Investigations of Structure and Conformation. Part 10.[1] Electron Spin Resonance and INDO Studies of Conformational Interconversion in the Tetrahydrofuran-2-yl and Tetrahydrothiophen-2-yl Radicals

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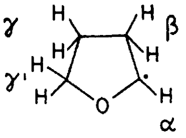
E.s.r. spectra have been recorded, over a wide range of temperature, for the radicals tetrahydrofuran-2-yl, 2,5-dimethyltetrahydrofuran-2-yl, and tetrahydrothiophen-2-yl. The spectra for tetrahydrofuran-2-yl indicate that, even at −125 °C, pseudorotation is rapid; in contrast, the spectra from its sulphur-containing analogue show that a preferred conformation is frozen out at low temperature. For 2,5-dimethyltetrahydrofuran-2-yl, the presence of the 5-methyl group causes conformational preferences to be established. Analysis of the splittings, in conjunction with INDO calculations on a variety of possible geometries, suggests that the favoured conformation in each case is a specific envelope type. For tetrahydrothiophen-2-yl, the barrier to pseudorotation (*ca.* 17.0 kJ mol^{-1}) is considerably greater than for the oxygen-containing radicals.

PREVIOUS e.s.r. studies of radicals derived from tetrahydrofuran and some analogous compounds can be grouped into two categories. In one type of study, radicals have been generated in liquid solution and at relatively high temperature by reaction of the parent molecules with, for example, $Bu^tO\cdot$ (generated photolytically) or $\cdot OH$ (generated in a flow system); examples include (1), generated [2] from $Bu^tO\cdot$ and THF at −40 °C and also [3] by reaction of THF at room temperature with $\cdot OH$ (from Ti^{III}–H_2O_2 in aqueous solution), and (2), generated [4,5] from $Bu^tO\cdot$ and tetrahydrothiophen (*e.g.* at [4] −60 °C). The second type of study has involved irradiation of solid matrices (*e.g.* in adamantane) containing 2-methyltetrahydrofuran,[6,7] tetrahydrothiophen, and 2-methyltetrahydrothiophen,[7] and this technique has allowed spectra to be recorded down to −196 °C. In the latter studies, evidence was obtained for conformational preferences by the detection of non-equivalent β-proton splittings both in (2), at very low temperature,[7] and in some asymmetrically substituted radicals [*e.g.* (3)].[6]



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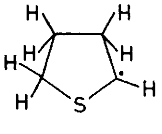

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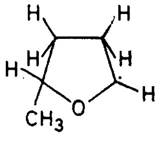

(3)

We have previously investigated the e.s.r. spectra of some photolytically generated dioxanyl [8] and dioxolanyl [9] radicals in fluid solution in the range from room temperature down to *ca.* −120 °C; the observation of line-width effects enabled ring inversion, in the former series, and radical-centre inversion, in the latter series, to be characterized. Conformational preferences of alkyl groups, and long-range interaction with γ-protons, were reported. The results of INDO calculations [10] on a variety of possible structures [8,9] suggest that this molecular orbital approach, when coupled with the analysis of e.s.r. splittings, provides a realistic method for the determination of the structure of cyclic radicals of these types. We have now investigated the e.s.r. spectra of radicals (1), (2), and some related species, in fluid solution down to −125 °C and below, in an attempt to provide a detailed conformational analysis. Our findings have been analysed in conjunction with the results of INDO calculations.

RESULTS AND DISCUSSION

E.s.r. Results.—(a) *Tetrahydrofuran-2-yl.* Reaction of $Bu^tO\cdot$ with tetrahydrofuran at all temperatures in the range 0 to −125 °C led to the detection of e.s.r. spectra clearly attributed to (1) (see Table 1 and refs. 2 and 3). Several features are noteworthy. The α-proton splitting is typical of a somewhat bent radical centre and it also possesses a significant temperature dependence over the temperature range achieved [$d|a(\alpha\text{-H})|/dT$ −0.60 μT °C^{-1}; *cf.*[11] −0.21 μT °C^{-1} for $\cdot CH_3$]. We attribute this to the tendency of a vibrating, and essentially bent, radical centre to flatten out and hence give an increased *negative* α-splitting as the temperature is lowered. The β-proton splittings remained equivalent down to the lowest temperature achieved, when the linewidth was such (0.01 mT) that the expected second-order effects on the β-proton splitting pattern could be resolved; this makes it clear that both conformational interconversion and radical-centre inversion must still be in the fast-exchange region. The assignment of the two pairs of γ-proton splittings, to the γ′-protons adjacent to oxygen [$a(\gamma'\text{-H})$ 0.195 mT at −125 °C] and to the remaining hydrogens [$a(\gamma\text{-H})$ 0.080 mT], follows from the results for the substituted derivative discussed next. At this

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[1] Part 9, C. Gaze, B. C. Gilbert, and M. C. R. Symons, *J.C.S. Perkin II*, 1978, 235.

