Investigations of Structure and Conformation. Part 7.[1] Long-range Interactions and Line-width Alternation associated with β- and γ-Proton Splittings in the E.s.r. Spectra of Radicals from Cyclic Ethers containing Six-membered Rings

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E.s.r. spectra from 1,3-dioxan-2-yl and 1,3,5-trioxanyl radicals at low temperatures show line-width alternation arising from conformational interconversion involving the rings. Both these radicals, which are pyramidal at the α-carbon atom, are found to have two pairs of γ-proton splittings of opposite sign, which accounts for the dramatic narrowing of the spectrum-width in each case as the temperature is raised: the contributions of hyperconjugation and of through-bond spin-polarization to spin transmission are discussed. Kinetic parameters are obtained for the chair–chair interconversion of the trioxanyl radical and also for 1,4-dioxanyl (the slow-exchange limit spectrum for which has been recorded). INDO calculations on these species are reported.

We have previously shown that at *ca.* −100 °C the radical $\cdot CH_2OCH_2OCH_3$ exhibits an e.s.r. spectrum with unusual line-width alternation; this was interpreted in terms of exchange not only of two non-equivalent α-proton splittings (*via* rotation about $\cdot C_\alpha$–O) but also of exchange (*via* rotation about O_β–C_γ) of two γ-proton splittings of opposite sign.[1] It was suggested that the opposite signs detected for the γ-protons in the slow-exchange limit probably reflect the operation of at least two modes of spin transmission, namely hyperconjugation involving spin-density on oxygen ($>\dot{C}-\ddot{O}-CH \longleftrightarrow >\overset{-}{\ddot{C}}-\overset{+\cdot}{O}-CH$), which should be angular-dependent, and spin-polarization *via* the bonding σ-electrons; these should give positive and negative contributions, respectively, to *a*(γ-H). In order to obtain more information about spin-transmission in such systems we have extended our study to some radicals from cyclic ethers, in particular those with six-membered rings (from 1,3-dioxan, 1,4-dioxan, and 1,3,5-trioxan). In this way it was hoped to obtain radicals for which the preferred conformations could be more reliably estimated than for the acyclic examples, so that the different mechanisms for spin transmission could be more easily studied. Added interest stems from the recognition that, for cyclic radicals in which two oxygen atoms flank the radical centre, there is considerable distortion from coplanarity of the bonds at the radical centre[2] (*i.e.* that the unpaired electron occupies an orbital with considerable *s*-character) and also that dramatic examples of long-range interaction often occur in cyclic systems.[3]

EXPERIMENTAL

Radicals were generated by *in situ* photolytic decomposition of di-t-butyl peroxide in the presence of suitable substrates; details of the photolysis apparatus, sample preparation, e.s.r. spectrometer and spectrum measurement, and computational procedures have been described.[1] The spectrum simulation program was provided by Dr. M. F. Chiu and was executed with an Elliott 4130 computer at the University of York; the INDO MO program[4] (obtained from the Quantum Chemistry Program Exchange, QCPE No. 141) was executed with a CDC 7600 computer at the University of Manchester Regional Computer Centre. The compounds employed (1,3-dioxan, 1,3,5-trioxan, 4-methyl-1,3-dioxan, and 1,4-dioxan) were commercial samples and, except for 1,3,5-trioxan (which was recrystallized from ethanol and from ether prior to use), were used without further purification.

RESULTS AND DISCUSSION

E.s.r. Spectra—(a) *The* 1,3-*dioxan*-2-*yl radical.* Figure 1(a) shows the e.s.r. spectrum obtained during the reaction of $Bu^tO\cdot$ with 1,3-dioxan at −63 °C. This is attributed to the 1,3-dioxan-2-yl radical (1), whose formation is expected on the basis of the activating influence of the two oxygen atoms to hydrogen abstraction from C-2. Several features are noteworthy. First, the small quartet splitting of 0.02 mT is attributed to the accidental equivalence of the δ-protons and the α-proton (the splitting of the latter is dramatically reduced from the value of *ca.* 1.7 mT for mono-oxygen conjugated analogues because of the bending introduced at the radical centre[2]). Secondly, the larger ' triplet ' is not of 1 : 2 : 1 type, and we have previously suggested[2] that it is a 1 : 4 : 1 pattern of sharp lines together with some broad undetected lines (as expected if γ-proton exchange involving two non-equivalent splittings occurs in the ' intermediate ' range).

