Investigations of Structure and Conformation. Part 8.[1,2] E.s.r. Studies of Conformational Preferences, Radical-centre Inversion, and Restricted Rotation about ·C–CH$_3$ in Some 1,3-Dioxolan-2-yl Radicals

By **Christopher Gaze** and **Bruce C. Gilbert**,* Department of Chemistry, University of York, Heslington, York YO1 5DD

The e.s.r. spectrum of 2-methyl-1,3-dioxolan-2-yl shows two temperature-dependent line width phenomena. As the temperature is lowered the central lines of the quartet from the methyl-group protons become broader than the outside lines and the quintet from the γ-protons shows line width alternation. These effects are interpreted in terms of restricted rotation about ·C–CH$_3$ (indicative of a bent radical centre) and radical-centre inversion, respectively. Conformational analysis of the low-temperature splittings for this and some ring-substituted radicals has been carried out with the aid of INDO calculations: it is concluded that preferred conformations, which are to a certain extent dependent on the ring substituents, are of a type intermediate between envelope and twist-chair forms (with a low barrier to pseudo rotation).

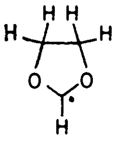
We have previously shown [1,2] that employment of e.s.r. spectroscopy in conjunction with low-temperature photolytic methods for radical generation enables interesting conformational information to be obtained. For example, restricted rotation about ·C$_\alpha$–O and O–C$_\gamma$ bonds in ·CH$_2$OCH$_2$OCH$_3$ has been demonstrated,[2] and kinetic parameters for ring-flipping in dioxanyl radicals have been measured;[1] for ·CH$_2$OCH$_2$OCH$_3$, 1,3-dioxan-2-yl, and 1,3,5-trioxanyl radicals the e.s.r. spectra exhibited novel and dramatic changes as the temperature was lowered and it was shown that in each case the preferred conformation has individual γ-proton splittings with opposite sign. We now report the results of a similar investigation into some five-membered ring species of related type (1,3-dioxolan-2-yl radicals). Our interest here was stimulated by the likelihood that the radical

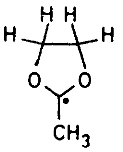
---

[1] Part 7, C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 754.

[2] Part 6, C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 116.

centre in 1,3-dioxolan-2-yl itself (1) is markedly bent, with $a(\alpha\text{-H})$ positive,[3,4] and by the report[5] of the non-equivalence of the γ-proton splittings in 2-methyl-1,3-dioxolan-2-yl (2) at low temperature. It was suggested[5] that the non-equivalence is a consequence of ' freezing out ' radical-centre inversion rather than conformational interconversion involving the ring (in contrast to the analogous six-membered cyclic radicals); INDO calculations on an envelope form predict[5] that the pairs of γ-proton splittings have *opposite* sign (*cf.* $\cdot CH_2OCH_2OCH_3$, 1,3,5-trioxanyl) but inspection of the spectra—and, in particular, the lack of narrowing of the γ-proton pattern at high temperatures—indicates that the splittings have the *same* sign. We have investigated these and related dioxolan radicals in order to characterize unambiguously both inversion at C_α and—*via* the study of ring-substituted analogues—conformational interconversion in the rings. INDO calculations[6] have been employed, in conjunction with experimental results, to estimate the degree of bending at C_α and the shape of the dioxolan ring in these species, and to delineate further the factors affecting spin-transmission to γ-protons in oxygen-conjugated radicals.


(1)


(2)

RESULTS AND DISCUSSION

E.s.r. spectra.—Radicals were generated by the *in situ* photolytic decomposition of di-t-butyl peroxide in the presence of the substrate:[1,2] solutions to be irradiated contained, typically, substrate, di-t-butyl peroxide, and cyclopropane in the volume ratio *ca.* 1 : 1 : 10. The temperature range over which radicals could be studied was quite extensive, ranging in one case (1,3-dioxolan-2-yl) from +24 to −127 °C; in most cases temperatures as low as *ca.* −125 °C were obtained. For the radicals from 4-methyl- and 2,4-dimethyl-1,3-dioxolan poor signal-to-noise ratios above *ca.* −50 °C precluded the acquisition of useful information above this temperature.

(a) *The* 1,3-*dioxolan*-2-*yl radical.* Figure 1 shows the e.s.r. spectrum obtained by reaction of $Bu^tO\cdot$ with 1,3-dioxolan at −127 °C; it is attributed to the 1,3-dioxolan-2-yl radical (1) formed by hydrogen-abstraction from C-2. At all temperatures between 24 and −127 °C the spectrum comprised a large doublet splitting from the α-proton together with a small quintet from the four γ-protons (see Table 1): no non-equivalence of the γ-protons, nor any line-broadening, was detected. Discussion of the likely conformation of this ring and sign of the γ-proton splitting is presented after the spectra from some substituted radicals have been described.

(b) *The* 2-*methyl*-1,3-*dioxolan*-2-*yl radical.* Figure 2(a) shows the spectrum of the radical, attributed the structure (2), derived from 2-methyl-1,3-dioxolan at −47 °C. The β-proton quartet and γ-proton quintet are clearly visible (data in Table 1). As the temperature is lowered, two linewidth phenomena become apparent. First, the amplitude of the central lines of the β-proton 1 : 3 : 3 : 1 quartet is lowered relative to that of the outside lines: a true 1 : 3 : 3 : 1 pattern is observed at 0 °C, some broadening has occurred by −47 °C [see Figure 2(a)] and by −100 °C [Figure 2(b)] the central lines have been dramatically reduced in intensity. Secondly, the γ-proton pattern shows selective broadening and by −100 °C has become resolved into a triplet of triplets [0.145 (2 H), 0.100 (2 H) mT, these splittings having the *same* sign, to give the high-temperature average, 0.120 (4 H) mT].