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

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[9] C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 1161.

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[11] I. A. Zlochower, W. R. Miller, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 3339.

stage it is perhaps worth noting that the size of the larger γ'-proton splitting presumably reflects to some extent the ease of transmission of spin density across the oxygen atom conjugated to the radical centre, although it must be remembered that the signs of these splittings are not yet established.

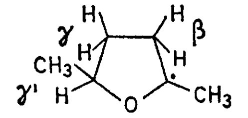
(b) 2,5-*Dimethyltetrahydrofuran*-2-*yl*. The spectrum detected when a mixture of *cis*- and *trans*-2,5-dimethyltetrahydrofuran was oxidised with Bu^{t}O· is ascribed to the radical (4) (see Table 1 for splittings). It is characterized by a splitting (1.900 mT) from three equivalent protons (evidently those of the methyl group at the radical centre) and splittings from two non-equivalent β-protons (2.135, 2.913 mT at −12 °C) and also from a pair of γ-protons (0.065 mT) and from the single γ'-proton across the oxygen atom (0.213 mT at −12 °C). Since only one radical is detected from both isomers, we believe that radical-centre inversion is rapid.

TABLE 1

Temperature dependence of the e.s.r. spectra of tetrahydrofuran-2-yl and tetrahydrothiophen-2-yl radicals [a]

		Hyperfine splittings (mT)			
Radical	T/°C	a(α-H)	a(β-H)	a(γ-H)	a(γ'-H)
(1)	0	1.325	2.775 (2 H)	0.075 (2 H)	0.180 (2 H)
	−73	1.358	2.798 (2 H)	0.075 (2 H)	0.188 (2 H)
	−125	1.400	2.820 (2 H)	0.080 (2 H)	0.195 (2 H)
(4)	−12		2.913 (1 H) 2.135 (1 H) 1.900 (3 H)	0.065 (2 H)	0.213 (1 H)
	−68		3.025 (1 H) 2.050 (1 H) 1.900 (3 H)	0.065 (2 H)	0.245 (1 H)
	−118		3.165 (1 H) 1.925 (1 H) 1.900 (3 H)	0.065 (2 H)	0.288 (1 H)
(2)	−50	1.700	2.606 (2 H)	0.083 (2 H)	0.225 (2 H)
	−124	1.733	2.629 (2 H)	0.088 (2 H)	0.438 (1 H)
	−150 [b]	1.750	3.750 (1 H) 1.500 (1 H)	0.088 (2 H)	0.440 (1 H)

[a] From Bu^{t}O· and parent substrate in cyclopropane. [b] In cyclopropane–propane mixture.



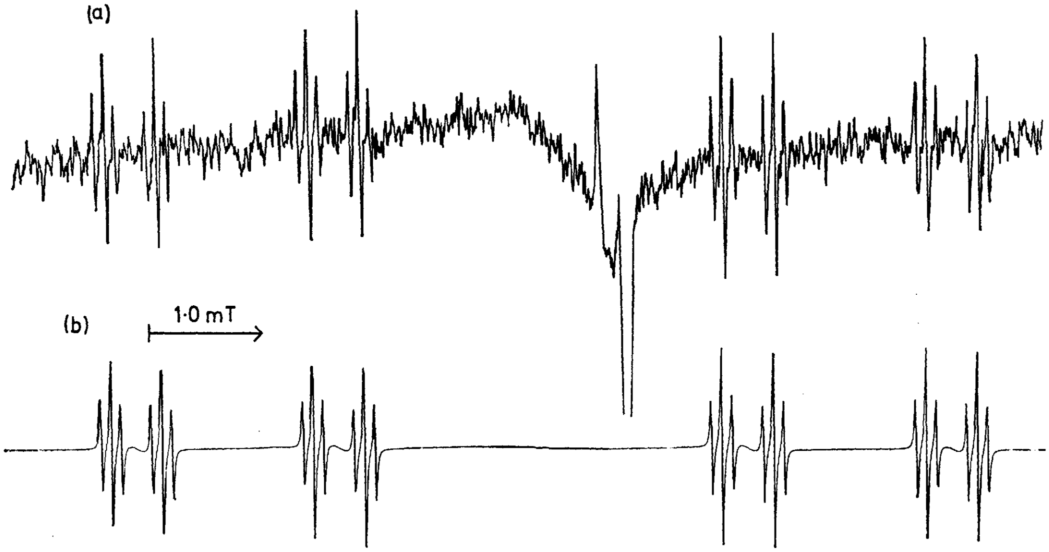
(4)