When the temperature was raised, the signal-to-noise ratio deteriorated and no further information could be obtained. However, when the temperature was lowered the spectra improved and changed dramatically: Figure 1(b) shows the spectrum at −87 °C: the γ-proton splitting pattern has become fully resolved into a septet of relative intensities 1 : 2 : 3 : 4 : 3 : 2 : 1, indicating splitting by two pairs of protons [*a* (2 H) 0.132, *a* (2 H) 0.065 mT], and the spectrum-width has dramatically increased. This behaviour can be explained if the two separate sets of γ-proton splittings (presumably from pseudoequatorial and pseudoaxial hydrogen atoms; see later) have opposite signs. Then, the average γ-proton splitting is *ca.* 0.03 mT and the spectrum is narrowed

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

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

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

[4] 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.

when the exchange rate is rapid: this is represented diagrammatically in Figure 2. Simulation of the spectra by using parameters given in Table 1 and a Bloch-equation treatment of exchange yields excellent agreement with experiment and provides confirmation of the analysis: for example, the spectrum at −63 °C is fitted by using an exchange rate between two equivalent forms [presumably (1a) and (1b)] of 10^7 Hz. Detailed assignment of splittings (with signs) to individual γ-protons (axial and equatorial) is made in later sections.

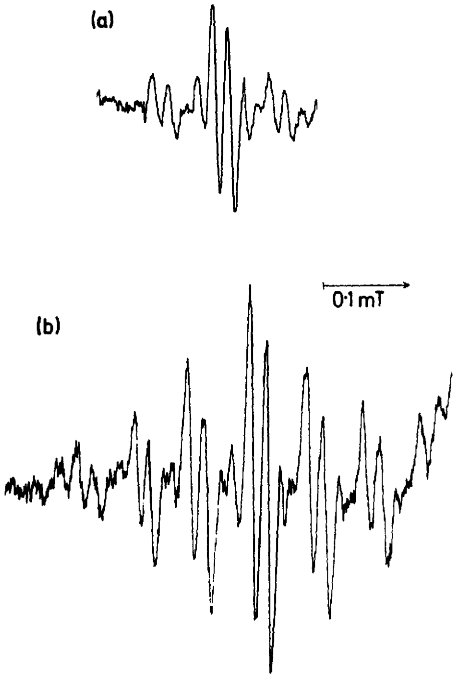
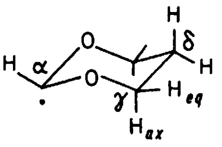
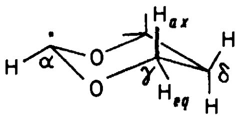


FIGURE 1 E.s.r. spectrum of the 1,3-dioxan-2-yl radical; (a) at −63 °C; (b) at −87 °C (the distortion at high field arises from radiation damage in the quartz cell)



(1a)



(1b)

(b) *The 4-methyl-1,3-dioxan-2-yl radical.* Support for the analysis presented above was obtained from the spectrum observed when t-butoxyl reacts with 4-methyl-1,3-dioxan. This, assigned to 4-methyl-1,3-dioxan-2-yl (2), bears some relationship to the low-temperature spectrum recorded for 1,3-dioxan-2-yl; it has two proton splittings [*a* (1 H) 0.14, *a* (2 H) 0.07 mT] attributed to the three γ-protons in (2) [*cf.* γ-proton h.f.s. in (1)] but with a fairly large line-width (*ca.* 0.05 mT) which, we believe, obscures the small α- and δ-proton splittings.

