Investigations of Structure and Conformation. Part 11.[1] Electron Spin Resonance Spectra of Sulphur- and Oxygen-conjugated Radicals derived from 1,3-Dithiolan, 1,3-Oxathiolan, and Related Compounds

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A variety of radicals with two α-heteroatom substituents (two sulphurs, a sulphur and an oxygen, and two oxygens), as well as in some cases an α-phenyl substituent, have been obtained by reaction of the parent compounds with $\mathrm{Bu^tO\cdot}$ generated photochemically. E.s.r. spectra confirm that sulphur exerts a significant delocalizing effect (spin-withdrawing parameter *ca.* 19%), and that when sulphur and oxygen α-substituents are both present the bending effect of the latter dominates. Two oxygen atoms at the radical centre induce significant bending except when a phenyl substituent is also conjugated with the unpaired electron; these effects are analysed on the basis of INDO and Hückel–McLachlan molecular orbital calculations.

Conformational effects in the sulphur-containing radicals are also reported.

E.S.R. spectra of α,α-di-oxygen substituted alkyl radicals provide evidence that these species, unlike unsubstituted alkyl radicals, are bent at the radical centre. Notable features of the spectra include the positive α-proton splitting in 1,3-dioxolan-2-yl,[2] the high α-^{13}C splittings in radicals of this type,[3] and also some effects which become manifest at very low temperatures, including the 'freezing-out' of radical-centre inversion in 2-methyl-1,3-dioxolan-2-yl [2,4] and restriction of rotation about $\cdot$C–CH$_3$ in this and related radicals. Radicals with a single sulphur atom at the radical centre are thought to be essentially planar, with more delocalization onto the heteroatom than for oxygen (see *e.g.* refs. 5—7); a few examples in which there are two sulphur atoms [6] or one oxygen and one sulphur atom [7] at the radical centre have been reported, but the structural variations and temperature ranges which have been studied are not extensive.

We have therefore prepared a series of radicals with two sulphur substituents, or an oxygen and a sulphur substituent, at the radical centre by oxidation of the parent thioethers with $\mathrm{Bu^tO\cdot}$ (produced photochemically from di-t-butyl peroxide). In an attempt to obtain information about the favoured conformations and configuration of sulphur-containing radicals (*cf.* the 'freezing-out' of preferred conformations of[8] $\cdot$CH$_2$OCH$_2$OCH$_3$ and dioxan-derived species[9]) we employed solvents (*e.g.* cyclopropane) which allow temperatures down to *ca.* −130 °C to be achieved. We have also studied some α,α'-dioxygen-substituted radicals and a series of radicals in which a phenyl group is conjugated with the radical-centre.

RESULTS AND DISCUSSION

E.s.r. Spectra from α,α-Di-sulphur-substituted Radicals

(a) *Radicals with Five-membered Rings.*—Photolysis of a mixture of 1,3-dithiolan and di-t-butyl peroxide in cyclopropane gave rise to the e.s.r. spectrum, as previously noted,[6] of the 1,3-dithiolan-2-yl radical (1) (see Table 1). The low α-proton splitting, small γ-proton splittings, and relatively high g-value are typical of radicals of this type.† Data were also obtained for the methyl-substituted analogues (2), (3), and (4), and for the 2-phenyl substituted derivative (5), each of which was detected as the dominant species during the reaction of the appropriate parent compound with $\mathrm{Bu^tO\cdot}$.

(i) *Configuration and delocalization.* The results for (1) and (2) indicate that it is not bending at the radical centre which reduces the α-proton splitting in (1) from the value expected for a planar unconjugated radical (*ca.* −2.2 mT) but rather delocalization of the unpaired electron onto sulphur. Thus the ratio a(Me) in (2) to $a(\alpha\text{-H})$ in (1) is 1.2 : 1, which is exactly as expected[11] for species with a planar radical centre [and similarly for the corresponding splittings in (4) and (3) respectively]. It is also notable that no broadening of the inner lines of the methyl protons' 1 : 3 : 3 : 1 quartet for (2) and (4) could be detected, even at temperatures below −100 °C; this is in marked contrast to the broadening detected for 2-methyl-1,3-dioxolan-2-yl and related species [2,12] where restriction of rotation about $\cdot$C–CH$_3$ is a consequence of the pyramidal geometry at the radical centre. Our results are consistent with a planar configuration for the sulphur-containing radicals.

