Investigations of Structure and Conformation. Part 9.[1] Electron Spin Resonance Evidence for Conformational Preferences and Hindered Rotation about ·C–CH$_3$ in Some αα-Dioxygen-substituted Alkyl Radicals. Determination of the Barriers to Rotation

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The e.s.r. spectra of some α-dioxygen-substituted α-methylalkyl radicals in fluid solution show a marked broadening of the inner (m_I $\pm\frac{1}{2}$) lines of the methyl proton hyperfine splitting pattern as the temperature is lowered. Results for the appropriate dioxolanyl and dioxanyl species trapped in solid matrices show that the preferred conformation of the methyl group is one in which one β-proton splitting is large (*ca.* 3.0 mT). INDO calculations support an interpretation in which this β-proton eclipses the orbital of the unpaired electron in a type of radical with considerable bending at the tervalent carbon atom. The barrier to rotation about ·C–CH$_3$ in these radicals is estimated as *ca.* 8 kJ mol^{-1}. α-Aryl αα-dioxygen-substituted radicals [*e.g.* ·C(C$_6$H$_5$)(OMe)$_2$] are found to be planar at the radical centre.

PREVIOUS applications[1-3] of e.s.r. spectroscopy in conjunction with u.v. irradiation of peroxides over a wide range of temperature have enabled interesting conformational information about oxygen-substituted radicals to be obtained. For example, restricted rotation about C–O bonds in open-chain radicals has been characterised,[3] ring-flipping motions in some cyclic radicals have been studied,[1,2] and evidence has been presented for radical-centre bending,[1,2] with, in some cases,[1] slow pyramidal inversion, in some αα-dioxygen-substituted radicals. An unusual form of line broadening, that from the inner lines of the 1 : 3 : 3 : 1 methyl group proton splitting in some 2-methyl-1,3-dioxolan-2-yl radicals, was tentatively interpreted[1] in terms of the restriction of rotation of the methyl group when attached to a markedly bent radical centre (*cf.* a similar broadening observed for the αα-difluoro radicals ·CF$_2$CF$_3$[4] and ·CF$_2$CH$_3$[5]).

We now report a detailed study of this phenomenon, as

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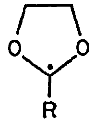
[1] Part 8, C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 1161.
[2] C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 754.
[3] C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 116.
[4] P. Meakin and P. J. Krusic, *J. Amer. Chem. Soc.*, 1973, **95**, 8185.
[5] K. S. Chen and J. K. Kochi (*a*) *J. Amer. Chem. Soc.*, 1974, **96**, 794; (*b*) *Canad. J. Chem.*, 1974, **52**, 3529.

exhibited by the 2-methyl-1,3-dioxolan-2-yl radical (1) and the related species 2-methyl-1,3-dioxan-2-yl (2) and 1,1-dimethoxyethyl (3). The radicals have been generated by a photolytic method and studied in fluid solution down to *ca.* −120 °C. An attempt has also been made to generate the radicals by γ-irradiation of solid matrices at −196 °C, in order to freeze out the favoured conformations. Our calculational approach has utilized the INDO method [6] [to explore the angular dependence of the β-proton splittings and the degree of bending at the radical centre in (1)—(3) and the corresponding unsubstituted radicals (4)—(6)]. Spectrum simulation techniques were used to determine barriers to rotation. The effect on the radicals' geometry of incorporating an aryl ring at the radical centre has also been studied.



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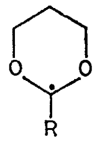
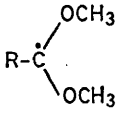
(4) R = H



(2) R = Me
(5) R = H



(3) R = Me
(6) R = H

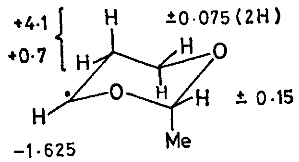
RESULTS AND DISCUSSION

Solution E.s.r. Spectra.—Radicals were generated by the *in situ* photolytic decomposition of di-t-butyl peroxide in the presence of the substrate. Solutions to be photolysed contained, typically, substrate, peroxide, and cyclopropane in the volume ratio *ca.* 1 : 1 : 10, and spectra were recorded over the range 0 to −125 °C.

(a) 2-*Methyl*-1,3-*dioxolan*. Radical (1) was obtained when this substrate was oxidised by $Bu^tO\cdot$; at 0 °C, the spectrum comprised a quartet (from the methyl group protons) and a quintet (from the four γ-protons) (parameters are given in Table 1: the assignment has been discussed previously [1]). As the temperature was lowered, two different broadening phenomena became noticeable: the inner lines of the quartet broadened (the intensity ratio for the four lines was 1 : 0.2 : 0.2 : 1 by −120 °C) and the γ-proton pattern showed alternating line-widths before resolving into a triplet of triplets. The latter effect has been attributed [1] to radical-centre inversion; we have now determined the energy barrier to this process by spectrum simulation (using the low-temperature γ-proton splittings given in Table 1) of the outer lines of the β-proton quartet (these are unaffected by the other line-broadening process). We find a value of 23.9 ± 2 kJ mol^{-1} (*cf.* a value of *ca.* 23 kJ mol^{-1} for the enthalpy of activation calculated [7] from a study of the inner lines of the quartet).