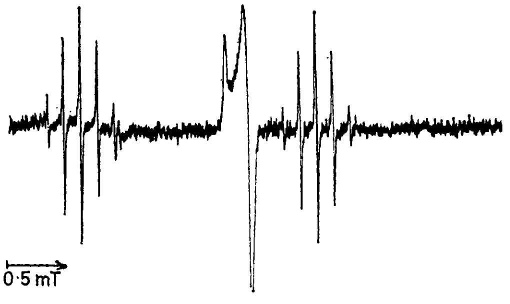


FIGURE 1 E.s.r. spectrum of 1,3-dioxolan-2-yl at −127 °C; the asymmetric resonance is from a paramagnetic impurity in the cell

It seems likely that the second phenomenon, involving interconversion of non-equivalent γ-proton splittings, is caused by ' freezing out ' of the radical-centre inversion process [(3) $\rightleftharpoons$ (4)], as previously suggested.[5] Thus conformational interconversion of the ring (see later) should not be dramatically affected by substitution of a methyl group at the radical centre [so that, from this point of view, (1) and (2) should be similar]. On the other hand, substitution of a methyl group at C_α in the oxiranyl radical does cause a considerable reduction in the

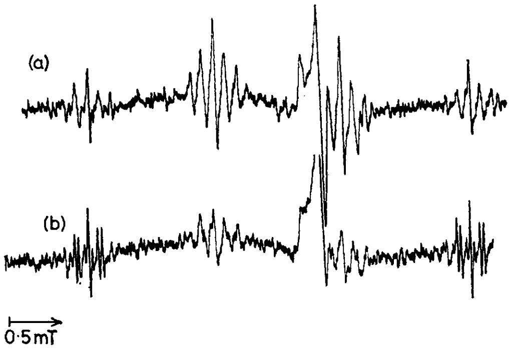


FIGURE 2 E.s.r. spectra of 2-methyl-1,3-dioxolan-2-yl (a) at −47 °C; (b) at −100 °C

---

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

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

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

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

rate of radical-centre inversion [7] and we believe that an analogous situation exists here. The measure of the activation energy for radical-centre inversion (*ca.* 23 kJ mol^{-1}) was taken [5] from a study of the broadened central lines of the quartet (which broadening was not previously observed and hence not taken into account) but it appears to be realistic.

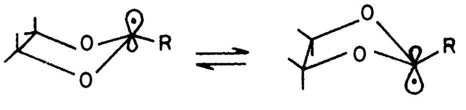
TABLE 1

Temperature-dependent e.s.r. spectra of some radicals derived from cyclic ethers containing five-membered rings

Radical	T/°C	Hyperfine splittings (mT) [a] a(α-H)	a(β-H)	a(γ-H)	g
(1)	+24	+2.104		0.135 (4 H)	2.003 3
	−76	+2.150		0.145 (4 H)	
	−127	+2.152		0.150 (4 H)	
(2)	0		+1.285 (3 H)	0.120 (4 H)	2.003 2
	−47		+1.290 (3 H)	0.120 (4 H)	
	−100		+1.295 (3 H)	(±) 0.140 (2 H), (±) 0.100 (2 H)	
	−111		+1.300 (3 H)	(±) 0.145 (2 H), (±) 0.100 (2 H)	
(7)	−48	+2.062		0.205 (2 H), 0.100 (1 H)	2.003 3
	−81	+2.054		0.210 (2 H), 0.100 (1 H)	
	−100	+2.082		0.220 (2 H), 0.090 (1 H)	
	−125	+2.077		0.220 (1 H), 0.240 (1 H) 0.080 (1 H)	
(8)	−8		+1.325 (3 H)	0.210 (2 H) [b]	2.003 1
	−49		+1.313 (3 H)	0.215 (2 H) [b]	
	−88		+1.331 (3 H)	0.385 (1 H), 0.055 (1 H)	
	−122		+1.325 (3 H)	0.400 (1 H), 0.075 (1 H)	
(9)	−56		+1.304 (3 H)	0.325 (1 H), 0.100 (1 H)	2.003 0
	−93		+1.308 (3 H)	0.312 (1 H), 0.100 (1 H)	
	−125		+1.308 (3 H)	0.175 (1 H),[c] 0.075 (1 H) 0.150 (1 H) [c]	
Me$\dot{\mathrm{C}}$(OMe)$_2$	−43		+1.372 (3 H)	0.066 (6 H)	2.003 0
	−60		+1.369 (3 H)	0.066 (6 H)	
	−98		+1.368 (3 H)	0.070 (6 H)	
	−130		+1.354 (3 H)	0.072 (6 H)	
CH$_2$OCHMeOMe	−43	−1.756 (2 H)		*ca.* 0.05	2.003 3
	−60	−1.756 (2 H)			
	−98	−1.794 (2 H)			
	−130	−1.864 (1 H), −1.717 (1 H)			

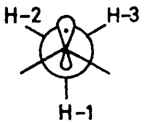
[a] ±0.005 mT. [b] From the sharp outer lines of the triplet. [c] Tentative assignment.

