Investigations of Structure and Conformation. Part 6.[1] Long-range Interactions and Line-width Alternation for γ-Proton Splittings in $\cdot CH_2OCH_2OCH_3$: Temperature-dependent Electron Spin Resonance Spectra

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E.s.r. spectra of $\cdot CH_2OCH_2OCH_3$ at low temperatures show line-width alternation in both the α- and the γ-proton hyperfine splitting patterns; conformational interconversion involving rotation around the O_β–C_γ bond has an energy barrier of 19 ±2 kJ mol^{-1}. In the radical's preferred conformation, the γ-proton splittings have opposite signs, which is understandable in terms of a combination of both hyperconjugation and through-bond spin-polarisation to spin transmission. INDO MO Calculations provide corroboration for the conformational analysis.

ATTENTION has previously been drawn to unusual structural features in oxygen-substituted alkyl radicals. For example, it has been concluded,[2,3] on the basis of ^{13}C and α-H splittings, that distortion from planarity at the radical centre occurs for $\cdot CH_2OH$ and related radicals and that bending is marked when two α-oxygen substituents are introduced (*e.g.* for 2-methyl-1,3-dioxolan-2-yl). For α,β-dioxygen substituted radicals (*e.g.* $\cdot CHOH$–CH_2OH), evidence from *a*(β-H) points[4] to an interaction which causes the β-C–O bond to eclipse the orbital of the unpaired electron. Previous studies on these and related radicals have mainly involved aqueous solution flow-system studies over a restricted temperature range, but development of low-temperature photolytic systems (see,

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[1] Part 5, B. C. Gilbert and M. Trenwith, *J.C.S. Perkin II*, 1975, 1083.

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

[3] A. L. J. Beckwith and P. K. Tindal, *Austral. J. Chem.*, 1971, **24**, 2099.

[4] B. C. Gilbert, M. Trenwith, and A. J. Dobbs, *J.C.S. Perkin II*, 1974, 1772.

e.g. ref. 5) suggests that much more detailed information may become available. Accordingly we have examined the e.s.r. spectra of some oxygen-substituted radicals over a wide temperature range. Particular emphasis is placed here on the radical $\cdot CH_2OCH_2OCH_3$ (from dimethoxymethane); unusual line-broadening phenomena involving the γ-proton splitting pattern are interpreted in terms of an unexpectedly high barrier to interconversion about O_β–C_γ,* together with the operation of at least two modes of spin transmission. These results, coupled with INDO calculations, provide a clear picture of the conformational preferences and motional processes in the radical.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E-3 X-band spectrometer employing 100 kHz modulation. The field scan was calibrated using Fremy's salt [6] and splittings were checked using a spectrum simulation program which incorporates routines for second-order effects and exchange processes. The radicals observed were generated by the photolytic decomposition of di-t-butyl peroxide and subsequent reactions of the t-butoxyl radical. An Hanovia 977B-1 1 kW mercury–xenon compact arc lamp was employed, and the temperature was controlled with a Varian variable temperature accessory; the temperature was monitored using a Comark 3015 Cr–Al digital thermometer and was found to be accurate and steady to within ±2 °C. Solutions to be photolysed contained, typically, substrate (reagent grade, used without further purification), di-t-butyl peroxide (purified on an activated alumina column), and cyclopropane (B.D.H.; 99%) in the volume ratio *ca.* 1 : 1 : 10. Substrate–peroxide solutions were rigorously degassed using a high-vacuum freeze–thaw technique before introduction of cyclopropane *via* the vacuum line; the sample tubes were then sealed. All glassware used was high quality quartz; a signal from the irradiated cell was produced in the region *g ca.* 2, but this did not interfere with spectral analysis. The spectrum simulation program was made available by Dr. M. F. Chiu and the INDO MO program [7] was obtained from the Quantum Chemistry Program Exchange (QCPE No. 141). The INDO program was executed on a CDC 7600 computer at the University of Manchester Regional Computer Centre; the spectral simulations were performed on the Elliott 4130 computer at the University of York.