The low temperature slow-exchange limit for radical-centre inversion was reached by *ca.* −120 °C, but we were unable to ' freeze out ' the motional process which causes modulation of the methyl proton splittings. Our attempts to obtain the slow-exchange spectrum by the use of solid matrices (and hence even lower temperatures) are described in a later section.

(b) 2-*Methyl*-1,3-*dioxan*. The reaction between this substrate and $Bu^tO\cdot$ produced the radicals (2) and (7) (above −58 °C the latter was not generated in sufficient concentration to allow spectrum interpretation). Structure (7) shows our assignment of the splittings for this radical at −58 °C; by −120 °C the two β-proton splittings had changed somewhat (though their sum had remained the same) and we believe that this change simply reflects an increased weighting for the conformation with the 2-methyl group equatorial in a rapidly equilibrating pair of structures, the other conformer having the methyl group axial. For (2), the spectrum comprised a large quartet of small quintets: at −30 °C the quartet intensities were 1 : 2.5 : 2.5 : 1 (rather than the expected 1 : 3 : 3 : 1) and the ratio was 1 : 1.2 : 1.2 : 1 by −120 °C, so that restricted rotation [as in (1)] presumably also occurs for this radical. Again, the low-temperature limit for this motional process could not be obtained from solution spectra. By analogy with the results [2] for the trioxanyl and 1,3-dioxan-2-yl radicals, where clearly resolved γ-proton splittings were only detected in the slow-exchange region for chair–chair interconversion, we believe that the observation of four γ-proton splittings in (2) (probably in two non-equivalent pairs: the relative intensities were not quite 1 : 4 : 6 : 4 : 1) indicates that ring-flipping is also slow for this radical. It seems likely that, as with 1,3-dioxan-2-yl and related radicals, the pairs of γ-protons (equatorial and axial) have splittings of opposite signs.



(7)

(c) 1,1-*Dimethoxyethane*. Figure 1a shows the spectra of radicals (3) and $\cdot CH_2OCHMeOMe$ derived by reaction of $Bu^tO\cdot$ with this substrate at −28 °C; the spectrum of the latter comprises an α-proton triplet [a(H) 1.75 mT] with some broadening of the middle line, whereas the former is the expected quartet of septets (see Table 1). At −120 °C (see Figure 1b) the spectra changed considerably, the lines due to $\cdot CH_2OCHMeOMe$ showing that the two α-protons have non-equivalent splittings [rotation about $\cdot C_\alpha$–O must now be occurring in the slow-exchange region (*cf.* $\cdot CH_2OCH_2OCH_3$ [3])] and the spectrum of (3) showing the marked broadening of the middle lines of the quartet (1 : 0.3 : 0.3 : 1 at this temperature) characteristic of radicals (1) and (2). We note that this type of broadening is almost identical in the three cases, as is

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

[7] S. O. Kobayashi and O. S. Simamura, *Chem. Letters*, 1973, 699.

TABLE 1

E.s.r. spectra of radicals derived from some dioxygen substituted compounds [a]

Substrate	Radical	T/°C	Hyperfine splittings (mT) [c]			g [d]
			a(α-H)	a(β-H)	a(γ-H)	
2-Methyl-1,3-dioxolan	(1)	0		+1.285 (3H)	±0.120 (4H)	2.003 2
		−111		+1.300 (3H)	±0.145 (2H) ±0.100 (2H)	
		−196 [b]		+2.9 (1H) +0.5 (2H)		
2-Methyl-1,3-dioxan	(2)	−30		+1.358 (3H)	±0.068 (2H) [e] ∓0.068 (2H) [e]	2 002 9
		−120		+1.375 (3H)	±0.075 (2H) [e] ∓0.075 (2H) [e]	
		−196 [b]		+2.9 (1H) +0.5 (2H)		
	(7)	−58	−1.625 (1H)	+4.100 (1H) +0.700 (1H)	±0.150 (1H) ±0.075 (2H)	2.003 1
		−120	−1.625 (1H)	+4.115 (1H) +0.688 (1H)	+0.150 (1H) ±0.075 (2H)	
1,1-Dimethoxyethane	(3)	−28		+1.373 (3H)	±0.066 (6H)	2.003 0
		−120		+1.360 (3H)	±0.072 (6H)	
	$\cdot CH_2OCHMeOMe$	−28	−1.750 (2H)			
		−120	−1.713 (1H) −1.863 (1H)			2.003 3
		−196 [b]	~(−) 1.9 (2H)			

[a] From Bu^{t}O. in cyclopropane unless stated otherwise. [b] γ-Irradiation of solid matrix. [c] ±0.005 for radicals in fluid solution. [d] ±0.000 1. [e] Two slightly inequivalent pairs of splittings (see text).

the magnitude of the hydrogen splitting from the methyl group (*i.e. ca.* 1.3 mT) which suggests that the three radicals possess closely similar geometric and dynamic properties.