As the temperature was lowered the spectrum showed some marked changes. The difference between the pair of β-proton splittings from the methylene group adjacent to the radical centre increased, as did the magnitude of the single γ'-proton splitting. There were no linewidth effects and we conclude that conformational interconversion involving different ring geometries is still fast. However, the non-equivalence of the β-methylene protons, and the increased difference as the temperature is lowered, indicates that the introduction of the γ'-methyl group has caused one particular conformation (or a range of closely related conformations within the lowest potential well on the total potential surface) to be weighted increasingly heavily in the equilibrating system. This is also reflected in the magnitude of the single γ'-proton splitting and in its increase as the temperature is lowered; evidently in the preferred conformation the remaining γ'-proton is in a favourable position for interaction with the unpaired electron, and a limiting value of *ca*. 0.3 mT seems indicated.

No inequivalence of the γ-protons could be resolved and it seems likely that in the preferred conformation they have similar splittings.

The sum of the two methylene β-splittings remained constant as the temperature was changed and it is also close to the sum of the two (equivalent) β-proton splittings in the unsubstituted radical (1). We believe that this implies that (1) and (4) have similar ring-shapes, the essential difference being that (1) undergoes rapid interconversion between two *equivalent* conformations whereas in (4) one conformation is increasingly favoured at low temperature. The spectrum from (3) in a matrix at very low temperature (−196 °C) shows two non-equivalent β-proton splittings of *ca*. 1.6 and 3.3 mT,[6,7] values which presumably refer to a fixed preferred conformation; the β-splittings for (4) show that these values are being approached as the temperature is lowered (*e.g.* they are *ca*. 1.9 and 3.2 mT at −125 °C) and it is clear that, by the lowest temperature reached in our experiment, the conformational preference has become almost completely established. Our calculational approach (see later) was to find a suitable model conformation (or range of conformations) in which individual β-proton splittings are calculated to have values of *ca*. 1.8 and 3.2 mT and in which γ'-protons are calculated to have splittings of *ca*. 0.3 mT and zero [*i.e.* for that γ'-proton in tetrahydrofuran-2-yl replaced by a methyl group in (4)].

(c) *Tetrahydrothiophen*-2-*yl*. Reaction of Bu^{t}O· with tetrahydrothiophen gave the spectrum from (2), whose splittings at higher temperatures were in agreement with those recorded previously.[4,5] However, as the temperature was lowered, broadening of the central lines of the β-methylene and γ'-methylene triplet patterns became detectable [alternating linewidths for the β-proton triplet became noticeable by *ca.* −50 °C, and the γ′-proton triplet showed analogous broadening by *ca.* −100 °C]. The Figure shows the spectrum at −124 °C, at which temperature the central lines of both β- and γ′-proton triplets have become broadened beyond detection. By −150 °C two non-equivalent β-proton splittings (3.750, 1.500 mT) were detected and the γ′-proton splitting pattern comprised a doublet (0.440 mT). The latter observation may indicate that the γ′-proton exchange has not been frozen out and that the doublet represents a 1 : broad : 1 pattern from two γ′-protons with different and exchanging splittings. However, we were unable to find any trace of such broadened inside lines, even at the lowest temperatures employed, and, especially in the light of the detection[7] of a single γ′-proton splitting for (2) in a solid matrix at −196 °C, we believe that the spectrum at −150 °C is characterized by γ′-proton splittings of *ca.* 0.440 and *ca.* 0.