RESULTS

E.s.r. Spectra.—Spectra have been recorded over a wide range of temperature for the radicals (1) and (2) from dimethoxymethane, and for (3) and (4) from 1,2-dimethoxyethane. The range available for the latter pair of radicals

$\cdot CH(OCH_3)_2$ (1)

$\cdot CH(OCH_3)CH_2OCH_3$ (3)

$\cdot CH_2OCH_2OCH_3$ (2)

$\cdot CH_2OCH_2CH_2OCH_3$ (4)

$\cdot CH_2OCH_3$ (5)

proved somewhat less than that for the former pair: signals from (3) and (4) were very weak at 0 °C and the solvent mixtures for 1,2-dimethoxyethane froze at *ca.* −100 °C. Details of the spectra are given in Table 1, which also contains data [8] on (5) for comparison.

TABLE 1

Temperature-dependent e.s.r. spectra of some radicals derived from ethers

Substrate	Radical	T/°C	Hyperfine splittings (mT) [a] a(α-H)	a(β-H)	a(γ-H)
$CH_2(OCH_3)_2$	(1)	0	(±) 1.11		(±) 0.08
		−130	(±) 1.21		(±) 0.08
	(2)	0	−1.78 (2 H)		(±) 0.08 (2 H)
		−130	−1.925, −1.81		(±) 0.19, (∓) 0.05
$CH_3OCH_2CH_2OCH_3$	(3)	−19	−1.68	+0.84	(±) 0.195
		−95	−1.73	+0.705	(±) 0.205
	(4)	−19	−1.70 (2 H)		(±) 0.215
		−95	−1.81, −1.66		(±) 0.235
CH_3OCH_3 [b]	(5)	−40	−1.724 (2 H)		(±) 0.204
		−100	−1.83, −1.68		(±) 0.21

[a] ±0.01 mT. [b] Data from ref. 8*a*.

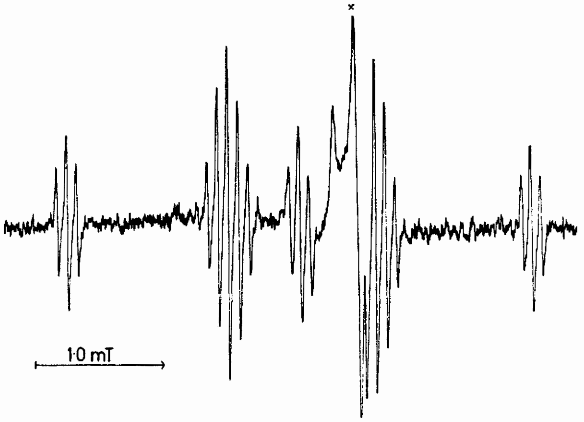

FIGURE 1 E.s.r. spectra of $\cdot CH_2OCH_2OCH_3$ and $\cdot CH(OCH_3)_2$, from dimethoxymethane, at −49 °C (a signal from the cell is indicated ×)

Figure 1 shows the e.s.r. spectra of the radicals (1) and (2) from dimethoxymethane at −49 °C; the signal from (1)

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* We employ the convention $\cdot\underset{\alpha}{C}–\underset{\beta}{O}–\underset{\gamma}{C}–\underset{\delta}{O}–C$ for labelling.

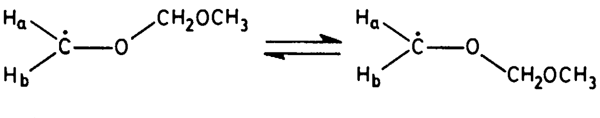
[5] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 7155, 7157.

[6] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[7] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201; D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, 1968, **48**, 5532.