The magnitude of a(Me) for (2) [and similarly for (4)] yields a value of 19% for the Fischer spin-withdrawal parameter for each sulphur atom (*cf.* ref. 13; such a calculation is not possible for the related oxygen-substituted analogues since the proton splittings in the latter are affected by changes in hybridization as well as delocalization). However, a comparison of the relative abilities of sulphur and oxygen for spin-withdrawal in radicals of this type should be possible on the basis of the spectra of the phenyl-conjugated radicals (5) and[12] (6) [these and other phenyl-substituted radicals were generated in toluene–isopentane mixtures at temperatures down to −90 °C; for (6), see also ref. 12]. These radicals are evidently planar at the radical centre, as judged by the ordering of ring-proton splittings $|a(4\text{-H})| > |a(2\text{-H})| \gg |a(3\text{-H})|$. In the sulphur-substituted radical (5) there is clearly considerable delocaliz-

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† The spectra from (1) also contained weak absorptions from the secondary radical $\mathrm{CH_3\dot{S}(OBu^t)_2}$ [a(3 H) 0.655 mT, g 2.0095, *cf.* ref. 10], the origin of which is unclear.

ation onto S [for the benzyl radical[14] the ring-proton splittings are 0.514, 0.175, and 0.614 mT, for 2-, 3-, and 4-H, respectively, so it appears that there is a reduction of *ca.* 25% of the spin density in the ring on going from benzyl to (5)]. In contrast, for the oxygen-conjugated radical (6) there is apparently little or no delocalization

TABLE 1

E.s.r. spectra of radicals from 1,3-dithiolan and related compounds[a]

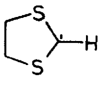
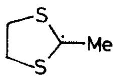
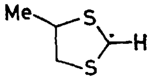
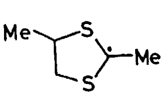
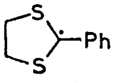
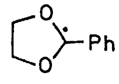
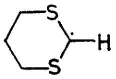
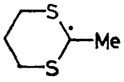
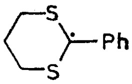
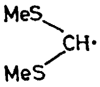
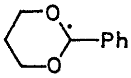
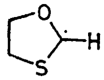
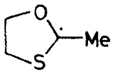
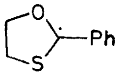
Radical	Hyperfine splittings/mT[b]					
	t/°C	a(α-H)	a(β-H)	a(γ-H)	a(other)	g[c]
 (1)	−52	1.414		0.123 (4 H)		2.0051
	−110	1.470		0.123 (4 H)[d]		
	−137[e]	1.495		0.123 (4 H)[d]		
 (2)	−72		1.782 (3 H)	0.083 (4 H)		2.0048
	−110		1.795 (3 H)	0.084 (4 H)[d]		
 (3)	−40	1.419		*f*	0.020 (CH_3)	2.0052
	−80	1.460		*f*	*f*	
 (4)	−66		1.825 (3 H)	0.125 (1 H)[g] 0.085 (2 H)		2.0047
	−91		1.825 (3 H)	0.112 (1 H)[g] 0.085 (2 H)		
	−127		1.825 (3 H)	(±)0.220 (1 H)[h] (±)0.245 (1 H) (∓)0.080 (1 H)		
 (5)	*i*			0.085 (4 H)	0.400 (2-H) 0.136 (3-H) 0.466 (4-H)	2.0044
 (6)	*j*			0.096 (4 H)	0.525 (2-H) 0.166 (3-H) 0.682 (4-H)	2.0032
 (9)	−45[k]	1.575		0.153 (4 H)		2.0053
	−100[k]	1.580		0.155 (4 H)[d]		
 (10)	−30		1.710 (3 H)	0.113 (4 H)		2.0047
	−80		1.727 (3 H)	0.100 (4 H)[d]		
	−108		1.727 (3 H)	0.100 (4 H)[d]		
 (11)	*i*			0.132 (4 H)	0.382 (2-H) 0.132 (3-H) 0.440 (4-H)	2.0046
 (12)	−58	1.488		0.175 (6 H)		2.0051
	−110	1.500		0.175 (6 H)		
 (13)	*i*			0.060 (4 H)	0.480 (2-H) 0.155 (3-H) 0.580 (4-H)	2.0029

