95**, 1516.

corroborative evidence for conclusions, based on hyperfine splittings, about structure and preferred conformations.

(*a*) $\cdot\mathrm{CH(OH)\cdot CH_2\overset{+}{N}H_3}$. The following bond lengths[14,15] were employed: R(C–H) 0·108, R(O–H) 0·096, R(C–O) 0·136, R(C–N) 0·152, and R(N–H) 0·103 nm. R(C–C) was set at 0·145 nm. The starting (eclipsing) geometry is depicted in Figure 2(a), with $\widehat{\mathrm{COH}}$ 107° (the O–H bond lies in the $\mathrm{OC_\alpha C_\beta}$ plane), $\widehat{\mathrm{HCO}}$ 120°, and all angles at the β-carbon and -nitrogen atoms tetrahedral. Figures 2(b) and (c) define the parameters ϕ (for bending), θ (rotation), and δ (distortion).

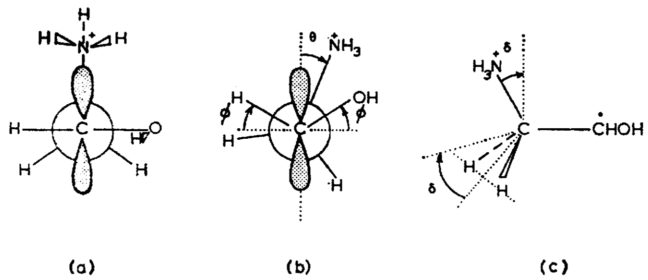

FIGURE 2 (a) Starting geometry for INDO calculations on $\cdot\mathrm{CH(OH)\cdot CH_2\overset{+}{N}H_3}$. (b) The variable parameters defining bending (ϕ) and rotation (θ); the angle ϕ is that made by the projection of the C–H or C–OH bond on the plane passing through the α-carbon parallel to the plane of the paper. (c) The angular parameter δ defining the distortion from tetrahedral geometry at the β-carbon

Keeping θ and δ 0° the total energy becomes more negative as bending at the radical centre is introduced; ϕ was increased in 1° steps and an energy minimum occurs at 7°. The same result is also obtained with[16] R(C–C) 0·140 nm, although the total energy is then less negative and the calculated splittings are in less good agreement with experiment. Table 2 displays calculated parameters for the planar and bent radical centre; the splittings, obtained before annihilation of the quartet spin state, correlate with the experimental values significantly better than post-annihilation splittings for this geometry and will here be considered exclusively. With ϕ 7°, distortion from tetrahedral geometry at the β-carbon was next simulated, and as δ was increased in 0·5° steps, a minimum in the total energy occurred for both C–C bond lengths at δ 2·5°; the minimum for R(C–C) 0·145 nm is lower in energy. [These results are in contrast to those for ·CH(OH)Me (see later) for which 8° bending but no distortion are predicted for the eclipsing (θ 0°) conformation.] The very low calculated β-hydrogen splitting of 0·549 mT, a consequence of bending and distortion, is to be noted.

Figure 3(a) shows the calculated energy of the radical $\cdot\mathrm{CH(OH)\cdot CH_2\overset{+}{N}H_3}$ as a function of rotation about the $\mathrm{C_\alpha}$–$\mathrm{C_\beta}$ bond [with R(C–C) 0·145 nm and δ 0°]. As expected for the preference of a conformation in which the β-nitrogen atom tends to eclipse the orbital of the unpaired electron, the curve is low in energy around θ 0° and shows a minimum at θ 20° with an associated a(β-H) of 1·026 mT. There is, however, another lower minimum at θ 110° which has an associated a(β-H) of 3·828 mT.

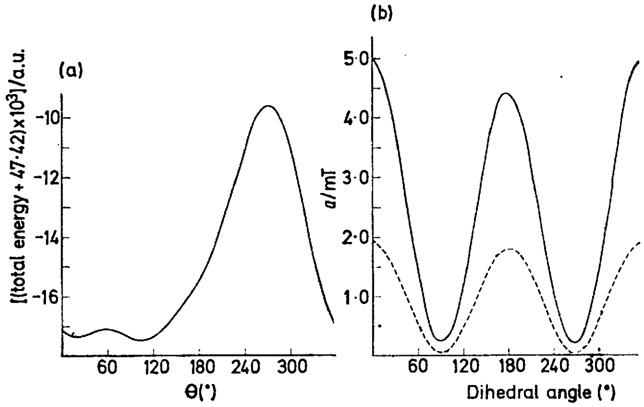

FIGURE 3 (a) Variation of total energy for $\cdot\mathrm{CH(OH)\cdot CH_2\overset{+}{N}H_3}$ with θ [see Figure 2(b)]. (b) β-Hydrogen (full line) and -nitrogen (broken line) splittings (before annihilation of the quartet spin state) for this radical as a function of dihedral angle. The values for a(β-H) are averages of different splittings for each β-hydrogen at the same rotation