[8] (*a*) A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **25**, 5311; (*b*) I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

is a doublet of septets, as expected, and that from (2) has large and small triplet splittings. The spectrum from (1) shows no temperature dependence, other than an increase in $|a(\alpha\text{-H})|$ (the sign of this splitting is not clearly established) as the temperature is lowered, whereas the spectrum from (2) shows some dramatic changes. First, we note that the central triplet in the larger 1 : 2 : 1 pattern expected from (2) is not twice the amplitude of the outside groups of lines (though the intensities are 1 : 2 : 1 at 0 °C). This phenomenon, noted before for $\cdot CH_2OCH_3$,[8] is explained in terms of the interconversion (1), at intermediate rates, of conformers with non-equivalent α-proton splittings. The radical $\cdot CH_2OCH_2CH_2OMe$ (4) behaves similarly.



(1)

As the temperature is lowered, the middle line in the spectrum of (2) becomes broader (Figure 2 shows the spectrum at −82°) and eventually becomes resolved into the pattern expected for two non-equivalent α-hydrogen splittings. However, by *ca.* −70 °C a line-width alternation pattern can be discerned on the formal 1 : 2 : 1 γ-proton triplet for this radical, and this broadening is pronounced by −82 °C. As the temperature is lowered still further, the central line of the γ-proton triplet broadens and then disappears completely (by −102 °C). At the lowest temperature employed (Figure 3 shows the spectrum at −130 °C) the γ-proton pattern has almost reached its slow-exchange limit (a doublet of doublets, indicating two non-equivalent γ-proton splittings). The interesting feature here, besides the inference that rotation about O_β–C_γ is evidently restricted, is that the broad central line from the γ-proton pattern, which disappears on cooling, reappears on the *outside* of the two γ-proton lines which remain sharp (rather than on the inside, which is normally the case). We also note that the total width of the γ-proton splitting pattern increases, from 0.16 mT (2 H, 0.08 mT) to 0.24 mT (0.19, 0.05 mT).

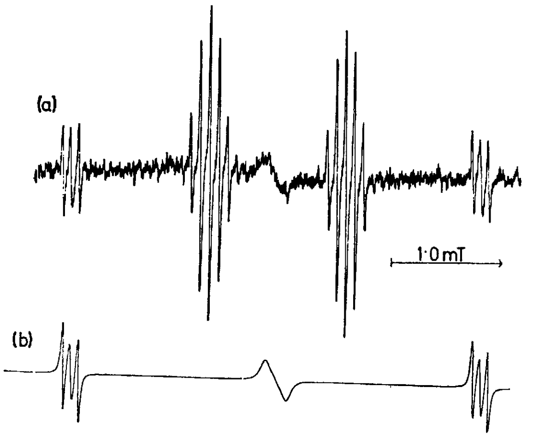


FIGURE 2 (a) E.s.r. spectra of $\cdot CH_2OCH_2OCH_3$ and $\cdot CH(OCH_3)_2$ at −82 °C. (b) Spectrum for $\cdot CH_2OCH_2OCH_3$ at −82 °C simulated using the splittings given in Table 1 and the following exchange rates: k_α 9 × 10^6 s^{-1}, k_γ 10^8 s^{-1}

This behaviour can be understood if the individual γ-protons in the preferred conformation have splittings of *opposite* sign. Then, the *average* of the splittings (±0.19, ∓0.05 mT) is ±0.07 (not ±0.12), and the spectrum becomes narrower when exchange is rapid. The broadened lines appear *outside* the sharp lines as the low-temperature limit is approached, as is indicated diagrammatically in Figures 4 and 5. This we believe to be the first observation of exchange of splittings, of opposite sign, associated with protons attached to the same carbon atom (though exchange involving fluorine splittings of opposite sign occurs [9] for the β-fluorines in $\cdot CF_2CF_3$).