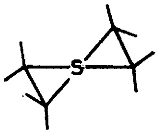


E.s.r. spectrum of the tetrahydrothiophen-2-yl radical at −124 °C: (a) observed; (b) simulated using the following parameters: *a*(α-H) 1.75, *a*(γ-H) 0.088 (2 H), *a*(β-H) 3.75, 1.50, *a*(γ′-H) 0.44, 0.0 mT, and an exchange routine which interchanges the individual β- and γ′-splittings simultaneously with *k* 5 × 10^7 Hz. The asymmetric peak in (a) is due to irradiation damage in the sample cell

Evidently conformational interconversion for (2), unlike (1), has been frozen out under the conditions employed. Our data on the ' frozen ' conformation are similar to those reported for (2) in an adamantane matrix at −196 °C [*e.g.* *a*(β-H) 3.18, 1.44 mT, *a*(γ′-H) 0.46 mT] although small but significant differences suggest that matrix effects may provide some conformational modification.

A higher barrier to interconversion for (2) than for (1) is implied by our results; we estimate from rate constants for the interconversion for (2) (obtained by spectrum simulation of line broadening using the low-temperature parameters) that the barrier to the dynamic process occurring for this radical is 17.0 ± 2.0 kJ mol^{-1}. However, it is noteworthy that the *splittings* for (2) and for the preferred conformation of (1) [as established by the low-temperature splittings for the radical (4)] suggest that fairly similar geometries are possessed by the oxygen- and sulphur-containing analogues.

INDO Calculations and Conformational Analysis.—It is generally accepted that cyclopentane and many related compounds containing a five-membered ring do not show a marked preference for a single geometry (in contrast, for example, to the adoption of a chair form for cyclohexane). For instance, vapour-phase electron-diffraction studies on tetrahydrofuran suggest[12] that this exhibits a very high degree of pseudorotation, with very small energy differences between half-chair, envelope, and intermediate conformations. For tetrahydrothiophen, evidence exists that the pseudorotation of the ring-puckering is more restricted, and both experimental measurements and theoretical treatments suggest[13] that the half-chair form (5) is more stable than other conformations, including the envelope form, (6), by *ca.* 10 kJ mol^{-1}.



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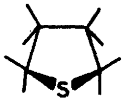

(6)

It would not necessarily be expected that the radicals (1) and (2) would possess geometries and dynamic properties closely similar to those of their parent molecules, but it is noteworthy that e.s.r. studies show that ring-flipping for radicals with five-membered rings is generally

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[12] A. Almenningen, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, 1969, **23**, 2748.

[13] Z. Náhlovská, B. Náhlovský, and H. M. Seip, *Acta Chem. Scand.*, 1969, **23**, 3534.

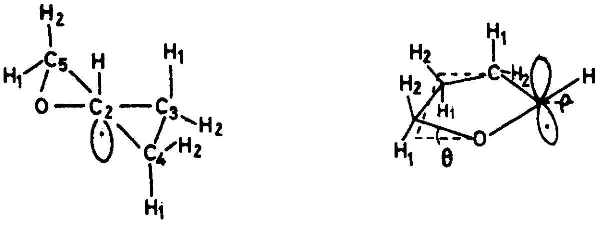
much faster than ring-flipping for radicals with six-membered rings (as judged by the many examples of ring ' locking ' at low temperatures in the latter systems; see, *e.g.* ref. 8 and references therein). In this respect, the freezing-out of at least some of the ring motion for (2) at low temperatures, and the effect of the 5-methyl substituent in causing conformational preference in (4), are unusual. Our results suggest that in these radicals a fairly well defined geometry *is* adopted; thus the detection of non-equivalent β- and γ'-proton splittings indicates that all conformations linked by pseudorotation cannot be significantly explored but that pseudorotation is to some extent frozen out. Perhaps a more realistic picture is one in which a range of geometries about a specific conformation, *i.e.* with a rather broad potential well, is adopted. With this in mind, we employed INDO calculations in an attempt to decide with which models for (1) and (2) the observed splittings are compatible.

(a) *INDO calculations on* (1). We chose bond lengths and angles as used previously [8,9] (with the length for the conjugated C–O bond taken as 0.139 nm) and carried out a series of INDO calculations [10] on a wide variety of possible geometries for radical (1).