The calculations indicate that the barrier to rotation about $\mathrm{C_\alpha}$–$\mathrm{C_\beta}$ $|E(\theta = 110°) - E(\theta = 270°)|$, is 20·8 kJ mol^{-1}. Employing R(C–C) 0·140 nm for $\cdot\mathrm{CH(OH)\cdot CH_2\overset{+}{N}H_3}$, we observe minima in the total energy curve at θ 110 and 10°; although the energies are both less negative than those obtained using R(C–C) 0·145 nm, it is encouraging to find an inversion in the order of magnitudes previously found which is in favour of the (almost) eclipsing conformation (6) [that this conformation is preferred is as expected from the magnitude of a(β-H) if a $\cos^2\theta$

TABLE 2

Hyperfine splitting constants[a] (mT) and total energies (a.u.) calculated for specified geometries[b] of the radical $\cdot\mathrm{CH(OH)\cdot CH_2\overset{+}{N}H_3}$

Geometry[b]	Total energy	a(α-H)	a(H-OH)[c]	a(O)	a(α-C)	a(β-C)	a(β-H)[d]	a(N)	a(H-NH)[c,e]
$\phi^f = \theta^f = \delta^f = 0°$	−47·4365407	−1·743	−0·349	0·520	2·940	−0·084	0·691	1·942	−0·027
$\phi = 7, \theta = \delta = 0°$	−47·4370950	−1·497	−0·323	0·502	3·742	0·254	0·590	1·927	−0·014
$\phi = 7, \theta = 0, \delta = 2·5°$	−47·4373047	−1·532	−0·309	0·500	3·632	0·204	0·549	2·005	0·013

[a] Before annihiliation of the quartet spin state. [b] See text for full details; R(C–C) = 0·145 nm. [c] Hydrogen splitting. [d] Mean of two values. [e] Arithmetic average of three values. [f] See Figure 2 for definition.

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[14] 'Tables of Interatomic Distances,' Chem. Soc. Special Publ. No. 11, London, 1958.

[15] 'Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 46th edn., 1965—1966.

[16] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201.

dependence is followed]. Distortion at the β-carbon at these four energy minima reveals the following results: with R(C–C) 0·145 nm θ 20, δ 1·5, and θ 110°, δ 1·5° and with R(C–C) 0·140 nm θ 10, δ 2·5, and θ 110°, δ 1·5°. That is, although some distortion is observed for the non-eclipsing conformations (θ 110°), the distortion appears to be greatest for the conformation which is more nearly eclipsing (θ 10°).

which correlate more satisfactorily with the experimental values than do post-annihilation splittings, are in Table 3. It is rather disappointing to find that, although some distortion, a shorter α-C–O, and longer β-C–O bond length are predicted [which is as expected from the mediation of structures related to (2)], the bending is somewhat greater than that (8°) for the radical ·CH(OH)Me (see later).

TABLE 3

Hyperfine splitting constants [a] (mT) and total energies (a.u.) calculated for minimum energy, eclipsing [b] conformations of the radicals $\cdot CH(OH)\cdot CH_2OH$ and $\cdot CH(OH)\cdot CH_2\overset{+}{O}H_2$

Radical	Total energy	a(α-H)	a(H-αOH) [c]	a(α-O)	a(α-C)	a(β-C)	a(β-H) [d]	a(β-O)	a(H-βOH) [c]
$\cdot CH(OH)CH_2OH$	−52·5559406	−1·420	−0·155	0·380	4·670	−0·848	0·850	1·378	0·405
$\cdot CH(OH)CH_2\overset{+}{O}H_2$ [e]	−52·9900033	−1·274	−0·350	0·574	4·160	0·863	0·325	3·531	0·561

[a] Before annihilation of the quartet spin state. [b] θ = 0°; see Figure 2(b). [c] Hydrogen splitting. [d] Mean of two values. [e] Splitting for the added proton −0·169 mT.