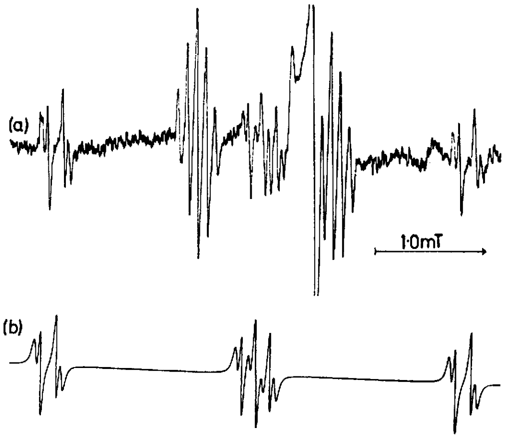


FIGURE 3 (a) E.s.r. spectra of $\cdot CH_2OCH_2OCH_3$ and $\cdot CH(OCH_3)_2$ at −130 °C. (b) Spectrum for $\cdot CH_2OCH_2OCH_3$ simulated using the splittings given in Table 1 and an exchange rate of k_γ 2.0 × 10^6 s^{-1} (k_α ' slow ' exchange)

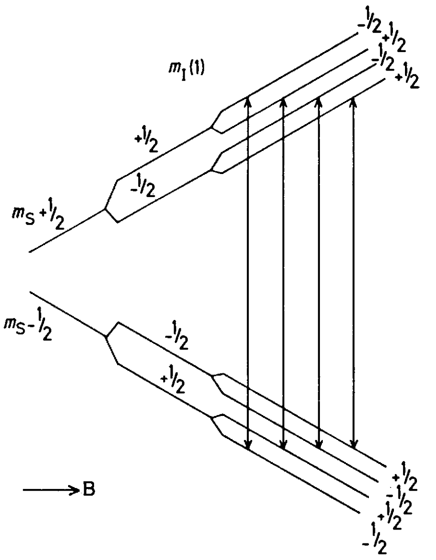


FIGURE 4 Energy-level diagram for interaction of the unpaired electron with two protons which have splittings of opposite sign

Spectrum simulation for $\cdot CH_2OCH_2OCH_3$ has been carried out using a simulation program incorporating a Bloch-equation treatment of exchange (for both α- and γ-protons); a second-order option was also included. The simulations are in excellent agreement with observed spectra over a range of temperature (see *e.g.*, Figure 3 for the lowest temperature achieved): in particular the unusual γ-splitting behaviour is well reproduced. Analysis of α- and γ-H ex-

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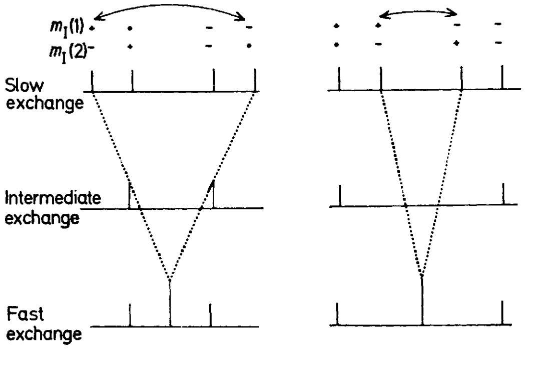
[9] P. Meakin and P. J. Krusic, *J. Amer. Chem. Soc.*, 1973, **95**, 8185.

change leads to the rate constants given in Table 2; from them we derive barriers to rotation about the C_α–O bond (17 ± 2 kJ mol^{-1}) and about the O_β–C_γ bond (19 ± 2 kJ mol^{-1}). The former value is to be compared with that (*ca.* 22 kJ mol^{-1}) estimated [8b] for (5).



(a) Nuclei with splittings of opposite sign

(b) Nuclei with splittings of same sign

FIGURE 5 Exchange patterns for the positional interchange of two protons which have splittings (a) of opposite sign; (b) of the same sign

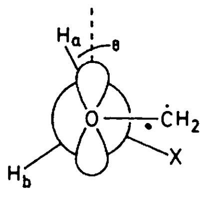
TABLE 2

Rates of exchange processes in $\cdot CH_2OCH_2OCH_3$

T/°C	Rate of rotation about $\cdot C_\alpha$–O_β ($10^{-6}k$/s^{-1})	Rate of rotation about O_β–C_γ ($10^{-6}k$/s^{-1})
−130	<0.1	2
−122	0.7	6
−112	0.9	9
−102	1	30
−96	5	50
−82	9	100
−76	15	200