We began by taking a model with a planar ring system in order to vary just the degree of bending at the radical centre. We found that an α-proton splitting of *ca.* −1.3 mT is calculated for a value of ρ (the angle between the α-C–H bond and the CCCCO plane) of 16° (*cf.* values of *ca.* 28°, to give α-proton splittings of approximately zero for 1,3-dioxan-2-yl and related radicals and of *ca.* 44° to give an α-proton splitting of +2.1 mT for 1,3-dioxolan-2-yl[1]). We employed this angle of bending in further calculations in which various ring geometries were assumed, and in all cases the calculated α-proton splitting remained close to −1.3 mT (as expected, its magnitude does not vary significantly with the ring shape, being primarily a function of radical-centre hybridisation).

We next carried out calculations on various geometries in which the C(3), C(2), and O atoms were held fixed and the C(4) and C(5) atoms were placed so as to give half-chair and envelope forms. In detail, these are the half-chair form (7), with C(4) and C(5) below and above the plane, respectively, the C(4) envelope form (8), with C(4) above the plane, and the C(5) envelope form (9). Further calculations were performed on other possible geometries, including the C(2) envelope (10), the C(3) envelope (11), and a variety of conformations (12) based on the geometry with oxygen at the ' flap ' of the envelope (and for which different amounts of half-chair character have also been included).

There are many model conformations in which the INDO method leads to α- and β-splittings in reasonable agreement with experiment (sample results are given in Table 2). The predictions for β-proton splittings are in accord with expectation based on a hyperconjugative interaction between the protons concerned and the unpaired electron, and hence on a $B\cos^2\theta'$ type relationship (θ' being the dihedral angle between the orbital of the unpaired electron and the β-C–H bond). Thus for the C(2) half-chair form (7), for instance, a[β-H(1)] is calculated to be greater than a[β-H(2)]; for θ (the angle of twist in the ring) 10° the calculated values are 3.662 and 2.243 mT, respectively; for an increased twist angle θ 15°, the values are 3.780 and 1.880 mT, respectively. As expected, the pseudoaxial β-proton has the larger interaction.



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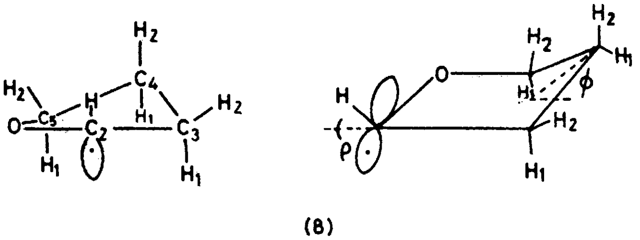

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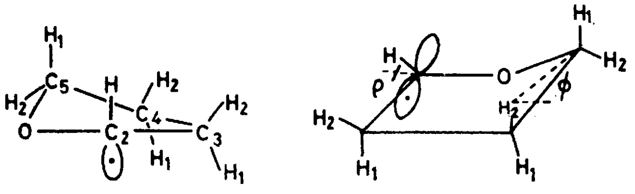

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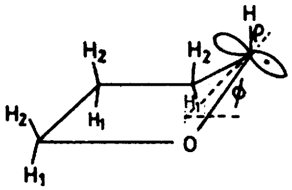

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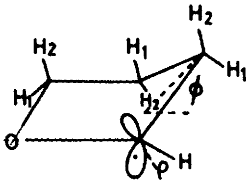

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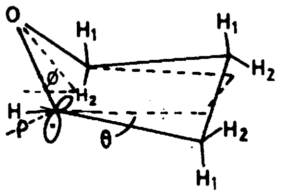

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The calculations generally overestimate to some extent the magnitude of the γ-proton splitting (although the two γ-protons are predicted in most cases to have splittings of the same sign and similar magnitude, as suggested by the experimental results). A further failing for most of the calculations is that, although significant differences between the individual γ'-proton splittings in the fixed conformation are predicted, the *averaged* γ'-proton splitting is considerably underestimated.

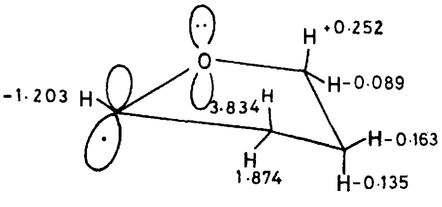
TABLE 2

INDO Calculations on the tetrahydrofuran-2-yl radical (**1**) [a]