Figure 3(b) displays the angular dependences of calculated (pre-annihilation) β-hydrogen and -nitrogen splittings for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$. The former is analysable approximately in terms of a relationship of the type $a(\beta\text{-H}) = B_0 + B\cos^2\omega$, where ω (= θ + 2π/3, θ + 4π/3) is the appropriate dihedral angle and B_0 and B are constants with values of 0·169 and 4·517 mT, respectively. [The difference between the INDO results and splittings calculated on this basis is further analysable as $\Delta a(\beta\text{-H}) = B'\cos\omega$, with B' 0·291 mT; the term $B\cos^2\omega$ clearly dominates, as expected for hyperconjugative interaction.] The values for a(β-N) are analysable approximately as $a(\beta\text{-N}) = B_0 + B\cos^2\theta$ with B_0 0·039 and B 1·848 mT; this provides support for the suggestion [3] that a β-nitrogen splitting in a ·C–C–N fragment arises *via* hyperconjugation.

Thus our calculations for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ give *splittings* in quite good accordance with those determined experimentally; although a degree of C_α–C_β rotation must be accommodated, the remarkably small a(β-H), less than the minimum value deduced from a $B\cos^2\theta$ relationship with θ 60° for each hydrogen, is apparently a consequence of the preference for the bent, distorted, and eclipsing radical geometry. The method does not give a single minimum *energy* for the appropriate conformation; we suggest, however, that this may be due to neglect of interactions of the radical with its environment (see also later). We also note that interchange between two equivalent conformations such as (6) and (7), with θ_N *ca.* 10°, could account for the unexpected line broadening observed [10] for the radicals from amino-alcohols discussed above.

(*b*) $\cdot CH(OH)\cdot CH_2OH$. Bond lengths, bond angles, and a starting geometry similar to that for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ (with the β-O–H bond in the $C_\alpha C_\beta O_\beta$ plane pointing away from the half-filled orbital) were used. Extensive minimisation of the total energy in the eclipsing (θ 0°) conformation yielded the following parameters: R(C–C) 0·145, R(α-C–O) 0·135, R(β-C–O) 0·139 nm and φ 10, δ 1·5°. The energy and pre-annihilation splittings,

Investigation of rotation about the C–C bond revealed that rotamers with θ *ca.* 90° are most stable. Here φ was found to be 9 and δ (encouragingly) 0°. The total energy as a function of θ, with φ 9, and δ 0° is shown in Figure 4. The curve has minima in the energy at θ 100 and 260° and maxima at θ 10 and 180°; the calculated energy barrier to rotation, |E(θ = 100°) − E(θ = 180°)|, is 10·2 kJ mol⁻¹. The angular dependence of the average

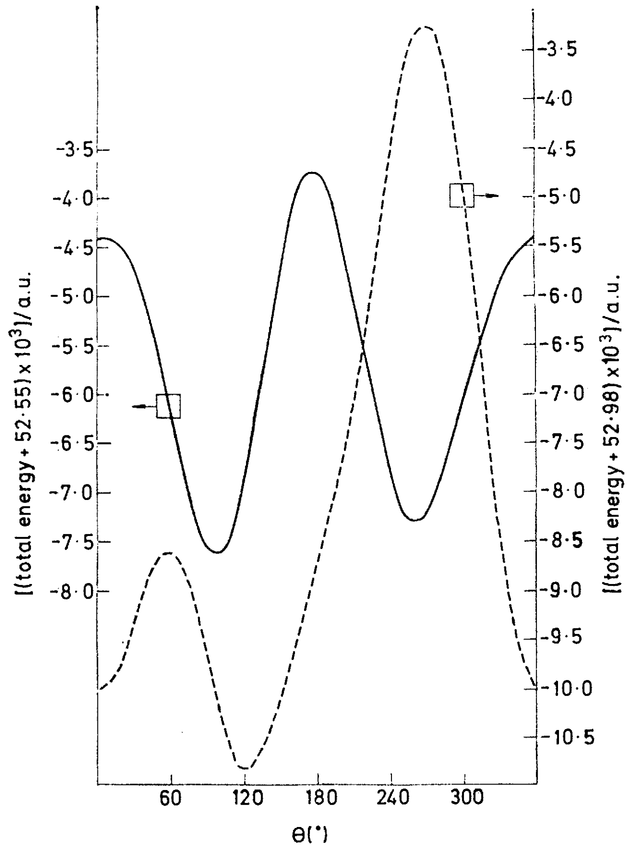

FIGURE 4 Calculated total energy as a function of θ for $\cdot CH(OH)\cdot CH_2OH$ (full line) and $\cdot CH(OH)\cdot CH_2\overset{+}{O}H_2$ (broken line)