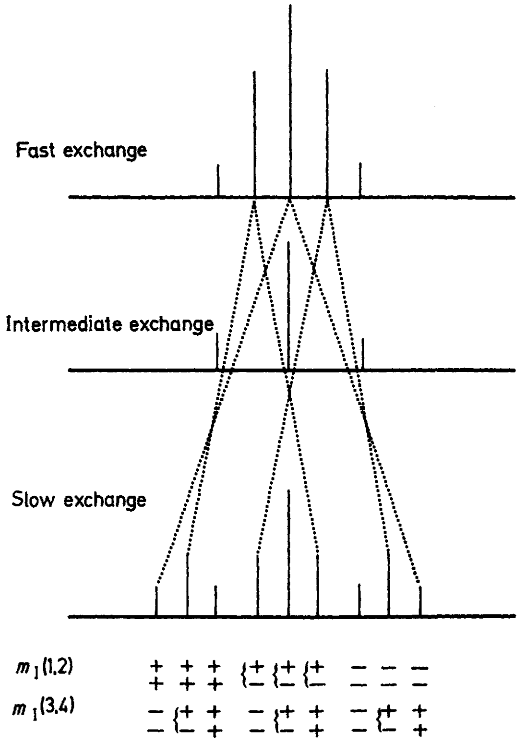


FIGURE 2 Diagrammatic representation of the effect of exchange on a spectrum from a radical exhibiting interaction with two pairs of protons with splittings of opposite sign ($|a[m_1(1,2)]| > |a[m_I(3,4)]|$).

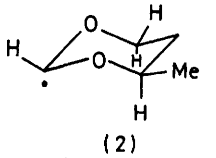
TABLE 1

E.s.r. spectra of radicals derived from some cyclic ethers [a]

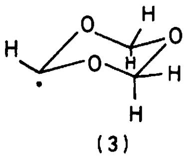
		Hyperfine splittings (mT) [b]			
Radical	t/°C	a(α-H)	a(β-H)	a(γ-H)	a(δ-H)
(1)	−14	(±) 0.02		*c*	(±) 0.02 (2 H)
	−87	(±) 0.02		(±) 0.132 (2 H) (∓) 0.065 (2 H)	(±) 0.02 (2 H)
(2)	−50	*d*		(±) 0.14 (1 H) (∓) 0.07 (2 H)	*d*
	−108	*d*			*d*
(3)	−29	(±) 0.03			
	−88	(±) 0.025		(±) 0.08 (2 H) (∓) 0.085 (2 H)	
(4)	R.t.[e]	(−) 1.738	(+) 2.269 (2 H) [c]	(±) 0.095 (2 H)	*d*
	−53	(−) 1.72	(+) 2.36 (2 H) [c]	(±) 0.075 (2 H)	*d*
	−88	(−) 1.75	(+) 3.875 (1 H) (+) 0.84 (1 H)	(±) 0.10 (2 H) [c]	*d*
•$CH_2OCH_2OCH_3$	−130	(−) 1.925 (−) 1.81		(+) 0.19 [f] (−) 0.05	

[a] From Bu^tO•. [b] ±0.005 mT. [c] Alternating line-widths; for analysis, see text. [d] Not resolved; see text. [e] Data for room temperature.[8] [f] Data from ref. 1.

The spectrum does not vary significantly with temperature, in contrast to that for (1); this is as anticipated since the 4-methyl group should provide almost complete conformational locking at the temperatures employed.[5] Since by comparison with the parent compound itself [5] we should expect that the methyl group is situated preferentially in the equatorial position, we can conclude that in the radicals (1) and (2) the γ-proton with the larger value of |a(H)| in each case is equatorial, rather than axial.