Table 1 (*Continued*)

Radical	Hyperfine splittings/mT [b]					
	t/°C	a(α-H	a(β-H)	a(γ-H)	a(other)	g [c]
 (14)	−60 −94 −105	0.507 0.486 0.481		0.119 (4 H) 0.119 (4 H) 0.119 (4 H)		2.0041
 (15)	−32		1.637 (3 H)	0.130 (2 H) 0.050 (2 H)		2.0040
	−60		1.630 (3 H)	0.130 (2 H) 0.050 (2 H)		
	−94		1.625 (3 H)	0.130 (2 H) 0.050 (2 H)		
 (16)	*i*			0.052 (4 H)	0.452 (2-H) 0.152 (3-H) 0.568 (4-H)	2.0035

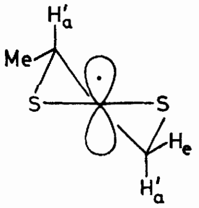
[a] Radical formed by reaction of parent compound with Bu^{t}O· in cyclopropane unless stated otherwise. [b] ±0.005 mT. [c] ±0.0001 mT. [d] Broadening of M_I ±1 lines. [e] In cyclopropane–propane solvent mixture. [f] Interpretation impossible. [g] Approximate analysis, see text. [h] Increase in spectrum width at low temperature, see text. [i] In toluene–isopentane mixture; the spectra were effectively independent of temperature between 0 and −90 °C. [j] Data from ref. 12; results identical in toluene–isopentane (*cf. i*). [k] In cyclopropane–oxiran.

onto oxygen—the 2-H and 4-H ring splittings are now greater than in benzyl. This rather surprising set of splittings is discussed again in a later section in the light of molecular orbital calculations.

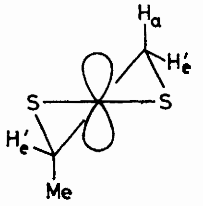
(ii) *Conformational aspects.* The γ-proton quintets in the spectra of (1) and (2) showed similar selective line-broadening of alternate lines as the temperature was lowered. For (1), for example, by −110 °C a 1 : *broad* : 4 : *broad* : 1 pattern resulted, and by −137 °C (the lowest temperature attainable, through the use of propane–cyclopropane solvent mixtures) the spectrum comprised a 1 : 4 : 1, with other lines completely broadened out. The slow-exchange limit could not be obtained.

This type of broadening, which was not detected for 1,3-dioxolan-2-yl, is evidently the result of the slowing down of the interconversion of ring-conformations with non-equivalent γ-proton splittings. Further evidence for this, and information about the probable magnitude of the splittings in the slow-exchange limit, derives from the dependence on temperature of the spectrum for the ring-substituted radical (4) [*n.b.* (3) behaved similarly but the spectra were also complicated by a δ-H splitting, and no detailed analysis proved possible]. At the higher temperatures the γ-proton splitting pattern for (4) indicated there to be an interaction with three protons; the pattern resembled a 1 : 3 : 3 : 1 with a(H) *ca.* 0.095 mT, though detailed analysis indicated that the three splittings were not identical (see Table 1). The observation of three virtually equivalent γ-splittings is as expected for rapid conformational interconversion with no particular conformation weighted preferentially [and an average γ-splitting similar to those for (1) and (2)]. At lower temperatures (*e.g.* −100 °C) the spectrum showed marked broadening of the inner lines (so that the γ-splitting pattern appeared as a doublet, *a ca.* 0.28 mT), and at still lower temperatures further lines appeared *outside* the sharp lines; by −127 °C, three separate splittings were resolved (0.245, 0.200, 0.080 mT). The increase in spectrum width coupled with the detection of broad—then sharper—lines outside the invariant lines, is typical of systems in which hydrogens with splittings of opposite sign are exchanged (*cf., e.g.* chair–chair interconversion, with γ-splittings of opposite sign, in 1,3-dioxan-2-yl [9]).