Further evidence for the considerable degree of bending at the radical centre in (2) [and, presumably, in (1) also] comes from the recognition that the first line-broadening phenomenon described for (2) is derived from restricted rotation about the ·C–CH$_3$ bond. There must be a considerable barrier to this rotation, which in turn means that, unlike radicals with a planar radical centre (which have essentially free rotation about ·C–CH$_3$) there must be pyramidal geometry at C$_\alpha$ [other examples where this effect has been detected include [8] ·CF$_2$CH$_3$ and [9] ·C(CH$_3$)=CH$_2$]. The pyramidal geometry at C$_\alpha$ produces a three-fold axis of rotation and creates a situation in which two protons have a splitting different from that of the third [*cf.* (5)], the positional interchange of which at ' intermediate ' rates gives rise to the observed line-broadening.

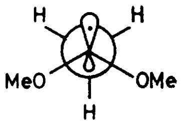


(3) (4)

We have been unable to observe the low-temperature slow-exchange limit spectrum for (2) and so cannot measure a(H-1) and a(H-2,H-3) in the preferred conformation, or, thence, estimate the barrier to rotation. We have found, however, that a similar phenomenon occurs for the radical ·CMe(OMe)$_2$, formed along with ·CH$_2$OCHMeOMe in the reaction of Bu^{t}O· with 1,1-dimethoxyethane (see Table 1). At −43 °C, the quartet splitting from ·CMe(OMe)$_2$ is a sharp 1 : 3 : 3 : 1 pattern, but by −60° the intensities have become 1 : 2 : 2 : 1, and by −98° they are 1 : 1.5 : 1.5 : 1; broadening of the central lines is virtually complete by −130 °C. Again, we were unable to achieve the low-temperature limit. Comparison of the broadenings for (2) and for ·CMe(OMe)$_2$ shows that the former becomes apparent before the latter as the temperature is lowered; we believe that the barrier to rotation (and hence degree of bending) is slightly greater in (2) than in the acyclic analogue (6) but we conclude that the acyclic species is also markedly distorted from planarity at C$_\alpha$. This indicates that in ·CH(OMe)$_2$, which would be expected to have closely similar geometry around C$_\alpha$ to ·CMe(OMe)$_2$, the α-proton



(5)



(6)

---

[7] H. Itzel and H. Fischer, *Helv. Chim. Acta*, 1976, **59**, 880.

[8] (*a*) P. Meakin and P. J. Krusic, *J. Amer. Chem. Soc.*, 1973, **95**, 8185; (*b*) K. S. Chen and J. K. Kochi, *ibid.*, 1974, **96**, 794.

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

splitting is probably positive (like that for 1,3-dioxolan-2-yl).

The similarities demonstrated here for the radicals (2), $\cdot CMe(OMe)_2$ and $\cdot CF_2CH_3$—and the fact that they possess similar methyl-proton splittings (*ca.* 1.3 mT, typical of a pyramidal radical centre)—suggests that the degree of bending is ***approximately*** the same in the three instances and that these alkoxy-substituted species have a similar barrier to rotation to [8] $\cdot CF_2CH_3$ (and hence probably *ca.* 12 kJ mol^{-1}).

(c) *The* 4-*methyl*-1,3-*dioxolan*-2-*yl radical.* The radical derived from 4-methyl-1,3-dioxolan is attributed the structure (7) on the basis of the typical α-proton doublet from a 1,3-dioxolan-2-yl radical [*ca.* (+) 2.05 mT] and the three γ-proton splittings. At −61 °C [see Figure 3(a)] the γ-proton pattern comprises a triplet [*a*(2 H) 0.2 mT] and doublet [*a*(1 H) 0.1 mT]; by −125 °C the three γ-protons all have different splittings [see Figure 3(b)]. The manner in which this non-equivalence is manifested on lowering the temperature is different from all the examples discussed so far. There is no broadening of certain lines as the temperature is lowered or re-appearance of sharp lines at other positions: we conclude that the two splittings are only *accidentally* equivalent at higher temperatures and that all the splittings vary with temperature. The spectra presumably reflect the weighted average of various possible conformations, one of which is more stable and becomes increasingly dominant as the temperature is lowered. The nature of these, and the preferred conformation of the methyl group, will be discussed later; however, we note here that ring motion is still rapid even at the lowest temperature obtained (there were no selective broadenings) and that the type of non-equivalence produced (as judged by the low-temperature γ-splittings) is distinct from that produced by the freezing out of radical-centre inversion.

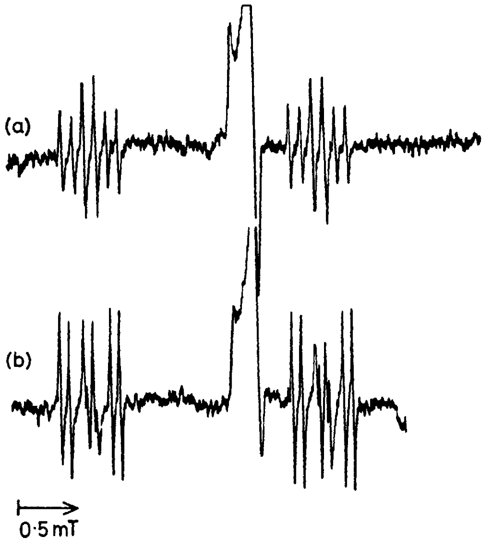
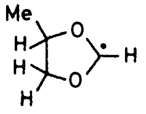
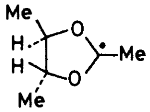


FIGURE 3 E.s.r. spectra of 4-methyl-1,3-dioxolan-2-yl (a) at −61 °C; (b) at −125 °C