(2)



(3)

(c) *The* 1,3,5-*trioxanyl radical.* Attention has previously been focussed (see, *e.g.* ref. 2 and references therein) on the extremely simple spectrum of radical (3), from trioxan, at ambient temperatures; the signal has a(1 H) 0.03 mT [see *e.g.* Figure 3(a)], which is ascribed to the anomalous α-proton splitting in a non-planar radical. Dramatic changes in this spectrum take place as the temperature is lowered; by −55 °C some broader lines are seen outside the sharp doublet [see Figure 3(b)] and by −100 °C the pattern has a(α-H) 0.025 mT, with a(γ-H) 0.08 (2 H) and 0.085 (2 H) mT [interaction with two pairs of protons, giving a spectrum which approaches a 1 : 4 : 6 : 4 : 1 pattern: see Figure 3(c)]. The tremendous increase in spectrum-width and the appearance of first broad, then sharp, lines outside the narrow doublet as the temperature is lowered can be understood if the γ-splittings of 0.08 and 0.085 mT have opposite signs. Then, rapid interconversion at higher temperatures produces an average splitting of almost zero (less than the line-width), so that the splitting is apparently removed at high temperatures. This is a special case of the phenomenon outlined for radical (1), with $a(\gamma\text{-H}_1) \simeq -a(\gamma\text{-H}_2)$, and the analysis is confirmed by the results of spectrum simulation by employing exchange effects and γ-proton splittings of opposite sign and similar magnitude [see *e.g.* Figure 3(b)]. Results for various temperatures are collected in Table 2; we estimate that the barrier to the interconversion process (presumably chair–chair ring flipping) is 27 ± 3 kJ mol^{-1}.

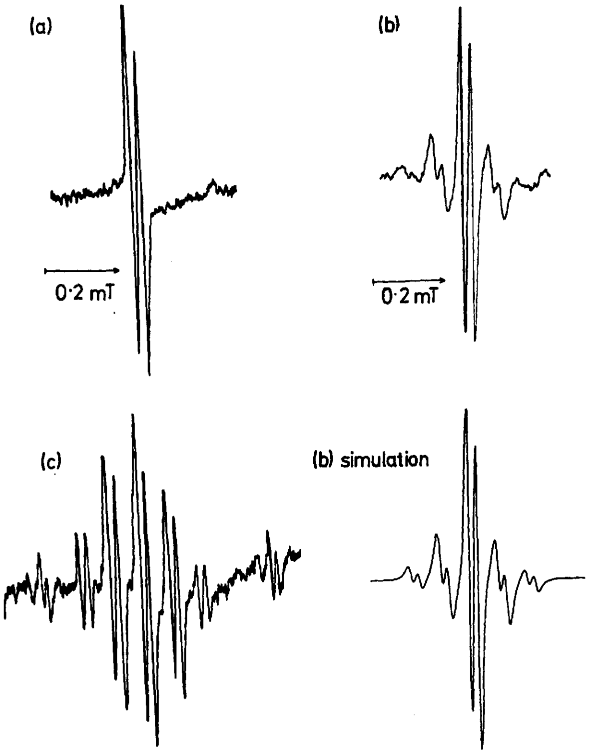


FIGURE 3 E.s.r. spectra of the 1,3,5-trioxanyl radical: (a) at −29 °C; (b) at −55 °C, with simulation by employing a rate for ring-flipping of 1.4 × 10^6 Hz (see text); (c) at −100 °C

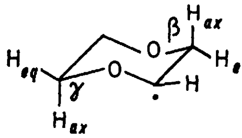
TABLE 2

Rate of chair–chair interconversion for the 1,3,5-trioxanyl radical (3)