The radicals from 1,2-dimethoxyethane deserve brief comment here. In (3) no non-equivalence becomes evident as the temperature is lowered; an interesting feature, referred to previously,[4] is the abnormally low a(β–H) which is indicative of an interaction which causes the C_β–O bond to eclipse the orbital of the unpaired electron and introduces distortion at C_β. For (4), the α-protons become non-equivalent on the e.s.r. time-scale, but the γ-proton splitting remains a clear 1 : 2 : 1 pattern down to −95 °C.

Since there is no evidence for slow or intermediate rotation about O_β–C_γ in $\cdot CH_2OCH_2CH_2OCH_3$ we believe that the unusual phenomenon detected for $\cdot CH_2OCH_2OCH_3$ is associated with the second oxygen on the γ-carbon, and INDO calculations (see later) provide corroboration for this claim.



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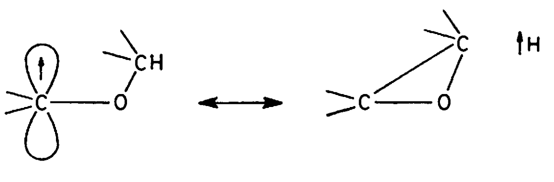
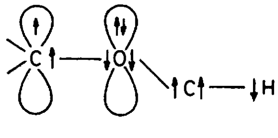


(9)

The opposite signs for the two γ-proton splittings can be understood in terms of the operation of two (at least) different mechanisms for spin transmission. One of these involves through-bond spin-polarisation [*cf.* (6)], which should provide a negative γ-proton splitting [10] which is not significantly dependent on the angle of rotation around C_γ–O_β. The other involves hyperconjugative interaction (7) between the γ-protons and the unpaired electron density in a $2p(\pi)$-orbital on oxygen (these radicals are best represented with some spin-delocalisation onto oxygen, $\cdot CH_2\ddot{O}R \longleftrightarrow \overset{-}{\ddot{C}}H_2-\overset{+\cdot}{O}R$,[2] the latter structure probably contributing to the extent of *ca.* 15%). The second interaction (7) should be angular dependent (*cf.* β-H coupling constants in a variety of radicals [11]) and of the form $a(\gamma\text{-H}) = \rho_O B \cos^2\theta$. It thus seems likely that for a conformation of the type (8), γ-H_a might have a positive splitting, as a result of its small dihedral angle θ, whereas γ-H_b might show a negative splitting as a result of the dominance of spin-polarisation when θ approaches 90°. We do not feel it necessary to include a contribution from homohyperconjugation (9), a mechanism proposed to contribute to long-range coupling in, for example, rigid bicyclic semidiones [12] and also simple alkyl radicals; [10] thus such an interaction appears to be significant only when the bond between β- and γ-atoms (O and C here) is at right angles to the plane containing C_α and H_α. For the radicals described here, evidence from the α-proton splittings for delocalisation and restriction to rotation about O_β–C_α suggests that H_α, C_α, O_β, and C_γ are all essentially coplanar.



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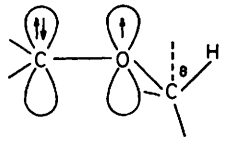

(7)

INDO MO Calculations.—Our calculational approach to the conformational analysis for $\cdot CH_2OCH_2OCH_3$ involved initial calculations on $\cdot CH_2OCH_3$, chosen as a model compound on which to optimise some of the parameters for the larger molecule. Our starting point was structure (10), based on the geometry of dimethyl ether [13] (with $\widehat{COC}$ 111°, but with C_α–O shortened somewhat to simulate the effect of the delocalisation of the unpaired electron onto oxygen from the radical centre); $H\widehat{C_\alpha}H$ was chosen to be 120°, the standard [7] C–H bond length of 0.108 nm was assumed, and C_α, O, C_γ, and Hγ-1 were fixed in the same plane. Table 3 lists the splittings calculated as a function of $\widehat{COC}$, from

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[10] G. R. Underwood, V. L. Vogel, and J-A. Iorio, *Mol. Phys.*, 1973, **25**, 1093.