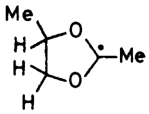
(d) *The* 2,r-4,t-5-*trimethyl*-1,3-*dioxolan*-2-*yl radical.* Reaction of $Bu^tO\cdot$ with 2,*r*-4,*t*-5-trimethyl-1,3-dioxolan led to the detection of a signal attributed to (8). At −31 °C, the spectrum has a large quartet splitting and what appears to be a single γ-proton splitting (see Table 1). As the temperature is lowered, two linewidth effects are noted: the 1 : 3 : 3 : 1 pattern again shows broadening of the central lines (by −119 °C the pattern is 1 : 2 : 2 : 1) evidently as a result of restricted rotation around $\cdot C_\alpha - CH_3$, as described for (2), and the γ-proton pattern develops broad lines, inside the sharp lines, which themselves become sharp, so that the low temperature spectrum is a doublet of doublets. At higher temperatures, exchange in the intermediate range presumably leads to a 1 : broad : 1 pattern. This phenomenon, as described for (2), is associated with inversion at the radical centre causing interconversion of two non-equivalent γ-protons [*cf.* (3) $\rightleftharpoons$ (4)]. The γ-proton splittings concerned have the same sign and, as far as can be ascertained, are not significantly temperature-dependent.



(7)



(8)



(9)

(e) *The* 2,4-*dimethyl*-1,3-*dioxolan*-2-*yl radical* (9). Radical (9) was generated by reaction of the parent dioxolan with $Bu^tO\cdot$. At −77 °C the spectrum has the expected methyl-group quartet [with *a*(H) *ca.* 1.3 mT] and a γ-proton splitting pattern comprising a doublet of doublets. When the temperature was lowered the methyl-group proton splitting showed the broadening diagnostic of restricted rotation about $\cdot C_\alpha - CH_3$ and the γ-proton pattern showed evidence of broad, then sharper, lines between the sharp absorptions. By analogy with results for (2) and (8) the latter effect is evidently associated with the slowing of radical-centre inversion. The γ-proton pattern could not be completely resolved, even at −125 °C, and the analysis given in Table 1 must be regarded as tentative.

Conformational Analysis and INDO Calculations.—Until recently, many studies of dioxolans of the type discussed here have presumed that either an ' envelope ' or ' half-chair ' form is appropriate (these conformations being essentially the same as those used to describe cyclopentane systems). However, more recent work [10] [11] indicates that this approach represents an oversimplification and that these systems do not have a well defined energy minimum in each case (*i.e.* corresponding to either the envelope or the half-chair) but rather that a number of conformations are of similar energy, with low barriers to interconversion so that they are interconverting rapidly: the ring thus cannot be regarded as having a unique shape. The interconversion process has been termed ' pseudorotation ' as it is envisaged that each ring atom in turn oscillates about the plane of the

---

[10] W. E. Willy, G. Binsch, and E. L. Eliel, *J. Amer. Chem. Soc.*, 1970, **92**, 5394.

[11] C. Altona, H. R. Buys, and E. Havinga, *Rec. Trav. chim.*, 1966, **85**, 973.

molecule. Substitution of the ring hydrogen atoms in 1,3-dioxolan or cyclopentane prevents complete pseudorotation while still permitting oscillation over a wide range of conformations: this is referred to as pseudolibration.[10,11] In some cases, further substitution may confine the ring to definite energy minima.

For the 1,3-dioxolan-2-yl radical (1) no temperature-dependent phenomena were observed in the e.s.r. spectra and it appears that radical-centre inversion and ring interconversion are occurring rapidly, even at low temperatures. The single γ-proton splitting is an *average* quantity—the individual splittings being averaged by *both* types of motion. However, the non-equivalences produced by substitution, at C_α and also in the $-CH_2-CH_2-$ framework, suggest that these effects can, to a certain extent, be studied separately. Accordingly we have employed INDO calculations (which yielded[1,2] results in excellent agreement with experiments for $\cdot CH_2OCH_2OCH_3$ and some six-membered cyclic radicals) in conjunction with observed values of $a(\alpha\text{-H})$, $a(\alpha\text{-}^{13}C)$, and $a(\gamma\text{-H})$—for C_2- and ring-substituted radicals—in order to provide a consistent conformational analysis. In carrying out the INDO calculations, particular emphasis has been placed on: (i) finding a configuration or configurations in which $a(\alpha\text{-}^{13}C)$ and, particularly, $a(\alpha\text{-H})$ values are reproduced [*e.g.* for (1), $a(\alpha\text{-H})$ is $+2.15$ mT at -127 °C; $a(\alpha\text{-}^{13}C)$ is 10.3 mT at room temperature;[3] for (2), $a(\alpha\text{-}^{13}C)$ is[3] 11.0 mT at room temperature]; (ii) finding a conformation or conformations of the ring in which the average γ-proton splitting calculated for (1) is not only similar to that observed [$(\pm)$ 0.15 mT] but in which separate pairs of proton splittings correspond to the values of $a(\gamma\text{-H})$ [$(\pm)$ 0.145, $(\pm)$ 0.10 mT, with the same sign] observed for (2), in which radical-centre inversion is frozen out.