t/°C	−100	−88	−70	−55	−52	−29
$10^{-5}k$/Hz	<1	1	5	14	18	70

Another unusual phenomenon associated with the spectrum from 1,3,5-trioxanyl is that, as the temperature is lowered, two groups of lines (with a separation of *ca.* 0.65 mT) appear on either side of the main signal (which has g 2.002 8); they are first noticed at *ca.* −33 °C (by using high modulation) and become more prominent as the temperature is lowered further [see Figure 3(c)]. This behaviour proved reproducible over a series of cycles in which the temperature was raised and lowered; it does not become enhanced after prolonged irradiation (and therefore does not apparently originate from any photoproduct), and was not removed even when the 1,3,5-trioxan was recrystallised several times before use. The lines appear to be too sharp—and occur at too high a temperature—to be attributed reliably to anisotropic features, and we tentatively suggest that the doublet may originate from the α-proton splitting in a conformation of 1,3,5-trioxanyl which is not the preferred chair form described above, but one of higher energy which is 'frozen out' when the ring-flipping is slowed. A twist-chair or skew-boat form might be appropriate.

(d) *The* 1,4-*dioxanyl radical.* Previous e.s.r. studies [6-8] have confirmed that in the radical (4), from 1,4-dioxan, the β-hydrogen splitting pattern at about room temperature appears as a 1 : (broad) : 1 triplet; the spectrum



(4)

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[5] (*a*) K. Pihlaja and S. Luoma, *Acta Chem. Scand.*, 1968, **22**, 2401; (*b*) E. L. Eliel and Sr. M. C. Knoeber, *J. Amer. Chem. Soc.*, 1968, **90**, 3444.

[6] A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **25**, 5311.

[7] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4850.

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

also contains an α-proton doublet splitting and a γ-proton triplet splitting (see Table 1). It is generally agreed that the origin of the alternating line-width effect for the β-proton pattern is the occurrence of chair–chair interconversion (at an intermediate rate) which exchanges the splittings from axial and equatorial β-protons.

We have now found that by −88 °C the β-proton splitting pattern has become completely resolved into a doublet of doublets [*a* 3.875 (1 H) and 0.84 (1 H) mT]; for these protons, then, the slow-exchange limit has been achieved. These splittings are presumably associated with the β-axial and β-equatorial protons, respectively, since the individual splittings should, to a first approximation, be proportional to $B\cos^2\theta$ (where θ is the dihedral angle between the C_β–H bonds and the orbital of the unpaired electron). In a perfect chair, with a planar radical centre, the appropriate values of θ are 30 and 90°, respectively: the splittings detected here (in particular, the non-zero value for the pseudoequatorial proton) suggests that some twisting of the ring has occurred, and values of θ of *ca.* 15 and 75° appear more appropriate [as previously suggested [8] for the 'locked' radical *N*-t-butylpiperidin-4-yl, for which *a*(β-H) values are 4.08 and 0.98 mT].

The ambient temperature γ-proton splitting pattern (1 : 2 : 1) shows broadening of the middle line as the temperature is lowered, and by −50 °C the central line has disappeared. At the lowest temperature obtained (−88 °C) the γ-proton pattern still remains a doublet, with no trace of a further splitting. We believe that the slow-exchange limit has been reached, so that the individual γ-proton splittings are probably *ca.* 0.20 mT and *ca.* zero (*i.e.* less than the line-width of *ca.* 0.05 mT). Spectra recorded over a range of temperatures have been successfully simulated by using the slow-exchange limit parameters given in Table 1 together with a Bloch-equation treatment of exchange: the energy barrier for ring flipping is found to be 32 ± 3 kJ mol^{-1}.

Interpretation of Long-range Splittings: *INDO Calculations*.—For our analysis of the magnitude and signs of the γ-proton splittings in the slow-exchange limit spectrum of $\cdot CH_2OCH_2OCH_3$,[1] INDO calculations gave results in general agreement with predictions based on a model in which spin density was transmitted both *via* hyperconjugation and *via* spin-polarization. A γ-proton for which the C–H bond subtends a small dihedral angle (θ *ca.* 30°) with the lone-pair *p* orbital on oxygen was attributed the *positive* splitting (of +0.19 mT), with a dominant contribution from hyperconjugation involving the structure $\overset{\cdot\cdot}{C}H_2\text{–}\overset{+\cdot}{O}\text{–}CH_\gamma$; the second γ-proton, evidently close to the nodal plane of the unpaired electron's orbital on C_α and O_β (with θ *ca.* 90°), was attributed the *negative* splitting of −0.05 mT (this reflecting mainly spin-polarization from C_α).