This behaviour evidently reflects a slowing down of conformational interconversion coupled with an increased weighting of a favoured conformation such that more or less complete weighting has occurred by −127 °C. We favour a half-chair structure, with the methyl group equatorial [*i.e.* (7)] as the preferred conformation for (3) (there is X-ray evidence [15] for a half-chair structure for the 1,3-dithiolan rings in 2,2′-bi-1,3-dithiolan; see also ref. 16). Thus by analogy with [8] $\cdot CH_2OCH_2OCH_3$ and, in particular,[9] 1,3-dioxan-2-yl, this would be expected to exhibit *positive* pseudo-axial γ-proton splittings [these would arise *via* hyperconjugation involving spin density in $p(\pi)$ orbitals on sulphur] and a negative pseudo-equatorial proton splitting (arising *via* spin polarization). In view of the significant spin density on sulphur (see above) we tentatively assign the *ca.* 0.2 mT splittings to the axial protons (with a positive sign) and the negative splitting of 0.080 mT to the equatorial proton. At higher temperatures, where faster pseudorotation occurs and where other conformations may contribute to the weighted average, the appearance will change. If (7) and the other half-chair form (8) interconvert rapidly, and ultimately have equal weightings, the resultant pattern should show three hydrogen splittings with values of *ca.* 0.7 mT (*i.e.* averages of *ca.* +0.22 and −0.08 mT). This is the type of behaviour observed. A full analysis would ideally make allowance for possible differences in the splittings for protons in essentially similar environments consequent upon introduction of the methyl group [*e.g.* the two pseudo-axial protons in (7)], expected slight differences between splittings for (7) and (8), and possible contributions from, *e.g.*, envelope forms at higher temperatures. We believe that this is impracticable and that, based on the data available, only a qualitative analysis is possible.



(7)



(8)

Spectrum simulation of the broadening for (1) on the assumption of individual pseudo-axial and equatorial splittings of (+)0.24 and (−)0.08 mT, respectively, leads to a series of rate constants for interconversion (*e.g.* 1×10^8 Hz at −100 °C) and a value for the barrier to interconversion of *ca.* 8 kJ mol^{-1}. We note finally that this barrier and the clear preference for a half-chair conformation (unlike the related dioxolan radicals) probably results from constraint imposed on the geometry by the low $\widehat{SCS}$ bond angle of[16] *ca.* 110°.

(b) *Radicals with Six-membered Rings.*—Table 1 also contains data on the e.s.r. spectra of the 1,3-dithian-2-yl radical (9), together with those for the 2-methyl and 2-phenyl derivatives (10) and (11). Data on the radical $\cdot CH(SMe)_2$ (12) [from $CH_2(SMe)_2$] are also included for comparison [no signals were detected from $\cdot CH_2SCH_2SMe$ although the spectra were complicated by the appearance of signals from secondary species, including $Me\dot{S}(OBu^t)_2$ (see above)]. We have also generated the 2-phenyl-1,3-dioxan-2-yl radical (13) for comparative purposes.

The essential features of the spectra closely resemble those from the corresponding five-membered ring radicals. Thus the low values of $a(\alpha\text{-H})$ for (9) and (12) are evidently a consequence of the spin-withdrawing propensity of sulphur, and the value of the spin-withdrawing parameter[13] for sulphur in radical (10) is calculated as 20%. The ratio a(Me) : a(H) for (10) : (9) is 1.09 : 1. The splittings for protons in the phenyl ring in (11) again indicate that the two sulphur atoms are effective in spin-withdrawal [compare, for example, the 4-H splitting of 0.440 mT in (11) with that of 0.614 in benzyl]. It is interesting to note that, as judged by the ring-splittings in (11) compared to (5), and the methyl-group splittings in (10) compared to (2), the dithian substituent is slightly more effective than the dithiolan substituent in spin-withdrawal. However, for the unsubstituted radicals (1), (9), and (12), the magnitudes of $a(\alpha\text{-H})$ suggest that spin-withdrawal is slightly greater for the five-membered ring system and for $\cdot CH(SMe)_2$ than for the six-membered ring species. The explanation for this anomaly may involve at least one of a variety of factors including spin-withdrawal and inductive effects of methyl and phenyl, hybridization changes, and the possible sensitivity of spin-polarization parameters to any or all of these. Further speculation seems unjustified.

The spectrum for (13) appears to show that there is little delocalization onto the two oxygen atoms, though the dioxan ring appears to be slightly more effective than the dioxolan ring [*cf.* (6)] in this respect.