The bond lengths employed for initial INDO calculations on (1) were: C–C 0.154, C–H 0.108, C–O 0.142 nm. Angles $H\widehat{C}H$ were taken as tetrahedral, and $H\widehat{C_\gamma}O$ and $H\widehat{C}C$ were set equal for all conformations studied. The initial structure taken comprised a *planar* ring with $O\widehat{C_\alpha}O$ 112°, and with $C\widehat{O}C$ and $C\widehat{C}O$ 107°. The first stage was to find the angle at which the C_α–H bond should be oriented to the plane of the ring to reproduce the observed values of $a(\alpha\text{-H})$ and $a(\alpha\text{-}^{13}C)$—*i.e.* to find the angle of bending at the radical centre. Here, and for all our other calculations, it was found that an angle of bending of 42.5° gave reasonable agreement with experiment (it proved to be essentially independent of ring conformation, as would be expected). Results for a planar ring, with a bent radical centre, do not give reasonable results for $a(\gamma\text{-H})$ [see Table 2, $\theta = 0$]: the averaged splitting is much too small, and pairs of protons have opposite signs, which is contrary to our experimental findings.

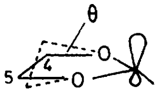
To discover whether any *half-chair* structure adequately describes the ring, the portion O–C–O was retained as before (with an angle of bending at C_α of 42.5°) and the portion C(4)–C(5) was twisted in relation to the $OC_\alpha O$ plane [*cf.* the half-chair form (10) and, in end elevation, (11)]. The amount of twist in the half-chair form was varied by altering θ in 5° steps (this involved a slight variation of angles $C\widehat{O}C$ and $C\widehat{C}O$) {consideration of the *X*-ray analysis of bis-1,3-dioxolan[12,13] indicates that the torsion angle Ω [where Ω is 2θ, see (12)] as shown cannot attain a value greater than 30°}. The results are shown in Table 2.

TABLE 2

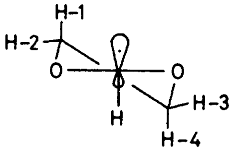
INDO MO calculations on the half-chair conformation of 1,3-dioxolan-2-yl [a]

				Calculated splittings [b]			
				$a(\gamma\text{-H})$			
θ/°	Energy [c]	$a(\alpha\text{-H})$	$a(\alpha\text{-}^{13}C)$	H-1	H-2	H-3	H-4
0	$-59.541\,235$	2.499	12.872	-0.154	$+0.173$	-0.154	$+0.173$
5	$-59.541\,013$	2.462	12.869	-0.144	$+0.122$	-0.148	$+0.177$
10	$-59.539\,673$	2.357	12.855	-0.137	$+0.044$	-0.100	$+0.120$
15	$-59.535\,064$	2.199	12.827	-0.146	-0.036	$+0.022$	$+0.014$

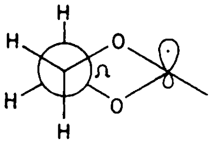
[a] For detailed geometry, see (10) and (11); θ measures the degree of twist in the ring; the ring is planar for $\theta = 0°$. An angle of bending of 42.5° at C_α is incorporated. [b] In mT. [c] In hartrees.



(10)



(11)



(12)

At this point it is necessary to consider which γ-proton splittings as calculated in Table 2 are interconverted by the processes previously discussed. For a half-chair structure with bent radical centre there are four possible conformations, as shown by structures (13)—(16). The *radical-centre inversion* process [exchanges (13) $\rightleftharpoons$ (15) and (14) $\rightleftharpoons$ (16)] leads to the averaging of the splittings of H-1 and H-4 and of the splittings of H-2 and H-3. The *flexible motion* of the ring or *ring-twisting* [exchanges (13) $\rightleftharpoons$ (14) and (15) $\rightleftharpoons$ (16)] leads to the averaging

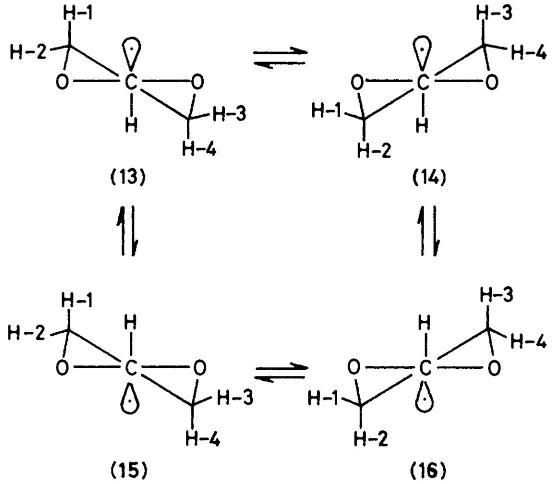
---

[12] S. Furberg and O. Hassel, *Acta Chem. Scand.*, 1950, **4**, 1584.

[13] C. Altona and A. P. M. van der Veek, *Tetrahedron*, 1968, **24**, 4377.

of the splittings of H-1 and H-3 and of the splittings of H-2 and H-4.

Consequently, for the unsubstituted radical (1) in which both processes are occurring freely, the observed simple quintet splitting will correspond to the overall



average of the calculated $a(\gamma\text{-H})$ values whereas, for the 2-methyl-substituted radical (2) in which the radical-centre inversion process has been frozen-out, the two pairs of observed splittings will correspond to the average of the calculated $a(\gamma\text{-H-1})$ and $a(\gamma\text{-H-3})$ $[a(\gamma\text{-H-1,H-3})_{av}]$ and the average of the calculated $a(\gamma\text{-H-2})$ and $a(\gamma\text{-H-4})$ $[a(\gamma\text{-H-2, H-4})_{av}]$. From the results in Table 2, no correlation can be found between the observed γ-proton splittings for either (1) or (2) and the corresponding average calculated splittings. It thus seems likely that the assumption of a perfect half-chair conformation does not offer a satisfactory explanation for the observed behaviour.