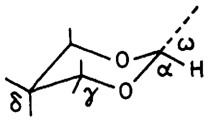
A similar approach has been employed here in an attempt to rationalize the observations concerning γ-proton splittings of opposite sign. It is of interest to determine whether INDO calculations lead to predictions of bent geometries (at C_α) in the radicals (1)—(3), and also, in particular, whether γ-proton splittings for (1) and (3) are calculated to have opposite signs (especially when the radicals are assumed to have chair-type structures, with pyramidal geometry at C_α).

INDO calculations on (1), (3), and (4) have been carried out. The following parameters have been employed: C–H 0.108, C–C 0.154, C–O (non-conjugated) 0.142, C–O (conjugated) 0.139 nm; $\widehat{CCC}$, $\widehat{HCH}$, and $\widehat{HCO}$ and $\widehat{HCC}$ (except for $\widehat{HC_\alpha O}$ and $\widehat{HC_\alpha C}$) tetrahedral. In addition, for (1) and (3) angles in the ring were taken as 110° except for $\cdot\widehat{C_\alpha OC}$ which was set equal to 120°; for (4), all angles in the ring were set at 110° except for $\cdot\widehat{C_\alpha OC}$ and $\cdot\widehat{C_\alpha CO}$, which were taken as 120°.

Table 3 shows the calculated energies and splittings for the 1,3-dioxan-2-yl radical as a function of the angle of bending (ω) at the radical centre. The calculated configuration of minimum energy has a considerable degree of bending at the radical centre (ω *ca.* +40°). However, of particular interest is the range ω +20 to +30°, where splittings close to those determined experimentally are obtained (as noted before,[1,2] INDO calculations seem to overestimate the degree of bending if the energy minimum, rather than best 'predicted' set of splittings, is used as the criterion). For example, for ω = +28°, the calculated α-proton splitting (−0.076 mT) is close to zero (the observed value is ±0.02 mT) and the α-^{13}C splitting predicted (8.854 mT) is in reasonable agreement with the experimental value for the related radical (3) [9.98 mT; [2] no ^{13}C data for (1) are available]. The γ-proton splittings are predicted to have opposite signs and somewhat different magnitudes, −0.105 and +0.047 mT, for equatorial and axial protons, respectively: these magnitudes are in good agreement with our finding [*a*(*eq*) (−) 0.132, *a*(*ax*) (+) 0.065 mT] and the signs are as expected if the axial γ-proton has a dominant

TABLE 3

INDO calculations of hyperfine splittings [a] for 1,3-dioxan-2-yl as a function of the extent of bending at the radical centre [b]