				Hyperfine splittings (mT)						
Geometry	ρ	θ	ϕ	$a(\alpha\text{-H})$	$a(\beta\text{-H}_1)$	$a(\beta\text{-H}_2)$	$a(\gamma\text{-H}_1)$	$a(\gamma\text{-H}_2)$	$a(\gamma'\text{-H}_1)$	$a(\gamma'\text{-H}_2)$
C_2 half chair (7)	+16	10		−1.256	3.662	2.243	−0.128	−0.143	−0.155	+0.117
	+16	15		−1.240	3.780	1.880	−0.128	−0.135	−0.039	−0.005
	−16	10		−1.371	3.479	2.127	−0.133	−0.091	−0.079	−0.030
C_4 envelope (8)	+16		30	−1.410	3.393	1.738	−0.027	−0.143	+0.080	+0.025
	+16		−20	−1.251	2.229	3.664	−0.132	−0.164	+0.250	−0.069
	+16		−30	−1.203	1.874	3.834	−0.135	−0.163	+0.252	−0.089
	+16		−40	−1.127	1.555	3.878	−0.132	−0.148	+0.244	−0.102
C_5 envelope (9)	+16		30	−1.345	2.761	3.147	−0.113	−0.140	+0.038	−0.095
	+16		−30	−1.395	3.207	2.780	−0.105	−0.136	−0.137	−0.065
C_2 envelope (10)	+16		20	−1.292	3.397	1.771	−0.069	−0.130	−0.206	+0.177
	+16		30	−1.383	3.321	1.227	+0.020	−0.133	−0.170	+0.105
C_3 envelope (11)	+16		−20	−1.100	3.571	1.621	−0.118	−0.115	−0.143	+0.180
	+16		−30	−1.037	3.568	1.010	−0.104	−0.118	−0.172	+0.175
O envelope and half-chair (12)	+16	5	0	−1.354	3.557	2.169	−0.134	−0.097	+0.098	−0.124
	−16	5	0	−1.337	3.847	2.333	−0.133	−0.150	−0.111	+0.099
	+16	0	−20	−1.248	3.353	2.383	−0.126	−0.117	+0.205	−0.191
	+16	0	−30	−1.210	3.398	2.029	−0.117	−0.114	+0.183	−0.172
	−16	10	+20	−1.213	3.839	2.014	−0.139	−0.141	−0.164	+0.166
	+16	10	+20	−1.462	3.575	1.883	−0.141	−0.053	−0.025	−0.082

[a] For definition of ρ, θ, and ϕ, see text.

However, there are a few conformations in which the α- and β-proton splittings have reasonable values and the γ'-proton splittings have the expected significant difference *and* a reasonable average value. These are of the C(4) envelope type. For example, for (**8**), ρ 16 ϕ −20°, the calculated values of $a(\gamma'\text{-H})$ are +0.250 and −0.069 mT (average +0.091) which may be compared with the observed values of *ca.* 0.3 mT and zero (with an average 0.180 mT at 0 °C). Optimum agreement with experiment is provided by the calculation for (**8**), ρ 16 ϕ −30°, in which both β- and γ'-protons are reasonably well reproduced [see (**13**); calculated splittings given in mT, *cf.* experimental results for (**1**) and (**4**) in Table 1].



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We believe that the marked differences between the individual β-proton splittings and also the γ'-proton splittings in the preferred conformation of the tetrahydrofuran-2-yl radical is best accounted for in terms of a C_4 envelope structure of this type (though geometric fluctuations of ρ and ϕ within a broad potential well would probably be occurring). Perhaps the most important feature of this type of structure is that the atoms C(5), O, C(2), and C(3) are all held in a plane; this maximises overlap between the unpaired electron and the *p*-lone-pair on oxygen (a feature which is of course not present in the parent molecule). The large positive splitting for the pseudo-axial γ'-proton presumably then results from hyperconjugation involving spin density in the *p*-orbital on oxygen [*i.e.* $\dot{C}{-}\ddot{O} \longleftrightarrow \overset{-}{\ddot{C}}{-}\overset{+}{\ddot{O}}$]. (We have previously shown [14] that in $\cdot CH_2OCH_2OCH_3$ the two γ-proton splittings have opposite signs in the conformation frozen out at low temperature, the positive (and large) splitting reflecting a dominance of hyperconjugation, the negative splitting being as a result of a dominant contribution from through-bond spin-polarization where a small dihedral angle reduces the effect of the former interaction). If the analysis presented here is correct, it implies that the 5-methyl group in (**4**) occupies preferentially the pseudoequatorial position.