[11] See, *e.g.* R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[12] G. R. Underwood and V. L. Vogel, *J. Amer. Chem. Soc.*, 1971, **93**, 1058.

[13] 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' Special Publication No. 11, The Chemical Society, 1958.

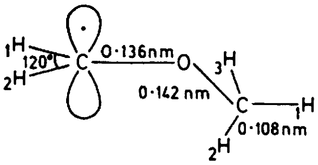
which it can be seen that, at least on the basis of calculated values of $a(\gamma\text{-H})$, a larger $\widehat{COC}$ angle than 111° is appropriate [the observed average value of $a(\gamma\text{-H})$ is *ca.* $\pm$ 0.2 mT]. Calculation with, for example, $\widehat{COC}$ 120° gives γ-splittings whose average is in considerably better agreement with experiment, assuming that $a(\gamma\text{-H})$ is *positive* in $\cdot CH_2OCH_3$ [this sign seems appropriate, especially in view of n.m.r. evidence[14] that $a(\gamma\text{-H})$ for the 4-methoxy-protons in 4-methoxyphenyl t-butyl nitroxide is positive]. For structure (10), with $\widehat{COC} = 120°$, and for similar structures which involve rotation about the $O\text{–}C_\gamma$ bond, we find that positive γ-proton splittings are predicted when the γ-H is situated away from the $H_\alpha COC$ plane (the nodal plane of the orbital of the unpaired electron) and that a small negative splitting is predicted when γ-H lies in or close to this plane (see, *e.g.*, Table 3). This is as anticipated from the earlier qualitative arguments concerning spin transmission.

TABLE 3

INDO Calculations on $\cdot CH_2OCH_3$[a,b]

$\widehat{COC}$ (°)	$a(H_\alpha\text{-}1)$	$a(H_\alpha\text{-}2)$	$a(H_\gamma\text{-}1)$	$a(H_\gamma\text{-}2)$	$a(H_\gamma\text{-}3)$
107	−2.006	−2.050	−0.074	−0.015	−0.015
111	−2.022	−2.023	−0.077	0.032	0.032
115	−2.037	−2.004	−0.079	0.076	0.076
120	−2.053	−1.976	−0.081	0.128	0.128

[a] For geometry, see text. [b] Splittings in mT.



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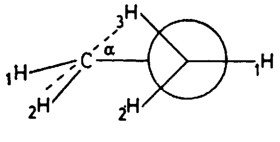
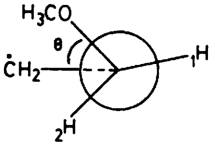


(11)

We have also investigated the effect of introducing a small amount of bending at the radical centre, as shown in (11), by carrying out calculations with α 5, 10, and 15° (with other parameters as above, and $\widehat{COC}$ 120°). As with $\cdot CH_2OH$, which is thought to be slightly bent,[2] the calculated energy decreases on bending and the α-proton splittings show improved agreement with experiment (though, as with $\cdot CH_2OH$,[2] energy considerations alone seem to exaggerate the extent of distortion): for (11), with $\alpha = 10°$, calculated α-proton splittings are $a(H_\alpha\text{-}1)$ −1.851, $a(H_\alpha\text{-}2)$ −1.802 mT. The γ-proton splittings appear to be fairly insensitive to this small amount of bending at the radical centre, and for this structure we calculate $a(H_\gamma\text{-}1)$ −0.076, $a(H_\gamma\text{-}2)$ 0.130, $a(H_\gamma\text{-}3)$ 0.125 mT (*cf.* results for the planar radical, in Table 3).