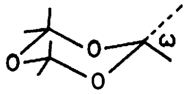
ω/°	*E*/Hartree [c]	*a*(α-H)	*a*(γ-*eq*)	*a*(γ-*ax*)	*a*(δ-*eq*)	*a*(δ-*ax*)	*a*(α-^{13}C)
−50	−67.974 950	+3.382	−0.010	−0.042	+0.496	+0.046	+16.137
−40	−67.980 899	+2.846	−0.021	−0.025	+0.459	+0.045	+14.004
−30	−67.982 300	+2.041	−0.037	−0.008	+0.420	+0.044	+11.589
−20	−67.980 327	+0.874	−0.060	+0.009	+0.375	+0.041	+8.907
−10	−67.976 717	−0.614	−0.093	+0.027	+0.315	+0.036	+6.173
0	−67.973 991	−1.952	−0.127	+0.042	+0.232	+0.028	+4.211
+10	−67.974 620	−2.202	−0.143	+0.049	+0.134	+0.017	+4.313
+20	−67.978 735	−1.190	−0.129	+0.048	+0.053	+0.007	+6.518
+22	−67.979 775	−0.914	−0.123	+0.048	+0.041	+0.005	+7.089
+24	−67.980 830	−0.633	−0.117	+0.048	+0.029	+0.004	+7.674
+26	−67.981 876	−0.352	−0.111	+0.047	+0.020	+0.002	+8.265
+28	−67.982 889	−0.076	−0.105	+0.047	+0.011	+0.001	+8.854
+30	−67.983 847	+0.190	−0.098	+0.048	+0.003	0.000	+9.435
+40	−67.987 198	+1.337	−0.065	+0.052	−0.022	−0.005	+12.102
+50	−67.986 882	+2.164	−0.034	+0.063	−0.034	−0.010	+14.280
+60	−67.981 681	+2.757	−0.007	+0.079	−0.038	−0.013	+15.979
[Observed, −87 °C:		(±)0.02	(±)0.132	(∓)0.065	(±)0.02 [d]	(±)0.02 [d]]	

[a] In mT. [b] ω positive for bending in the downward direction, as shown. [c] 1 Hartree = 2 625 kJ mol^{-1}. [d] Individual splittings not resolved.

hyperconjugation contribution and the equatorial γ-splitting arises almost solely *via* spin-polarization. The positive splitting (if we assume that our assignments are correct) is considerably lower than that detected for $\cdot CH_2OCH_2OCH_3$; this may reflect a smaller extent of overlap between the unpaired electron on C_α and the *p*-lone pair on oxygen in the cyclic, as compared with the acyclic, example (in the latter it seems likely that this overlap is maximized).

TABLE 4

INDO calculations of hyperfine splittings [a] for the 1,3,5-trioxanyl radical as a function of the extent of bending at the radical centre [b]



ω/°	*E*/Hartree [c].	*a*(α-H)	*a*(γ-*eq*)	*a*(γ-*ax*)	*a*(α-^{13}C)
−50	−77.159 263	+3.694	−0.085	+0.138	+15.950
−40	−77.164 505	+3.050	−0.092	+0.148	+13.906
−30	−77.165 208	−2.145	−0.101	+0.158	+11.520
−20	−77.162 585	+0.860	−0.115	+0.167	+8.798
−10	−77.158 507	−0.745	−0.130	+0.172	+5.980
0	−77.155 739	−2.075	−0.134	+0.163	+4.054
+10	−77.156 788	−2.074	−0.109	+0.135	+4.440
+20	−77.161 292	−0.810	−0.061	+0.100	+6.885
+22	−77.162 364	−0.504	−0.051	+0.094	+7.475
+24	−77.163 431	−0.199	−0.041	+0.089	+8.071
+26	−77.164 470	+0.099	−0.030	+0.083	+8.665
+28	−77.165 457	+0.388	−0.021	+0.079	+9.250
+30	−77.166 373	+0.665	−0.011	+0.075	+9.822
+40	−77.169 285	+1.835	+0.033	+0.065	+12.395
+50	−77.168 246	+2.674	+0.067	+0.059	+14.481
+60	−77.162 126	+3.304	+0.097	+0.064	+16.090
[Observed: [d]		(±) 0.025	(±) 0.085	(∓) 0.08	(+) 9.98]

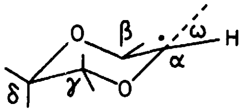
[a] In mT. [b] ω positive indicates downward distortion, as indicated. [c] 1 Hartree = 2 625 kJ mol^{-1}. [d] This work and ref. 2 [for *a*(α-^{13}C)].