One observation of conformational interest is that in 1,3-dithian-2-yl (9) the γ-proton quintet showed line-width alternation at the lowest temperatures achieved (*ca.* −100 °C). However, the slow-exchange limit spectrum could not be ' frozen out '. In the absence of the appropriate splittings, the rate constants for interconversion cannot be estimated, but it seems likely that the barrier to conformational interconversion in (9) is lower than that in the analogous 1,3-dioxan-2-yl, since the low-temperature slow-exchange limit for the latter was achieved[9] by −87 °C. This presumably reflects a flattening of at least part of the ring in (9) (*i.e.* C–S–C–S–C) as a result of the considerable delocalization of the unpaired electron over the two sulphur atoms.

E.s.r. Spectra of α-Oxygen-α-sulphur-substituted Radicals.—Reaction of $Bu^tO\cdot$ with 1,3-oxathiolan, 2-methyl-1,3-oxathiolan, and 2-phenyl-1,3-oxathiolan led to the detection of signals unambiguously assigned to the oxathiolan-2-yl radicals (14)—(16) respectively.

Radical (14) is characterized by a low $a(\alpha\text{-H})$ which presumably reflects a considerable degree of bending at the radical centre; the sign of this splitting is unknown (as is pointed out in ref. 3, the sign of the temperature coefficients cannot necessarily be reliably used to determine this) but it is clear that the extent of bending is less than for $\cdot CH(OMe)_2$ and 1,3-dioxolan-2-yl [$a(\alpha\text{-H})$[2,8] *ca.* +1.2 and +2.1 mT, respectively]. Despite the considerable delocalizing influence of sulphur (as judged by the magnitude of the g-value), a significant bending at the radical centre is produced by the oxygen substituent; our finding supports the previous assertion[7] that the configurations of radicals with both $\alpha\text{-OMR}_n$ and $\alpha\text{-SMR}_n$ substituents are governed by the bending effect of alkoxy-groups. However, the bending produced is greater than that when just a single oxygen atom is present (*cf.*[1] tetrahydrofuran-2-yl) so that the introduction of sulphur does assist the bending effect of oxygen. The γ-proton quintet from (14) showed no line-broadening as the temperature was lowered.

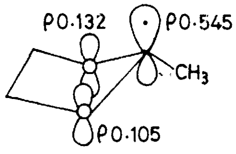
Further evidence for significant bending in (14) and (15) derives from the observation of a broadening in the inner lines of the methyl protons' quartet splitting in the spectrum from the latter at low temperature: by −94 °C the ratio was 1 : 0.9 : 0.9 : 1. Again, this effect is presumably induced by the presence of the oxygen substituent [*cf.* 2-methyl-1,3-dioxolan-2-yl but contrast the behaviour of (2) and (4)]. It is impossible to determine the extent of delocalization of the unpaired electron onto sulphur [though the g-value and low $a(\alpha\text{-Me})$ indicate this to be significant] because of the effect of bending at C_α in producing a reduction of the methyl-group's splitting.

One surprising feature is that in (15), unlike the radicals (14) and (16), two pairs of γ-proton splittings were detected (0.130, 0.050 mT): we tentatively assign these to the two hydrogens next to sulphur and those next to oxygen, respectively (the former are *usually* greater than the latter, presumably on account of the more effective spin-transmission across sulphur than across oxygen). No changes in the γ-proton pattern, other than increase in resolution, were detected as the temperature was lowered. The difference in behaviour of (14) and (15) must reflect a change in configuration (at C_α), change in spin density at C_α, or a change in ring-conformation—or a combination of any of these factors—on the introduction of the methyl group. Changes in ring-geometry seem least likely, in our view, but we note that an α-methyl group would be expected to reduce the spin-density at C_α by *ca.* 8% and to cause increased bending. These effects may then cause quite marked changes on the long-range transmission of spin-density to γ-protons.

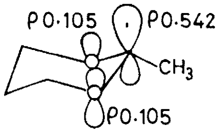
Finally, the effect of the phenyl-substituent in (16) is, as judged by the relative magnitudes of the ring-splittings [$|a(4\text{-H})| > |a(2\text{-H})| \gg |a(3\text{-H})|$], to produce an essentially planar benzyl-type radical centre [*cf.* (5), (6), and (11)]. Comparison with the data for (5) and (6) indicates that the spin density in the ring is intermediate between those for the dioxolan and dithiolan substituents, presumably reflecting the predominant delocalizing effect of the single sulphur atom.