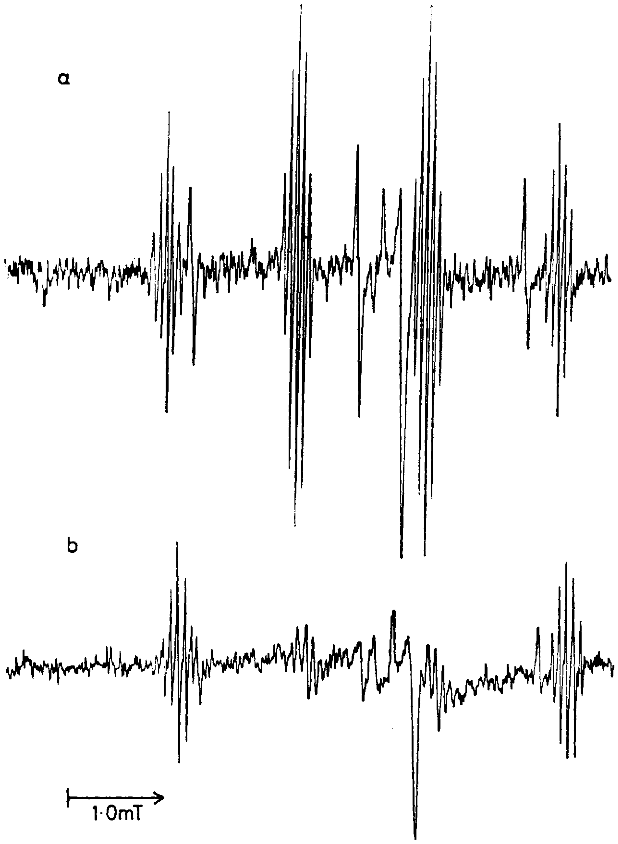
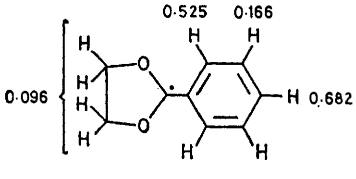


FIGURE 1 E.s.r. spectra of radical (3) and of $\cdot CH_2OCHMeOMe$ from 1,1-dimethoxyethane: a, at −28 °C; b, at −120 °C

(d) *Aromatic substrates.* Oxidation of 2-phenyl-1,3-dioxolan with Bu^{t}O· under conditions similar to those described for the aliphatic analogues led to a complex spectrum which could nevertheless be satisfactorily analysed and simulated; our assignment is to the 2-phenyl-1,3-dioxolan-2-yl radical (8). Similarly, oxidation of 2-(4-fluorophenyl)-1,3-dioxolan gave the analogous 4-phenyl-substituted radical [a(γ-H) 0.090, a(^{19}F) 1.50, a(2-H) 0.552, a(3-H) 0.180 mT], and oxidation of benzaldehyde dimethyl acetal gave a spectrum attributed to (9). The spectra from these radicals were effectively temperature independent.



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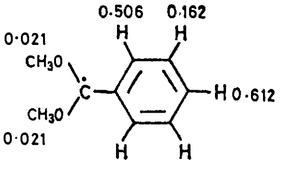

(9)

The pattern of ring-proton splittings in (8) and (9) [*i.e.* a(4-H) > a(2-H) ≫ a(3-H)] is exactly as expected for a *planar* geometry at the radical centre [*cf.* the planar π-type species benzyl,[8] phenoxyl,[9] *etc.*] rather than that obtained when the ring is attached to a bent radical centre [*e.g.* $C_6H_5\dot{S}O_2$, with[10] a(2-H) > a(3-H), a(4-H)]. We thus conclude that the conjugation between the unpaired electron and the aromatic ring π-orbitals in (8) and (9) is sufficient to outweigh the incipient bending effect of the two oxygen atoms substituted at the radical

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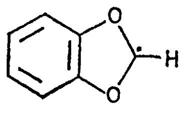
[8] A. Carrington and I. C. P. Smith, *Mol. Phys.*, 1965, **9**, 137.

[9] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.

[10] A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626; M. McMillan and W. A. Waters, *J. Chem. Soc.* (*B*), 1966, 422.

centre. [This situation parallels that in which introduction of a phenyl group at the radical centre of the vinyl radical (which itself is a bent σ-species with the unpaired electron localised in an sp^2-type orbital on carbon) leads to the 'linear' radical $CH_2{=}\dot{C}(C_6H_5)$;[11] in the latter the unpaired electron occupies a molecular orbital composed of a *p*-orbital on the central carbon and the ring *p*-orbitals (orthogonal to the *p*-orbitals of the double bond)]. We also note that comparison of the splittings for (8) and (9) with those for benzyl indicates that the two oxygen atoms are ineffective at withdrawing spin density from the radical centre.