Table 4 shows the energies and splittings calculated for 1,3,5-trioxanyl (3), again as a function of the extent of bending at the radical centre. As for (1), consideration of calculated energies and splittings provides further support for the concept of a bent radical centre for this 1,1-dioxygen-substituted species. Again, a bent configuration is found which gives a very low *a*(α-H) and high *a*(α-^{13}C) [calculated for ω = +26°; *a*(α-H) +0.099, *a*(α-^{13}C) +8.7 mT; observed values ±0.025 (at −88 °C) and [2] 9.98 mT, respectively]. Of particular interest is that, for ω in this region, the γ-proton splittings are calculated to be of opposite sign, and closer together in magnitude, than the corresponding protons in (1) [as observed: for (3), ω = +26°, we calculate *a*(γ-H) −0.03 (*eq*), *a*(γ-H) +0.083 mT (*ax*), in comparison with observed values of (±) 0.08 and (∓) 0.085 mT]. Since the geometries of (1) and (3) (particularly around the radical centres, the adjacent oxygen atoms, and the γ-carbon atoms) are very similar, it seems likely that these differences observed (and calculated) for the two radicals stem from electronic changes associated with the replacement of CH_2 [in (1)] by oxygen; the transmission of spin density to the γ-protons (particularly by the spin-polarization mode) may well be affected by the electronegativity of the atoms attached to the γ-carbon.

INDO calculations on the 1,4-dioxanyl radical are presented in Table 5. Consideration of energy minima and also of optimized splittings suggests that, in comparison with (1) and (3), the degree of bending at the radical centre is less pronounced; thus for ω *ca.* +10°, and also for ω in the region −10 to −20°, calculated values of *a*(α-H) are in the appropriate region. Further, the β-proton splittings are in good agreement with experiment and with expectation based on the *B*cos^{2}θ dependence, and the γ-proton splittings are predicted to be different, with one close to zero (as observed) and the other having a significant negative splitting. An interesting feature is that for most configurations one δ-proton is predicted to give a splitting of detectable magnitude, which is contrary to our findings. Optimum overall agreement is obtained in the region with ω −10 to −20°, where not only are the β-proton and γ-proton splittings well reproduced but also the δ-proton splitting

TABLE 5

INDO calculations of proton hyperfine splittings [a] for 1,4-dioxanyl as a function of the extent of bending at the radical centre [b]



ω/°	*E*/Hartree [c]	*a*(α-H)	*a*(β-*ax*)	*a*(β-*eq*)	*a*(γ-*ax*)	*a*(γ-*eq*)	*a*(δ-*ax*)	*a*(δ-*eq*)
−40	−67.965 555	−0.242	+4.009	+0.643	+0.101	−0.107	−0.005	+0.020
−30	−67.965 569	−0.885	+4.140	+0.647	+0.081	−0.134	−0.001	+0.058
−20	−67.963 880	−1.559	+4.154	+0.638	+0.065	−0.154	+0.003	+0.111
−10	−67.961 956	−2.033	+3.987	+0.613	+0.047	−0.162	+0.008	+0.177
0	−67.960 949	−2.056	+3.611	+0.558	+0.025	−0.152	+0.013	+0.248
+10	−67.961 089	−1.601	+3.079	+0.475	0.000	−0.131	+0.017	+0.314
+20	−67.961 589	−0.894	+2.492	+0.378	−0.026	−0.108	+0.020	+0.369
+30	−67.961 148	−0.191	+1.933	+0.285	−0.049	−0.091	+0.021	+0.413
+40	−67.958 487	+0.341	+1.438	+0.209	−0.071	−0.083	+0.022	+0.450
[Observed:		(−) 1.75	(+) 3.875	(+) 0.84	(±) 0.20 (1 H) *ca.* 0 (1 H)			

[a] In mT. [b] ω positive for bending in the downward direction, as shown. [c] 1 Hartree = 2 625 kJ mol^{-1}.

is considerably lowered. We do not suggest that the radical is ' locked ' in this bent configuration: indeed, it is presumably inverting rapidly at the radical centre between two minimum-energy configurations (one with ω positive, the other with ω negative). However, on the basis of the calculations we speculate that the potential well of lowest energy has ω negative.

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