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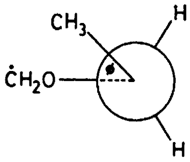

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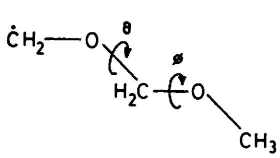

(14)

We have extended our calculations to $\cdot CH_2OCH_2OCH_3$; we chose, in the first place, a planar geometry around C_α (for calculational simplicity: the γ hyperfine splitting appears not to be sensitive to small amounts of bending), $\widehat{COC}$ 120°, and other bond lengths and angles as for $\cdot CH_2OCH_3$, together with $\widehat{OCO}$ tetrahedral and $C_\gamma \widehat{O_\delta} C_\epsilon$ 120°. The geometry was varied by changing θ, the dihedral angle between the $O_\delta\text{–}C_\gamma$ bond and the $C_\alpha OC_\gamma$ plane, and ϕ, the dihedral angle between the $O_\delta\text{–}CH_3$ and the $O_\beta\text{–}C_\gamma$ bonds [see (12)—(14)]. For each value of θ, values of ϕ starting at 0° and increasing in 60° steps were chosen; positive angles refer to movement in a clockwise direction as shown. The adoption of a planar radical centre means that only $0° < \theta < 180°$ need be considered.

For each value of θ taken, the value of ϕ giving minimum energy, and the proton splittings for the appropriate conformation, are given in Table 4. Before considering this, it is worth noting our finding that for a given value of θ, variation in ϕ makes little difference to the calculated γ-splittings $a(\gamma\text{-H})$; this is as expected, since the γ-proton splitting's conformational dependence should reflect mainly the angle of rotation about $O_\beta\text{–}C_\gamma$. The columns headed $a(H_\gamma\text{-}1)$, $a(H_\gamma\text{-}2)$ thus provide a picture of the angular dependence (on θ) of $a(\gamma\text{-H})$. The dependence is as expected from the qualitative arguments presented earlier; thus when θ [as defined in structure (12)] is zero, the γ-protons (dihedral angle 30°) are predicted to have a positive splitting of 0.11 mT (with hyperconjugative interaction dominant), and when θ increases, $a(H_\gamma\text{-}1)$ decreases and $a(H_\gamma\text{-}2)$ increases. For example, when θ is 60°, H_γ-1 is in the nodal plane and has a(Calc) −0.08 (from spin polarisation), whereas H_γ-2 makes a dihedral angle of 30° [a(Calc) +0.13 mT]; when θ is 30° H_γ-2 eclipses the orbital of the unpaired electron and a maximum positive splitting (+0.18 mT) is predicted.

TABLE 4

INDO Calculations on $\cdot CH_2OCH_2OCH_3$[a]

θ(°)	ϕ(°) for minimum energy	Energy (Hartree)[b]	$a(H_\alpha\text{-}1)$	$a(H_\alpha\text{-}2)$	$a(H_\gamma\text{-}1)$	$a(H_\gamma\text{-}2)$[c]
0	180	−60.961 907	−2.05	−2.02	0.11	0.11
20	60	−60.963 851	−2.04	−2.03	0.03	0.18
30	60	−60.964 509	−2.05	−2.01	−0.02	0.18
40	60	−60.964 108	−2.06	−2.00	−0.06	0.17
60	0	−60.964 654	−2.04	−2.03	−0.08	0.13
80	−60	−60.964 487	−2.05	−2.00	−0.06	0.04
90	−60	−60.963 566	−2.05	−1.99	−0.04	0.01
110	−60	−60.962 032	−2.04	−1.99	0.02	−0.03
120	60	−60.961 810	−2.05	−1.99	0.06	−0.02
140	0	−60.961 984	−2.05	−1.99	0.09	0.01
150	0	−60.962 192	−2.05	−1.99	0.11	0.04
170	0	−60.962 535	−2.06	−1.98	0.12	0.10
180	0	−60.962 587	−2.06	−1.98	0.12	0.12

[a] For geometry, see text: θ refers to rotation around $O_\beta\text{–}C_\gamma$, for each value of which the value of ϕ (rotation around $C_\gamma\text{–}O_\delta$) was varied until the energy was minimised. [b] 1 Hartree = 2 625 kJ mol^{-1}. [c] Splittings in mT.