We have also reinvestigated the report[12] that radical (10), from 1,2-methylenedioxybenzene exhibits a spectrum with a large doublet and a *sextet* indicating interaction with a further five protons. We have studied the spectrum produced over a range of temperature and find under all circumstances that the observed species has a large doublet splitting [2.382 mT, presumably *positive*, see ref. 1] and two triplet splittings [*a*(2H) 0.042, *a*(2H) 0.033 mT], exactly as expected for (10). In this case, very little delocalisation onto the ring has occurred and we conclude that the radical is markedly bent at the α-carbon [*cf.* (1)—(6)].



(10)

Solid-state Spectra.—Experiments have been carried out in which solid samples of substrates (both as pure compounds and as 5% solutions in CD_3OD) have been γ-irradiated (for *ca.* 1 h at a dose rate of 2 Mrad h^{-1}). Spectra have been recorded for the irradiated samples at −196 °C and also as the temperature was raised so that the solids could anneal.

The spectra obtained from 2-methyl-1,3-dioxan and -dioxolan at −196 °C showed a close resemblance to each other, as did their behaviour as the temperature was raised. For example the pure irradiated solids show, at −196 °C, a dominant doublet splitting (with little anisotropy) of *ca.* 3.0 mT (see Figure 2a), accompanied by traces of signals from other radicals including ·CHO and $\cdot CH_3$ (see *e.g.* ref. 13). When the samples were allowed to anneal, the doublet spectrum gradually changed until a clear 1 : 3 : 3 : 1 pattern [*a*(3H) 1.3 mT], with approximately the same overall width, was obtained (see Figure 2b). Irradiated solid solutions of each substrate in CD_3OD at −196 °C showed, in addition to signals from $\cdot CD_2OD$, $\cdot CD_3$, and ·CHO, the same doublet spectrum in which further hyperfine splitting is also apparent. This spectrum (see Figure 2c) is analysed in terms of a doublet [*a*(1H) 2.9 mT] and triplet [*a*(2H) 0.5 mT], *g ca.* 2.003 0, with some broadening of the inner lines compared with the two outside lines.

The observation of quartets with the expected splitting and *g* value in the annealed spectra confirms that the major radicals produced are the same as those generated in the reactions with $Bu^tO\cdot$, namely (1) from 2-methyl-1,3-dioxolan and (2) from 2-methyl-1,3-dioxan. We conclude that at the lowest temperature employed (−196 °C) the doublet appearance indicates that the methyl groups in the two radicals are more or less 'locked' in a conformation in which one proton shows a large interaction with the unpaired electron, the other two having a small splitting [*cf.* Figure 2c]. This is as

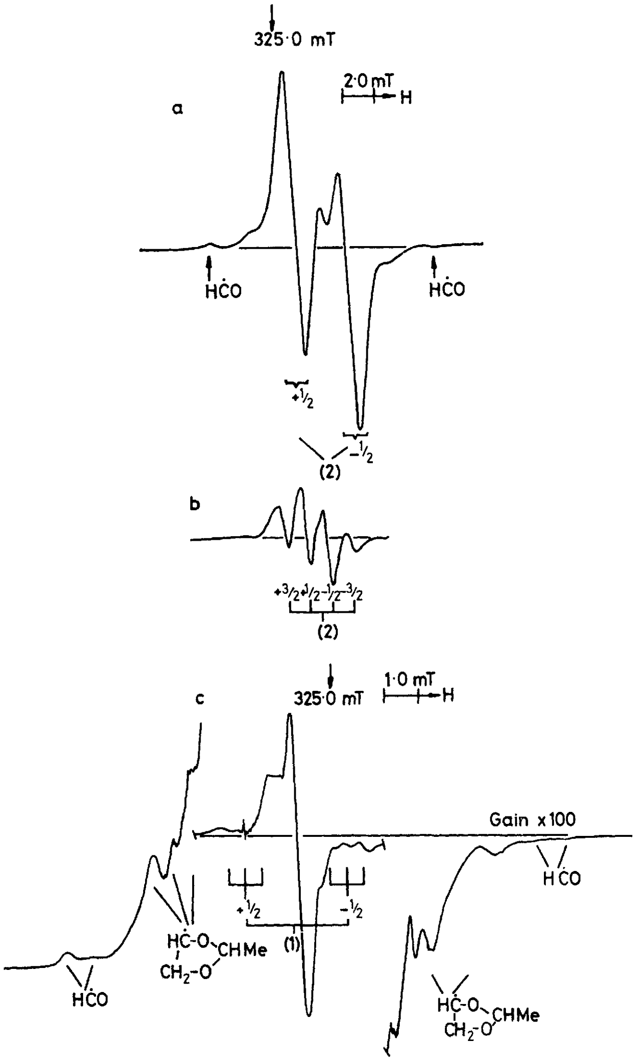


FIGURE 2 First derivative X-band e.s.r. spectra for 2-methyl-1,3-dioxan and -dioxolan after exposure to ^{60}Co γ-rays at −196 °C. a, 2-Methyl-1,3-dioxan at −196 °C showing features assigned to ·HCO and radical (2); b, as a during the annealing process showing the reversible change to a quartet for radical (2); c, 2-methyl-1,3-dioxolan in CD_3OD at −196 °C showing features assigned to ·HCO, $\cdot CH{-}CH_2{-}O{-}CHMe{-}O$, and radical (1). The central line is due to e^-_t and to $\cdot CD_2OD$ and $\cdot CD_3$ radicals