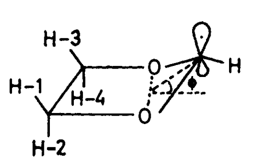
TABLE 3

INDO MO calculations on the envelope conformation of 1,3-dioxolan-2-yl [a]

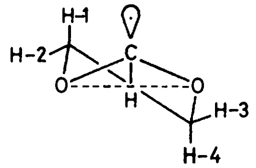
		Calculated splittings [b]					
				$a(\gamma\text{-H})$			
$\phi/°$	Energy [c]	$a(\alpha\text{-H})$	$a(\alpha\text{-}^{13}\text{C})$	H-1	H-2	H-3	H-4
0	−59.541 235	2.499	12.872	−0.154	+0.173	−0.154	+0.173
10	−59.542 531	2.315	12.943	−0.130	+0.123	−0.130	+0.123
20	−59.543 495	2.089	13.032	−0.107	+0.040	−0.107	+0.040
30	−59.544 142	1.893	13.198	−0.099	−0.058	−0.099	−0.058
40	−59.544 767	1.817	13.516	−0.118	−0.129	−0.118	−0.129
50	−59.546 145	1.963	14.047	−0.160	−0.089	−0.160	−0.089
60	−59.549 652	2.438	14.785	−0.205	+0.197	−0.205	+0.197
70	−59.556 855	3.302	15.592	−0.208	+0.900	−0.208	+0.900

[a] For geometry, see (17): ϕ measures the angle between the ' flap ' and the planar portion of the envelope. The angle of bending at C_α was taken as 42.5°. [b] In mT. [c] In hartrees.

Next, the possibility that an *envelope* configuration could adequately describe the dioxolan ring was investigated *via* INDO calculations on configurations in which the angle of bend (ϕ) in the envelope was varied as shown in (17) [ϕ is the angle between the OCCO and $OC_\alpha O$ planes defined such that H_α is *trans* to the ring]. The results are in Table 3. It can be seen that a value of ϕ of *ca.* 40° appears appropriate: then the two calculated averaged pairs of splittings $a(\gamma\text{-H-1,H-3})_{av}$ and $a(\gamma\text{-H-2, H-4})_{av}$ of −0.118 and −0.129 mT give reasonable agreement with the observed values for (2) [(±) 0.100 (2 H), (±) 0.145 (2 H)]. Larger values of ϕ enhance the difference between the pairs (for $\phi = 50°$, calculated values are −0.089 and −0.160) and a value of *ca.* 45° would presumably give optimum agreement. [A value of ϕ of 47° is calculated for the envelope form of cyclopentane itself from the published co-ordinates [11] of the ring carbon atoms; we note that on the basis of a study [14] of the nematic phase n.m.r. spectrum of 1,3-dioxolan it is concluded that an envelope configuration, with ϕ 42°, provides a reasonable description of the ring system]. We note that a small value of ϕ (*e.g. ca.* 20°) gives reasonable average pairs of splittings, but with *opposite* signs.



(17)



(18)

Despite the good correlation between these calculations on the envelope form of (1) and the experimentally observed splittings for (1) and (2), the possibility that the dioxolan ring has preferred conformations intermediate between half-chair and envelope forms (with, probably, dynamic interconversion involving a variety of structures) cannot be ignored, especially in the light of n.m.r. evidence to support this view.[10,11,13] In particular, the half-chair form rather than the envelope form minimises eclipsing 1,2-interactions between the γ-C–H bonds. Therefore, further calculations were performed in which both θ [*cf.* (10) and (11)] and ϕ [*cf.* (17)] were varied as indicated by (18) [*i.e.* on configurations having elements of both envelope and half-chair structures]; the results are in Table 4.

The best correlations between the calculated $a(\gamma\text{-H})_{av}$ and the observed values are obtained for $\theta = 5°$, $\phi = 40°$ (calculated γ-splittings are then −0.130, −0.102 mT); reasonable values are also obtained for $\theta = 10°$, $\phi = 30°$ (−0.148, −0.029) and $\theta = 15°$, $\phi = 20°$ (−0.152, −0.010 mT).

Final INDO calculations on (1) were performed for a

---

[14] C. A. de Lange, *J. Magnetic Resonance*, 1976, **21**, 37.

selection of configurations corresponding to $\phi = 40$ and 50° with $\theta = 0$, 5, 10, and 15° but with the conjugated bond C_α–O shortened to 0.139 nm (the value used previously[1,2]). In this case, this shortened bond length had little effect on the calculated splittings (see Table 5).

TABLE 4

INDO MO calculations on intermediate conformations of 1,3-dioxolan-2-yl[a]

		Calculated splittings (mT)					
				$a(\gamma\text{-H})$			
θ/°	ϕ/°	$a(\alpha\text{-H})$	$a(\alpha\text{-}^{13}C)$	H-1	H-2	H-3	H-4
5	20	2.078	13.042	−0.112	−0.037	−0.120	+0.099
5	30	1.900	13.219	−0.131	−0.108	−0.097	+0.004
5	40	1.842	13.546	−0.174	−0.107	−0.086	−0.098
5	50	2.005	14.083	−0.212	+0.076	−0.098	−0.148
5	60	2.491	14.817	−0.178	+0.614	−0.136	−0.047
10	20	2.053	13.078	−0.147	−0.099	−0.130	+0.118
10	30	1.930	13.287	−0.188	−0.109	−0.109	+0.051
10	40	1.931	13.648	−0.220	+0.014	−0.081	−0.046
10	50	2.150	14.205	−0.164	+0.410	−0.060	−0.138
10	60	2.667	14.927	+0.130	+1.280	−0.057	−0.161
15	20	2.041	13.152	−0.200	−0.106	−0.104	+0.085
15	30	2.024	13.431	−0.221	−0.007	−0.110	+0.063
15	40	2.142	13.859	−0.140	+0.310	−0.088	0.000
15	50	2.467	14.457	+0.214	+1.011	−0.052	−0.089
15	60	3.011	15.148	+1.120	+2.288	−0.017	−0.174

[a] For geometry, see (18); θ is the angle of twist in the ring, ϕ the angle at the envelope.