Spin-density Distribution Calculations.—As noted above, the spin-delocalizing effect of a sulphur atom conjugated with the radical centre can be reliably estimated as *ca.* 20% for radicals of the type described here. Changes in hybridization induced by α-oxygen substituents mean that changes in $a(\alpha\text{-H})$ and $a(\alpha\text{-CH}_3)$ cannot be used with confidence to derive a spin-withdrawal parameter for oxygen. Although it is generally believed that oxygen does exert a spin-delocalizing effect ($\dot{\mathrm{C}}{-}\ddot{\mathrm{O}}{-} \longleftrightarrow \overset{-}{\dot{\mathrm{C}}}{-}\overset{+}{\dot{\mathrm{O}}}$: for example, the occurrence of γ-proton splittings in radicals of this type points[8,9,12] strongly to there being significant spin density in a p^π-orbital on oxygen) the results for the planar phenyl-substituted radicals (6) and (13) appear to be anomalous in that, by comparison with splittings for benzyl, they indicate that oxygen is at best weakly capable [*cf.* (13)] or totally ineffective [*cf.* (6)] at spin-withdrawal. The explanation for this anomaly is, we believe, that the presence of the attached oxygen atoms alters significantly the electronegativity of the central benzyl-like carbon and that this causes significant redistribution of the unpaired electron between the radical centre and the ring [*cf.*, for example, benzyl *vs.* phenoxyl[17]]. This effect will mask the real electron-withdrawing (*delocalizing*) effect of oxygen. In order to determine the extent of delocalization onto oxygen we have employed two approaches, namely to carry out INDO calculations[18] (which yield reasonable values for γ-proton splittings in radicals of this type) in order to estimate $\rho_O(\pi)$, and also to perform Hückel–McLachlan calculations,[19] incorporating both inductive and conjugative models for oxygen, on the aromatic radicals.

(i) *INDO calculations.* We have previously[8] carried out INDO calculations on a variety of configurations and conformations for $\cdot CH_2OCH_2OCH_3$; for the calculated minimum energy conformation (with an angle of bending 10° at the radical centre) the splittings (particularly those from the non-equivalent γ-protons) were in excellent agreement with those obtained experimentally. We now find that the calculated spin-density distribution for this structure has $\rho_\pi(\alpha\text{-C})$ 0.830, $\rho_\pi(\text{O})$ 0.128. We have similarly carried out[12] INDO calculations designed to obtain optimum agreement with ^{13}C, α-CH$_3$, and γ-H splittings for low-temperature spectra from 2-methyl-1,3-dioxolan-2-yl (17) and 2-methyl-1,3-dioxan-2-yl (18); the spin densities in the oxygens' π-orbitals are again calculated to be of the order of 10% [see ref. 12 for details of optimum geometries].



(17)



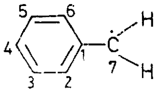
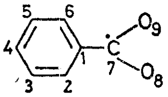
(18)

(ii) *Hückel–McLachlan calculations.* We have carried out a series of calculations on the planar benzyl radical using values of the resonance integrals[20] β for the 1—7, 2—3, and 5—6 C–C bonds which are different from those for the other C–C bonds, as suggested by Allendoerfer and Pollock[21] (see Table 2). The resultant spin-densities have been converted into splittings using the McConnell equation[22] with $Q_{\mathrm{CH}}{}^{\mathrm{H}}$ -2.687 mT (*cf.* ref. 21); the resulting splittings for benzyl (Table 2, entry for $h_7 = 0$) are in excellent agreement with experiment.[14] We have investigated the effect of changes in the electronegativity of the central carbon (C-7) consequent upon the introduction of oxygen substituents at the radical centre first by incorporating different values of h_C for that atom. It can be seen that using this simple 'inductive' model leads to increased values of $a(2\text{-H})$ and $a(4\text{-H})$ when h is varied in either negative or positive directions (corresponding to overall electron donation or electron withdrawal, respectively).