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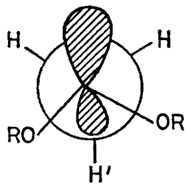
[11] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1971, **9**, 460.

[12] E. A. C. Lucken and B. Poncioni, *J.C.S. Perkin II*, 1976, 777.

[13] M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 297.

expected for a conformation of the type (11), with $a(\mathrm{H}')$ large, if we assume that the β-proton splitting has an angular dependence which is broadly governed by a $B\cos^2\theta$ relationship (as expected for hyperconjugative interaction).



(11)

The broadening of the inner lines in the solid state spectrum, and of the central lines of the fluid solution spectra as the temperature is lowered, can be simply understood in terms of the correlation diagram shown in Figure 3 (details of simulation of the spectra are described later). The observation of this broadening pattern, and the constancy of the overall width of the spectrum, indicates that the two splittings in the low temperature spectrum have the same sign. The low-temperature limit spectrum for $\cdot\mathrm{CF_2CF_3}$ also has one large and two small β-splittings, as expected for a favoured conformation akin to (11), although in this case the splittings have opposite sign.[4]

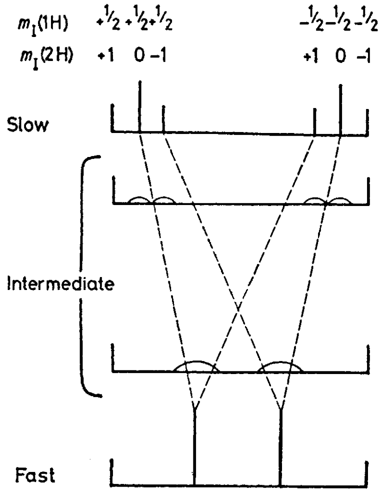


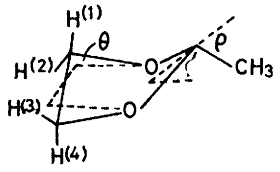
FIGURE 3 Correlation diagram showing the relationship between the fast exchange, intermediate exchange, and slow exchange spectra for a methyl group ($\cdot\mathrm{C{-}CH_3}$) undergoing restricted rotation

γ-Irradiated solid samples of $\mathrm{MeCH(OMe)_2}$ did not give spectra attributable to $\cdot\mathrm{CMe(OMe)_2}$, as had been hoped. Instead, the spectra showed a dominant signal comprising a triplet [a(2H) *ca.* 1.9 mT] with anisotropy as expected for a radical with two α-protons: this is attributable to $\cdot\mathrm{CH_2OCHMeOMe}$. It is not clear why this radical, rather than $\cdot\mathrm{CMe(OMe)_2}$, should be preferentially produced, especially in the light of results for the cyclic species.

INDO MO Calculations.—We have previously found that INDO MO calculations in conjunction with optimization of radical geometry can give a good account of many of the unusual features shown by oxygen-substituted radicals; these include high ^{13}C splittings,[1,2] near-zero[2] or positive[1] α-hydrogen splittings (all of which are characteristic of radicals with a bent trigonal carbon), and γ-proton splittings which within the same radical can possess both positive and negative signs.[2,3] We have now extended this approach to the α-methyl-substituted radicals described here, with particular emphasis on the degree of bending at the radical centre and on the preferred conformation(s) of the methyl group.

1,3-*Dioxolan-2-yl radicals*. Our calculational approach to (1) was simple, and involved the use of that conformation and configuration at the radical centre previously[1] estimated for (4). Accordingly, an initial geometry was taken as described by structure (12), with θ 5° (angle of twist, of half-chair type, in the ring), ϕ 40° (angle at the envelope), and ρ 42.5° (angle of bending) (other bond lengths and angles were as used previously,[1] with a bond length for $\cdot\mathrm{C_\alpha{-}O}$ of 0.139 nm and $\mathrm{C_\alpha \widehat{C_\beta} H} = \mathrm{H\widehat{C_\beta}H} = 109°\ 28'$). The orientation of the methyl group was studied by varying the torsional angle ω, as shown in (13).