(b) *INDO calculations on* (**2**). We have also carried out INDO calculations on the tetrahydrothiophen-2-yl radical using a modification [15] of the standard INDO programme which includes the CNDO/2 parametrization for second-row elements [16] and the Slater and Condon parameters suggested by Benson and Hudson [17] for second-row elements. We have also carried out calculations using the parameters for sulphur proposed by Stevenson and Burkey.[18]

Calculations have been performed for a variety of possible ring geometries (*e.g.* half-chair geometries,

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

[15] A. R. Gregory, *Chem. Phys. Letters*, 1974, **60**, 3713.

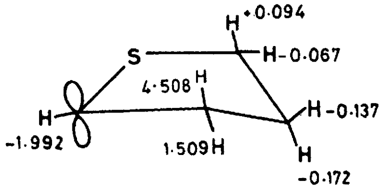
[16] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

[17] H. G. Benson and A. Hudson, *Theor. Chim. Acta*, 1971, **23**, 259.

[18] P. E. Stevenson and D. L. Burkey, *J. Amer. Chem. Soc.*, 1974, **96**, 3061; 1975, **97**, 1988.

envelopes) in which in each case we chose a *planar* arrangement of the atoms around the radical centre, $C{-}\dot{C}(H){-}S$. It has previously been argued[19] that α-sulphur-substituted alkyl radicals are planar (unlike their oxygen-substituted analogues); it was suggested, for example, that the ratio $|a(CH_3)/a(H)|$ for radicals of the type $\cdot CH(CH_3)X$ is a good guide to hybridization, a value of *ca.* 1.2 being typical of planar radicals (*e.g.* X = R, COR, SR) whereas a greater value for radicals of the type $\cdot CH(CH_3)OR$ reflects the decreasing magnitude of $|a(\alpha\text{-}H)|$ as the radical centre bends. On the other hand, the relatively low values of $a(\alpha\text{-}H)$ and $a(CH_3)$ and the high values of $a(\gamma\text{-}H)$ (*e.g. ca.* 0.3 mT in[20] radicals of the type $\cdot C{-}S{-}CH_3$) are entirely consistent with there being considerable delocalization onto sulphur $[\cdot C{-}\ddot{S}{-}R \longleftrightarrow {>}\overset{-}{\ddot{C}}{-}\overset{+\cdot}{S}R \longleftrightarrow {>}C{=}\dot{S}R]$.

The results of our INDO calculations (with both sets of parameters) show that for a *planar* radical centre the extent of spin delocalization onto sulphur is considerably underestimated (in particular, the calculated α-proton splitting is too high, as are the calculated β-proton splittings, and the γ-proton splittings are underestimated); we have established that this is also so for simple radicals of the type $\cdot CH_2SCH_3$. An example is the result for the C_4-envelope structure (14), the analogue of the preferred conformation which we believe is adopted by (1) [bond lengths $S{-}\dot{C}$ 0.180, S–C 0.184, C–C 0.154, and C–H 0.108 nm, and bond angles $C\hat{C}C$ 105° and $H\hat{C}H$ 109° 28′, with $\phi = 40°$, were employed]. Although the results have some features expected by comparison with the experimental observations for (2), namely the marked difference between the individual β-proton splittings and the inequivalence of the γ′-protons, the overall agreement is unsatisfactory. Thus the α-proton splitting is overemphasized, and the magnitude of the calculated splitting for the γ′-proton in the pseudoaxial position also suggests that too little delocalization onto sulphur is predicted.



(14)

INDO Calculations in which bending is introduced at the radical centre do have lower values for the calculated α-proton splitting, but we believe that such results are unrealistic and do not reflect differences in the radical-centre geometry and delocalization conferred on a radical by the substitution of a sulphur atom for an oxygen atom.

We conclude tentatively on the basis of the *observed* splittings for (2) that the preferred conformation is of the envelope form (14) with the pseudoaxial γ′-proton having the large (positive) splitting (0.44 mT) as a result of hyperconjugation involving spin on sulphur. We are unable to suggest a reason for the failure of the INDO calculations and believe that alternative parametrization schemes are necessary.

EXPERIMENTAL

The spectrometer, photolytic apparatus, and methods for generating, recording, calibrating, and simulating spectra have been previously described,[14] as have the computational details. Compounds were commercial materials, used without further purification.

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[7/1466 *Received*, 12*th August*, 1977]

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[20] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.