calculated β-hydrogen splitting for $\cdot CH(OH)\cdot CH_2OH$ is expressible in the form $a(\beta\text{-H})/\text{mT} = 0{\cdot}092 + 0{\cdot}466 \cos\omega + 5{\cdot}489 \cos^2\omega$; deviation from a strict $\cos^2\omega$ dependence is evidently rather more than for the ethanolamine-derived radical. Calculations therefore give reasonable agreement with the observed *splittings* for $\cdot CH(OH)\cdot CH_2OH$ if a bent, distorted, eclipsing geometry similar to that found for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ is highly preferred. However, results for the energy variation for rotation about the C–C bond are clearly not in agreement with experiment.

The relative success of calculations for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ and the possibility that effects of the medium should receive attention prompted us to simulate the effect of solvation by placing a proton near to the β-oxygen atom of $\cdot CH(OH)\cdot CH_2OH$ (the $\widehat{HOH}$ angle used was 104·45°) in the best energy, eclipsing conformation. The effect on the splittings is quite marked (*cf.* Table 3); in particular, the decrease in $a(\beta\text{-H})$ is to be noted. The total energy as a function of θ for $\cdot CH(OH)\cdot CH_2\overset{+}{O}H_2$ is in Figure 4 (broken line). The resemblance to the curve for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ is noteworthy; minima in the energy occur at θ 0 and 120° and maxima at θ 60 and 270°. The calculated energy barrier to rotation, $|E(\theta = 120°) - E(\theta = 270°)|$, is 19·9 kJ mol^{-1} [*cf.* the result for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$]. The better agreement with experiment achieved in this way may be due to the enhanced $-I$ effect of the β-substituent or to the increased steric requirement of the $\overset{+}{O}H_2$ system; indeed both factors may be significant.

(*c*) $\cdot CH_2\cdot CH_2OH$. Our calculations (see also ref. 17) employed bond angles and lengths [R(C–C) 0·145 nm], the starting geometry, and angular variables defined above. Rotation about the C–C bond maintaining ϕ, δ 0° revealed an energy minimum at θ 90° in accordance with the experimental prediction [*cf.* structure (4)] and a maximum at θ 0°; the barrier to rotation is calculated as 17·3 kJ mol^{-1}. The pre-annihilation splittings for the θ 90° rotamer are $a(\alpha\text{-H})$ −2·014, $a(\alpha\text{-}^{13}C)$ 3·813, and $a(\beta\text{-H})$ 5·687 mT. [We find the angular dependence of the calculated β-H splitting is well fitted by the relation $a(\beta\text{-H})/\text{mT} = 0{\cdot}217 + 6{\cdot}816 \cos^2\omega$]. For this geometry, no bending or distortion is indicated. However, for the eclipsing, higher energy conformation (θ 0°), 6° bending and 3·5° distortion are predicted by INDO. This suggests that a β-oxygen substituent may exhibit an interaction with the radical centre when it is in the eclipsing conformation but that, although this tends to produce distortion at the β-carbon, it is not strong enough to lead to a preference for the eclipsing conformation (unlike that which causes the dominant distorted eclipsing conformation [18] for $\cdot CH_2\cdot CH_2Cl$).

(*d*) $\cdot CH(OH)Me$. Calculations employed bond angles, bond lengths, and the starting geometry quoted for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ (with H replacing $\overset{+}{N}H_3$). Minimisation of the energy with respect to radical geometry in the eclipsing conformation yielded the following parameters: R(α-C–H) 0·112, R(C–O) 0·135, R(C–C) 0·144 nm, the angles made by the α-C–H and C–O bonds with the projection of the C_β–C_α bond 56 and 60°, respectively, and ϕ 8, δ 0°. It was confirmed that the conformation of the α-O–H bond depicted in Figure 2(a) is the one of lowest energy. Pre-annihilation splittings calculated for this geometry are $a(\alpha\text{-H})$ −1·644, $a(\alpha\text{-}^{13}C)$ 4·197, and $a(\beta\text{-H})$ 3·139 mT. Rotation about the C–C bond maintaining this geometry revealed that the θ 0° rotamer is lowest in energy and the θ 70° rotamer highest; the calculated barrier is 1·8 kJ mol^{-1}. The angular dependence of the theoretical β-hydrogen splitting is of the form $a(\beta\text{-H})/\text{mT} = 0{\cdot}184 + 0{\cdot}346 \cos\theta + 5{\cdot}954 \cos^2\theta$; the dependence on cos θ [as also for $\cdot CH(OH)\cdot CH_2OH$ and $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ but not for $\cdot CH_2\cdot CH_2OH$, which is planar at the radical centre] may reflect the deviation from planarity at the α-carbon.