For a series of calculations with ω varied from 0 to 120°, a distinct energy minimum was found for ω 60° [*i.e.* conformation (14)]; Table 2 shows some typical results, with ω varied in the range 0—60° [results for ω and (120 − ω) bear a close resemblance to each other]. The calculated splittings are in good agreement with experiment; for all values of ω the calculated average β-proton splitting is close to the observed value of 1.30 mT [*e.g.* 1.335, 1.338 mT for ω 30, 60° respectively], and, in particular, for ω 60° [structure (14)] the calculated β-proton splittings of 0.322, 0.338, and 3.344 mT for H(1), H(2), and H(3), respectively, are close to the separate values detected for the low-temperature



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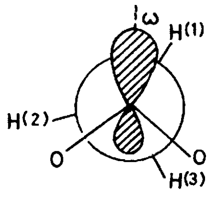

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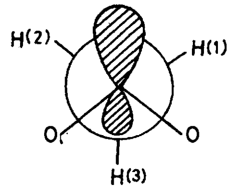

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spectrum in which methyl group rotation has been frozen out (*ca.* 0.5, 0.5, 2.9 mT). The INDO results thus provide corroboration for the conclusion about conformational preferences presented earlier.

With this value of ω, we varied the angle of bending ρ to determine the value which gives the best fit for a(Me); this is found for ρ 44°. The calculated splittings (see Table 2) are $a(\beta\text{-H})_{\text{av}}$ 1.302 (individual values 0.305, 0.319, 3.283 mT), $a(\alpha\text{-}^{13}\text{C})$ 12.563, and averaged γ-proton splittings (to take into account ring flipping[1]) $a[\gamma\text{-H(1), H(3)}]_{\text{av}}$ −0.138, $a[\gamma\text{-H(2), H(4)}]_{\text{av}}$ −0.098 mT: the experimental values are, respectively, 1.30, 11.0,[14] 0.145 (2H), and 0.100 (2H) mT, the γ-proton splittings having the same sign. In a related series of calculations on the radical (4), in which θ and φ were retained as here and ρ was varied, optimum agreement with experiment was also achieved with ρ 44° [*e.g.* then, a(α-H) is calculated as 2.147 mT; *cf.* a(α-H) (+) 2.152 mT at −127 °C [1]].

TABLE 2

INDO MO Calculations on 2-methyl-1,3-dioxolan-2-yl [a]

			Calculated hyperfine splittings (mT)							
			$a(\beta\text{-H})$ [b]			$a(\alpha\text{-}^{13}\text{C})$	$a(\gamma\text{-H})$ [c]			
ω/°	ρ/°	E/hartree	H(1)	H(2)	H(3)		H(1)	H(2)	H(3)	H(4)
0	42.5	−68.002 275	1.892	1.040	1.073	12.225	−0.180	−0.079	−0.083	−0.117
10	42.5	−68.002 383	1.820	0.585	1.600	12.223	−0.180	−0.079	−0.083	−0.118
20	42.5	−68.002 675	1.624	0.243	2.137	12.221	−0.179	−0.078	−0.083	−0.119
30	42.5	−68.003 032	1.332	0.046	2.626	12.218	−0.179	−0.078	−0.082	−0.119
40	42.5	−68.003 412	0.988	0.010	3.014	12.272	−0.184	−0.076	−0.091	−0.117
50	42.5	−68.003 675	0.632	0.110	3.262	12.241	−0.181	−0.078	−0.087	−0.118
60	42.5	−68.003 746	0.322	0.338	3.344	12.241	−0.181	−0.078	−0.087	−0.118
60	44.0	−68.002 978	0.305	0.319	3.283	12.563	−0.184	−0.083	−0.092	−0.113

[a] For geometry, see text. θ and φ define the twist (half-chair) and envelope character, see structure (12); ρ defines the angle of bending (12) and ω defines the angle of rotation of the methyl group. [b] See (13). [c] See (12).

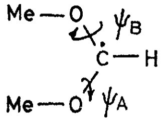
We have also used the calculated slow-exchange splittings for (1) [with ω 60, ρ 44°] in a spectrum simulation program to match the broadening of the inner lines of the methyl proton quartet in the observed spectrum. In this way we have obtained rates of interconversion (*i.e.* rates of rotation about ·C–CH$_3$) over a wide temperature range (we find, for example, rates of 2×10^{10} Hz at −50 °C, 5×10^{9} Hz at −110 °C). From our data we estimate that the barrier to rotation is 7.4 ± 2 kJ mol^{-1}.

1,3-Dioxan-2-yl radicals. In an earlier series of INDO calculations on the unsubstituted radical (5) we found[2] that a chair form with an angle of bending at the radical centre of 28° gave optimum agreement with experiment [in particular, it yielded a calculated near-zero value, as observed, for a(α-H)]. Adoption of this basic geometry for the methylated analogue (2), along with $\text{C}_\alpha\text{–C}_\beta$ 0.154, C_β–H 0.108 nm, and $\widehat{\text{C}_\alpha\text{C}_\beta\text{H}} = \widehat{\text{HC}_\beta\text{H}} = 109°\,28'$, and variation of the torsional angle ω (as above) gave a minimum energy conformation with ω 60° and β-H splittings of 4.0 (1H) and 0.63 (2H) mT. Variation of ρ gave optimum agreement with the experimental average value of 1.375 mT for ρ 42° [$a(\beta\text{-H})_{\text{av}}$ calculated, 1.381 mT]; the individual splittings of 3.44 (1H) and 0.352 (2H) are again in reasonable agreement with those in the solid-state spectrum. Spectral simulation with these values leads to an energy barrier to rotation about ·C–CH$_3$ in (2) of 8.56 ± 2 kJ mol^{-1}.