We have, secondly, carried out Hückel–McLachlan calculations in which conjugation with oxygen was simulated by incorporating two extra (oxygen) atoms in the π-framework, with appropriate parameters.[20] It is interesting to note that calculations with h_{C7} zero (*i.e.* as for benzyl) yield splittings very close indeed to those obtained in the calculations on benzyl itself (though with an *enhanced para*-proton splitting, of -0.683 mT) and

TABLE 2

Hückel–McLachlan calculations on benzyl-type radicals

Radical π-framework [a]	h_7	Calculated hyperfine splittings/mT				ρ_π (oxygen)
		a(7-H)	a(2,6-H)	a(3,5-H)	a(4-H)	
	-1.0	-0.975	-0.519	0.140	-0.838	
	-0.8	-1.145	-0.521	0.150	-0.782	
	-0.5	-1.416	-0.516	0.164	-0.685	
	-0.3	-1.583	-0.510	0.169	-0.626	
	0.0	-1.750	-0.505	0.177	-0.562	
		[(–)1.635	(–)0.514	0.175	(–)0.614] [b]	
	$+0.3$	-1.744	-0.511	0.177	-0.551	
	$+0.7$	-1.488	-0.519	0.164	-0.623	
	$+0.9$	-1.290	-0.516	0.148	-0.680	
	-1.0		-0.474	0.105	-0.916	0.012
	-0.5		-0.500	0.131	-0.808	0.017
	0.0		-0.496	0.146	-0.683	0.028
	$+0.5$		-0.474	0.150	-0.580	0.046
	$+1.0$		-0.457	0.147	-0.543	0.065
			[(–)0.480	0.155	(–)0.580] [c]	

[a] Parameters for benzyl: $\beta_{12} = \beta_{16} = \beta_{24} = \beta_{45} = 1.0$, $\beta_{23} = \beta_{56} = 1.125$, $\beta_{17} = 1.185$, $\lambda = 0.93$, $Q = -2.687$ mT (see ref. 21); parameters for α,α-dioxygen-substituted analogue as for benzyl together with $h_8 = h_9 = 2.0$, $\beta_{78} = \beta_{79} = 0.8$ (see ref. 20). [b] Data for benzyl, ref. 14. [c] Data for (13), this work.

predict *ca.* 3% of the spin density in the oxygen $p(\pi)$ orbitals. Of particular note is that for positive values of h_{C7} the spin density on each oxygen increases (being 6.5% for h 1.0) whilst at the same time the ring splittings show little or no evidence [see, *e.g.*, a(4-H)] for overall spin-withdrawal [giving good agreement with observed splittings for (13), see Table 2]. There evidently *is* considerable delocalization (probably 5—6% on each oxygen, being less than the 10% for aliphatic radicals because of the delocalizing effect of the ring) together with a redistribution of spin density between C-7 and the ring. We interpret the *positive* value of h_{C7} suggested by the calculations as implying that the central carbon atom (C-7) is rendered effectively more electronegative than C-7 in benzyl, evidently as a result of the $-I$ effect of oxygen.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E-104 X-band e.s.r. spectrometer employing 100 kHz modulation. Details of spectrum measurement, calibration, and simulation have been described previously,[8] as have details of sample preparation and the photolytic apparatus. The spectrum simulation,[8] INDO,[8] and Hückel–McLachlan programs (the last-named of which was kindly made available by Dr. D. R. Burnham) were executed on a DEC-KL10 computer at the University of York.

1,3-Dithian was obtained commercially and was used without further purification. Bis(thiomethyl)methane was prepared by the method of Schönberg and Praefcke [23] and characterized by its boiling point, and 1,3-dithiolan, 2-methyl-1,3-dithiolan, 4-methyl-1,3-dithiolan, and 2,4-dimethyl-1,3-dithiolan (as a mixture of diastereoisomers) were prepared by the method of Keskinen *et al.*[16] and characterized *via* their boiling points. 2-Phenyl-1,3-dithiolan was prepared by the acid-catalysed condensation of benzaldehyde and ethane-1,2-dithiol [24] and was characterized *via* its n.m.r. spectrum [25] and boiling point.[26] 2-Methyl- and 2-phenyl-1,3-dithian were prepared by the method of Seebach *et al.*[27] and were characterized *via* measurement of the boiling point [28] and freezing point,[27] respectively. The 1,3-oxathiolans were prepared by the method of Pihlaja [29] and characterized *via* their boiling points [29,30] and n.m.r. spectra.[29,31,32] 2-Phenyl-1,3-dioxan was prepared from benzaldehyde and propane-1,3-diol [33] and characterized *via* its boiling point.[34]

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