For the unsubstituted radical (1) and the 2-methyl-substituted radical (2) it can be concluded, on the basis of INDO calculations, that a configuration of envelope type with an angle of bend of 42.5° at the radical centre and with ϕ *ca.* 40°, but with a small degree of twist (θ in the range 0—10°) would account for the hyperfine splittings observed.

It was also of interest to see whether the calculations presented so far permit conclusions to be drawn regarding the structure of any of the ring-substituted radicals. It is apparent from the non-equivalence of the γ-proton splittings induced by the presence of one or two methyl groups, that unsymmetrical structures [with different $a(\gamma\text{-H})$ values] are involved. Presumably some degree of conformational weighting is introduced, as indicated by the temperature dependent $a(\gamma\text{-H})$ values in, for example, the 4-methyl-substituted radical (7) where the e.s.r. spectrum presumably resembles that of the preferred conformation to an increased extent as the temperature is lowered. It is perhaps surprising, however, that the $a(\gamma\text{-H})$ values detected are in some cases significantly greater than any observed for (1) and (2) [though it should be remembered that the latter are averaged splittings]. For example, for (7) $a(\gamma\text{-H})$ values of *ca.* 0.2 mT are seen, and for (8) one splitting is as high as 0.4 mT. Bearing in mind that it is not known[10] whether a single ring substituent would be preferentially axial or equatorial and since the ring shapes for radicals (7)—(10) may not closely resemble those for (1) and (2), it would not necessarily be expected that there exists a correlation between the hyperfine splittings of these radicals and the results of the INDO calculations presented so far. However, some tentative conclusions may be drawn.

TABLE 5

Sample INDO calculations on 1,3-dioxolan-2-yl using a shortened C_α–O bond length of 0.139 nm

		Calculated splittings[a]					
				$a(\gamma\text{-H})$			
θ/°	ϕ/°	$a(\alpha\text{-H})$	$a(\alpha\text{-}^{13}C)$	H-1	H-2	H-3	H-4
0	40	1.978	13.869	−0.127	−0.137	−0.127	−0.137
	50	2.143	14.404	−0.169	−0.087	−0.169	−0.087
5	40	2.003	13.892	−0.187	−0.106	−0.093	−0.111
	50	2.186	14.431	−0.225	+0.096	−0.104	−0.156
10	40	2.093	13.972	−0.233	+0.032	−0.085	−0.063
	50	2.336	14.525	−0.176	+0.458	−0.064	−0.153
15	40	2.311	14.144	−0.145	+0.356	−0.089	−0.020
	50	2.663	14.725	+0.219	+1.099	−0.054	−0.111

[a] In mT.

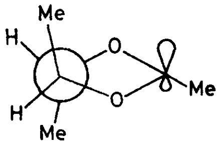
For (7) a configuration having two averaged $a(\gamma\text{-H})$ values of at least 0.2 mT is required (radical-centre inversion will still be occurring rapidly at the lowest temperature of observation so that splittings from H-1 and H-4 are averaged, as are splittings from H-2 and -3) [structures (13)—(16), with distortion as indicated by (18)]; it must also be remembered that complete weighting of the preferred conformation may not have been achieved. Structures can be found which lead to predicted splittings for (7) in reasonable agreement with observation. For example for $\theta = 5°$, $\phi = 50°$, with the methyl group replacing γ-H-3, the configuration has $a(\gamma\text{-H-1})$ −0.212, $a(\gamma\text{-H-4})$ −0.148, and $a(\gamma\text{-H-2})$ +0.076 mT: averaging of the splittings from H-1 and H-4 by the rapid radical-centre inversion gives calculated splittings of $a(\gamma\text{-H-1,H-4})_{av} = -0.180$ (2 H) and $a(\gamma\text{-H-2}) = +0.076$ mT (1 H), in reasonable agreement with the observed values. On the other hand, if the larger γ-splittings in (7) are positive, possible structures include that with $\theta = 5°$, ϕ *ca.* 60° [with H-1 replaced by methyl, and $a(\gamma\text{-H-2})$ and $a(\gamma\text{-H-3})$ averaged by rapid radical-centre inversion: calculated splittings are then $a(\gamma\text{-H-2, H-3})_{av}$ +0.239 (2 H), $a(\gamma\text{-H-4})$ −0.047 mT (1 H)]; similarly, those conformations with $\theta = 10°$, ϕ *ca.* 50° and $\theta = 15°$, ϕ *ca.* 40—50° could also be appropriate. Clearly no definite conclusions can be drawn regarding the shape of the ring in this radical without knowledge of the absolute signs of the γ-splittings.