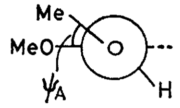
It is interesting to note that whereas the dioxolan radicals (1) and (4) appear to have essentially the same degree of bending at α-C, the methylated dioxanyl radical (2) and the unsubstituted analogue (5) do not show the same correspondence. For (2) the bending appears to be about the same as that for (1), as suggested by the similarities between their a(β-H) values and also between their barriers to rotation. For (5), in contrast, the bending is less than for (2) and also less than for the corresponding dioxolan radical (4) [indeed, this would certainly be the simplest interpretation for the large difference in their values of a(α-H), *i.e.* + 2.1 mT for[1] (4), (±) 0.02 mT for[2] (5)].

Other radicals. We have also carried out INDO calculations on ·CH(OMe)$_2$ (6) and ·CMe(OMe)$_2$ (3). The latter has more degrees of freedom than its cyclic counterparts described above, and in order to fix some of the degrees of freedom we carried out initial calculations on (6).

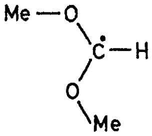
We used the following bond lengths and angles: $\cdot\text{C}_\alpha\text{–O}_\beta$ 0.139, C–H 0.108, $\text{O}_\beta\text{–C}_\gamma$ 0.142 nm, $\widehat{\text{COC}} = \widehat{\text{OCO}} = 110°$, $\widehat{\text{HCH}} = \widehat{\text{HCO}} = 109°\,28'$. We commenced with a geometry in which atoms COCOC were all in one plane [and the methyl groups *cis*, see (15)] and with an angle of bending ρ of 26°. This gave a(α-H) + 1.096 mT (observed 1.212 mT). The torsional angle ψ_A was then varied [see (16)] and a minimum in the energy found for ψ_A 180°. The energy minimum with respect to rotation about the other ·C–O bond was found to occur for ψ_A 0°,



(15)



(16)



(17)

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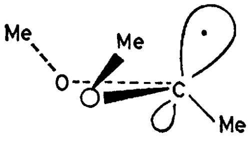
[14] A. L. J. Beckwith and P. K. Tindal, *Austral. J. Chem.*, 1971, **24**, 2099.

giving structure (17) (with COCOC atoms all in one plane) as the resulting geometry. The angle of bending was then adjusted (see Table 3) to give an optimum fit with the experimentally observed value of a(α-H). The result is for ρ 29°, though the γ-proton hyperfine interaction is somewhat underestimated.

The calculations were then extended to the methylated radical (3) (with C–C 0.154 nm, $\widehat{CCH} = \widehat{HCH} = 109° 28'$). We fixed ρ at 40° initially [*cf.* calculations on (1) and (2)] and varied first ψ_A, then ψ_B, as for $\cdot CH(OMe)_2$. Values of 210 and 30°, respectively, gave a calculated minimum energy (selected values are given in Table 4). The plan view of this geometry is as in (17), with Me replacing α-H, but as the elevation [structure (18)] indicates, both methoxy methyl groups are above the $O\dot{C}O$ plane, the α-CH_3 group being below it. Finally ω (the angle of rotation of the α-methyl group) was varied systematically and ρ altered slightly to obtain the best fit for the observed parameters. The energy minimum with respect to rotation again occurs for ω 60°; individual values of a(β-H) for ω 60, ρ 42° are 0.303, 0.365, and 3.386 mT with an average value of 1.351 mT. This is to be compared with an experimental value of 1.360 mT [in this case, the individual values could not be obtained from the solid-state spectrum but we expect that they would closely resemble those seen for the cyclic analogues, namely *ca.* 2.9 (1H) and 0.5 (2H) mT]. We have used the low-temperature splittings as indicated by the INDO calculations to generate simulated spectra which match those observed. The resulting rates of rotation have been employed to determine an energy barrier to rotation around $\cdot C{-}CH_3$ in $\cdot CMe(OMe)_2$ of 9.16 ± 2 kJ mol^{-1}.