Conclusions.—INDO Calculations demonstrate for radicals of the type $\cdot CH(OH)R$ that the radical centre is non-planar for all C_α–C_β conformations. Evidence is also provided for conclusions drawn from the magnitudes of α- and β-hyperfine splittings that for $\cdot CH(OH)\cdot CH_2OH$ and $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ in the preferred, near eclipsing conformations, distortion from tetrahedral geometry at the β-carbon is implicated, which can account, in particular, for the low values of $a(\beta\text{-H})$; these are smaller than the minimum splitting estimated using a $B\cos^2\theta$ relationship. Calculations of the energy as a function of rotation about the C–C bond in these species give somewhat unexpected results, the cause of which discrepancies may be neglect of effects of the solvent in our calculations. Theoretical findings for $\cdot CH_2\cdot CH_2OH$ concur with the experimental conclusion that the radical adopts a conformation in which the β-C–O bond subtends a dihedral angle of 90° with the orbital of the unpaired electron and in which the radical centre is planar. The calculated energy barriers to rotation for $\cdot CH(OH)\cdot CH_2\overset{+}{N}H_3$ (20·8) and for $\cdot CH(OH)\cdot CH_2\overset{+}{O}H_2$ (19·9) are somewhat larger than that (17·3 kJ mol^{-1}) for $\cdot CH_2\cdot CH_2OH$ suggesting, as does consideration of the magnitude of $a(\beta\text{-H})$ values, that restriction of rotation is greater for the first two radicals, for which conformation and structure are dictated by the electronic interaction.

Finally, we suggest that such electronic interactions as we have considered may be more extensive and could govern the conformations assumed by substituted nitro-anion-radicals ($RNO_2^{\cdot-}$) and nitroxides ($R_2NO\cdot$). Thus for radicals containing the YCH_2N group, $a(\alpha\text{-N})$ and other splittings [including $a(\beta\text{-H})$] appear [8] to exhibit characteristic variations with the nature of Y which are diagnostic of conformational preferences; this recog-

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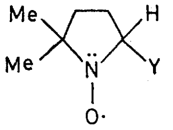
[17] D. Bahier and J. Maruani, *Compt. rend.*, 1972, **275C**, 257.

[18] I. Biddles and A. Hudson, *Chem. Phys. Letters*, 1973, **18**, 45.

nition could facilitate radical identification in spin-trapping experiments employing $CH_2=NO_2^-$ [19-22] and $CH_2=\overset{+}{N}(Bu^t)O^-$.[23,24] Such proposals may also rationalise the dramatic changes of the splittings in radicals [25] of type (8) with the nature of Y. When Y is alkyl, *a*(N) is *ca.* 1·43 and *a*(β-H) *ca.* 2·05 mT, as expected if Y is disposed pseudo-equatorially in a puckered ring. However, when Y is OR (say), nitrogen (1·31—1·36), and hydrogen (0·68—0·79 mT) splittings are appreciably smaller. Thus alkoxy and other electronegative substituents prefer an eclipsing, pseudo-axial position [26] (possibly because of a stabilising interaction similar to that discussed above) so that a small splitting from the *equatorial* hydrogen atom results. We believe that the lowering of *a*(N) derives either from flattening at nitrogen (if the nitroxide function is slightly non-planar) or because hyperconjugation actually increases spin density at oxygen [*i.e.* a greater contribution of canonical form (9)]. In practice, both may contribute.



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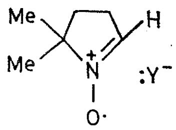

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We are grateful to the S.R.C. for a Research Studentship (to M. T.).

[4/978 *Received, 20th May,* 1974]

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[19] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

[20] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

[21] D. Behar and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 2752.

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

[23] G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 401.

[23] E. G. Janzen and I. G. Lopp, *J. Magnetic Resonance*, 1972, **7**, 107.

[25] E. G. Janzen and J. I.-P. Liu, *J. Magnetic Resonance*, 1973, **9**, 510.

[26] E. G. Janzen, C. A. Evans, and J. I.-P. Liu, *J. Magnetic Resonance*, 1973, **9**, 513.