The case of radical (8) is different, since at low temperature the radical-centre inversion process is frozen out [two very different $a(\gamma\text{-H})$ values of the *same* sign are observed]: furthermore the positions of the sharp γ-lines remain constant over a wide temperature range. This suggests not only that the radical-centre inversion is slowed at low temperature, but also that the radical may be more or less 'locked' in one specific configuration at the back of the ring (*i.e.* θ remains fixed): by analogy with some 1,2-dihalogenocyclopentanes[11,15] it seems likely that this fixed conformation is the result of a preference for the two *trans*-ring-methyl substituents to be axial or pseudoaxial (19). The remaining two equatorial γ-proton splittings should then correspond to

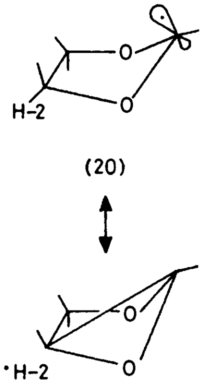
---

[15] C. Altona, H. R. Buys, and E. Havinga, *Rec. Trav. chim.*, 1966, **85**, 983, 998.

$a(\gamma$-H-2) and $a(\gamma$-H-3) in Tables 2—5. From these Tables, the configurations which have either $a(\gamma$-H-2) or $a(\gamma$-H-3) *ca.* 0.4 mT (and which have a significant value of θ consistent with this shape) are $\theta = 10°$, $\phi = 50°$ and $\theta = 15°$, $\phi = 40°$; for example, the former has $a(\gamma$-H-2) $+0.41$ and $a(\gamma$-H-3) -0.06 mT. Furthermore a reasonably large value of θ seems appropriate since this decreases steric hindrance between the two methyl groups. On the basis of these results, it appears likely that the dioxolan ring in 2,4,5-trimethyl-1,3-dioxolan-2-yl (8) is more puckered than in radicals (1) and (2) and that this arises from increases in both θ and ϕ. Although the details of the calculations on (1), as applied to this radical (8), are not necessarily reliable, it is interesting that only for high values of θ and ϕ are γ-proton splittings as large as 0.4 mT detected, and in every case this large splitting is predicted to be positive; this seems reasonable as in these very puckered conformations (*i.e.* high θ and ϕ), one particular γ-proton (H-2, as predicted by the calculations) is ideally situated [see (20)] to allow transference of positive spin density from the radical centre to the γ-protons *via* a homohyperconjugation mechanism.[16,17] This is an example of the typical W (zig-zag) arrangement of bonds which is often associated with long-range interaction.



(19)



(20)

Here, as elsewhere, it is desirable to know the absolute signs of the splittings. However, it is impossible to achieve this without the assistance of n.m.r., and clearly the radicals studied here are not stable enough for this method to be used. It is possible that the INDO approach—coupled with a knowledge of the relative signs of splittings as indicated by linewidth alternation effects—provides a realistic alternative to n.m.r. under these circumstances.

It is apparent that the result of spin-transmission to γ-protons is different for the more markedly bent dioxolan radicals (both splittings the same sign, probably negative for unsubstituted examples) than for the dioxan species (splittings of opposite sign). It seems likely that the effect giving rise to a positive contribution to spin density (hyperconjugation arising from positive spin density on β-oxygen) has decreased for the five-membered ring radicals as compared with the six-membered analogues: this decrease may be a consequence of increasing bending at C_α or, more probably, because the γ-protons are not positioned in those regions of space where the hyperconjugative transmission is most effective (*cf.* axial γ-protons in the six-membered ring, with dihedral angles close to zero). By contrast, the spin-polarization mechanism, which is a through-bond effect, probably becomes more effective as the degree of bending at C_α is increased.

EXPERIMENTAL

Details of the e.s.r. spectrometer, photolytic arrangement, sample preparation, and generation of radicals have been given previously.[1,2]

With the exception of the following compounds, all chemicals employed were obtained commercially and used without further purification. 2,4-Dimethyl-1,3-dioxolan[10] was prepared by the acid-catalysed condensation[18] of propane-1,2-diol and acetaldehyde, with dichloromethane as a solvent. A similar method was employed to prepare 2,4,5-trimethyl-1,3-dioxolan from acetaldehyde and butane-2,3-diol [this being obtained from Aldrich Ltd. as a mixture of *meso* and ($\pm$)-forms]. The n.m.r. spectrum of the product showed that the *trans*-form $\{\tau[C(4,5)H]\ 6.45\}$ constituted >80% of the reaction mixture: some *cis*-form $\{\tau[C(4,5)H]\ 6.00\}$ was also obtained (these assignments are based on the n.m.r. spectra of the *syn*- and *anti*-forms of 2,*r*-4,*c*-5-trimethyl-1,3-dioxolan[10] and of *c*- and *t*-4,5-dimethyl-1,3-dioxolan[19]). The e.s.r. spectra derived from the product showed a strong signal attributed to the radical from the *trans*-isomer, together with some weak unassigned lines probably associated with a radical from the *cis*-compound.

We thank the S.R.C. for a studentship (for C. G.).

[6/2009 *Received*, 29*th October*, 1976]

---

[16] G. R. Underwood, V. L. Vogel, and J.-A. Iorio, *Mol. Phys.*, 1973, **25**, 1093; G. R. Underwood and V. L. Vogel, *J. Amer. Chem. Soc.*, 1971, **93**, 1058.

[17] F. W. King, *Chem. Rev.*, 1976, **76**, 157.

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

[19] M. Gianni, J. Saavedra, R. Myhalyk, and K. Wursthorn, *J. Phys. Chem.*, 1970, **74**, 210.