(18)

TABLE 3

Sample INDO MO calculations on $\cdot CH(OMe)_2$ [a]

ρ/°	ψ_A/°	ψ_B/°	E/hartree	Hyperfine splittings (mT) a(α-H)	a(α-^{13}C)	a(γ-H)$_{av}$
26	0	0	−58.724 765	+1.096	9.486	−0.007
26	180	0	−60.988 277	+0.830	9.506	−0.018
28	180	0	−60.988 961	+1.088	10.047	−0.017
29	180	0	−60.989 267	+1.211	10.312	−0.016
30	180	0	−60.989 547	+1.331	10.574	−0.015

[a] For bond lengths and angles see text: ρ is the angle of bending at the radical centre, ψ_A and ψ_B describe the angles of rotation about $\cdot C_\alpha$-O [see (15) and (16)].

TABLE 4

Sample INDO MO calculations on $\cdot CMe(OMe)_2$ [a]

					Hyperfine splittings (mT)				
				a(β-H)				a(α-^{13}C)	a(γ-H)$_{av}$
ρ/°	ψ_A/°	ψ_B/°	ω/°	E/hartree	H(1)	H(2)	H(3)	Average		
40	180	0	60	−69.429 896	0.285	0.356	3.429	1.357	11.505	−0.008
40	210	0	60	−69.436 219	0.282	0.398	3.456	1.379	11.581	−0.009
40	210	30	60	−69.436 496	0.331	0.394	3.467	1.398	11.606	−0.035
41	210	30	60	−69.436 231	0.317	0.379	3.427	1.374	11.835	−0.034
42	210	30	0	−69.434 847	1.885	1.029	1.147	1.354	12.084	−0.029
42	210	30	20	−69.435 171	1.602	0.245	2.222	1.356	12.060	−0.031
42	210	30	40	−69.435 697	0.957	0.021	3.086	1.355	12.049	−0.032
42	210	30	60	−69.435 918	0.303	0.365	3.386	1.351	12.061	−0.033
43	210	30	60	−69.435 556	0.289	0.350	3.335	1.328	12.284	−0.032

[a] For parameters, see text; ρ defines the angle of bending at the radical centre, ψ_A and ψ_B the angles of rotation about $\cdot C{-}O$, an ω defines the angle of rotation about $\cdot C{-}CH_3$.

Concluding Remarks.—It is interesting to note that on the basis of the INDO calculations it appears that the radical $\cdot CMe(OMe)_2$ (3) has approximately the same geometry at the radical centre as its analogues (1) and (2) [calculated angles of bending for (1)—(3) are 44, 42, and 42°, respectively; they have similar values for a(Me) and also for ΔE]. In contrast, the radical $\cdot CH(OMe)_2$ appears to be somewhat less bent [ρ *ca.* 29°: *cf.* 28° for (5), 44° for (4)].

The reasons for this variation in the geometry of the unsubstituted radicals, in contrast with the similarity in geometry for the methylated radicals, is unclear. However, we note that the incorporation of a methyl group at the radical centre evidently causes an increase in bending for the strain-free six-membered ring and the open-chain radical (*cf.* also evidence [15] for an increase in bending from $\cdot CH_2OH$ to $\cdot CMe_2OH$). This may arise because the methyl group interacts primarily *via* its doubly occupied group $(\sigma\pi)_2$ orbitals, *i.e.*, that it may be regarded as a pseudo electron-pair donor (with a $+M$

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

effect; see *e.g.* ref. 16). The lack of a corresponding increase in bending for the dioxolan-2-yl species on introduction of methyl may simply reflect the already greater extent of distortion in the unsubstituted ring-strained species; thus the extent of bending here may already have achieved a limiting value for a dioxygen substituted radical of *ca.* 44°.

EXPERIMENTAL

The generation of radicals in fluid solution was carried out at the University of York; details of the e.s.r. spectrometer, photolytic arrangement, sample preparation, generation of radicals, and spectral simulation techniques have been described previously.[2,3] γ-Irradiation was carried out at the University of Leicester; samples were irradiated in a Vickrad ^{60}Co γ-ray source, and e.s.r. spectra were measured with a Varian E109 spectrometer.

With the following exceptions, all chemicals employed were obtained commercially and were used without further purification. Commercial grade di-t-butyl peroxide was purified on an activated alumina column; 2-methyl-1,3-dioxan [17] was prepared by the acid-catalysed condensation [18] of propane-1,3-diol and acetyldehyde in dichloromethane as solvent, 2-phenyl-1,3-dioxolan [19] was similarly prepared from benzaldehyde and ethane-1,2-diol, and benzaldehyde dimethyl acetal was prepared by the method of Huang and Lee.[20]

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[7/979 *Received*, 8*th June*, 1977]

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[16] P. J. Krusic and R. C. Bingham, *J. Amer. Chem. Soc.*, 1976, **98**, 230.

[17] K. Pihlaja and J. Heikkila, *Acta Chem. Scand.*, 1967, **21**, 2390.

[18] I. L. Finar, ' Organic Chemistry, Volume 1, The Fundamental Principles ', Longman, London, 1967, 5th edn., p. 278.

[19] E. S. Huyser and Z. Garcia, *J. Org. Chem.*, 1962, **27**, 2716.

[20] R. L. Huang and K. H. Lee, *J. Chem. Soc.*, 1964, 5957.