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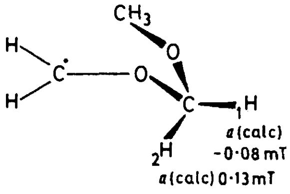
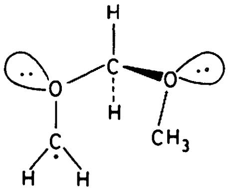
[14] J. Goldman, T. E. Petersen, and K. Torssell, *Tetrahedron*, 1973, **29**, 3833.

For a given value of θ, the calculated energy varies significantly with the position of the methoxy group (*i.e.* with ϕ), and details are given only for the minimum energy configuration for each θ. There appears to be a preference for the O–CH_3 bond to eclipse (or come close to eclipsing) the O_β–C_γ bond (at least for $30° < \theta < 180°$, for which the preference for ϕ is $-60° < \phi < 60°$), though an exception is when θ is small, when the methoxy-group clearly prefers to avoid the radical centre ($\phi = 180°$).

The *overall* minimum energy geometry has $\theta = 60$, $\phi = 0°$, as indicated in structure (15). Certainly a value of $\theta = 60°$ looks appropriate, since it provides a large positive γ-proton splitting (H-2) and a small negative value (H-1), thus giving excellent agreement with experiment (on the assumption that the *signs* are correctly assigned, as seems intuitively reasonable). It is perhaps a little surprising that the energy is a minimum for $\theta = 60°$ rather than $\theta = 120°$ (which would have the C_γ–O_δ bond pointing away from C_α) and that for $\theta = 60°$ the O–CH_3 group is predicted to point towards, rather than away from the radical centre. It is possible that the lower energy calculated for (15) reflects the most favourable arrangement of the sp^2 lone-pairs on the two oxygen atoms [*cf.* structure (16)]. This minimum energy structure bears a close resemblance to that deduced from an electron diffraction study for the parent molecule itself:[15] this is thought to have a gauche-gauche conformation (with the dihedral angle C–O–C–O 66°; this angle corresponds to our θ) rather than an all-*anti*-arrangement.



(15)



(16)

Finally, we have investigated the effect of introducing a small amount of bending at the radical centre in structure (15): as for $\cdot CH_2OCH_3$, the angle of bending α at the radical centre was varied (5, 10, 15°) in the two possible directions. The calculated energy decreases when a mode of bending is introduced which lowers the two α-protons: when $\alpha = 10°$, the resultant calculated splittings are in excellent agreement with experiment [$a(H_\alpha\text{-}1)$ -1.771, $a(H_\alpha\text{-}2)$ -1.952, $a(H_\gamma\text{-}1)$ -0.080, $a(H_\gamma\text{-}2)$ $+ 0.139$ mT: *cf.* observed values $(-)1.81$, $(-)1.925$, $(\pm)0.05$, $(\mp)0.19$ mT, respectively].

Conclusions.—INDO Calculations provide further evidence that radicals of the type $\cdot CH_2OR$ are slightly bent at the radical centre and that, in agreement with semiquantitative considerations, their γ-proton splittings arise *via* a combination of hyperconjugation interaction (usually dominant) and spin-polarisation. The calculations also provide some support for conclusions based on the low-temperature e.s.r. spectra for $\cdot CH_2OCH_2OCH_3$ that the presence of the second oxygen atom confers unusual conformational preferences on the radical: in particular, the opposite signs of $a(\gamma\text{-H})$ in the fixed conformation are predicted. We believe that interelectronic repulsion between lone-pairs may account for the preference of this conformtion. We also envisage that, as the temperature is raised, an increased rate of rotation about O_β–C_γ (coupled with some synchronous rotation about C_γ–OMe) provides the mechanism for averaging of $a(\gamma\text{-H})$.

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[15] E. E. Astrup, *Acta Chem. Scand.*, 1971, **25**, 1494.