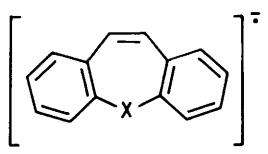
An Electron Spin Resonance Investigation of Electronic and Conformational Effects in Phenoxyl Radicals with *para*-Substituents: A Comparison of Carbonyl and Sulphur Substituents [-S(O)$_n$R, n = 0, 1, 2]

Bruce C. Gilbert, Peter Hanson,* William J. Isham, and Adrian C. Whitwood
Department of Chemistry, University of York, Heslington, York, YO1 5DD

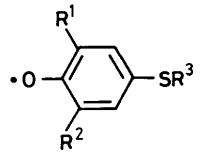
Line-width alternation in the e.s.r. spectra of some 4-substituted phenoxyl radicals $\cdot OC_6H_4X$ [X = C(O)R, SR, SAr] reveals restricted rotation about the C(4)–X bond. Though the barrier heights are similar for the carbonyl- and thio-substituted phenoxyl radicals, the considerably higher values of ring proton splittings for the former reflect the inductive effect of the CO substituent in redistributing spin density between (phenoxyl) oxygen and the ring. There is no evidence that sulphinyl and sulphonyl substituents are effective in spin-withdrawal, though their inductive effects on spin distribution are marked. A general model for the analysis of inductive and mesomeric effects in phenoxyl radicals is proposed. Barriers to rotation in the acetyl- and thio-substituted phenoxyl radicals are compared with those of their phenolic precursors.

It is perhaps not surprising that there is a general correlation between the spin density distribution in delocalised radicals such as aminomethyl, acetonyl, and allyl and the extent of stabilisation (*e.g.* as measured from barriers to rotation).[1] We have interpreted[2] e.s.r. α-proton splittings for radicals $^{\bullet}CH_2S(O)_nMe$ in terms of decreased spin delocalisation along the series sulphenyl > sulphinyl > sulphonyl [a(α-H) is 1.65, 2.00, and 2.23 mT for n 0, 1, and 2, respectively] and argued that the high value for $^{\bullet}CH_2SO_2Me$ (*cf.* 2.3 mT for Me$^{\bullet}$) implies that there is effectively no delocalisation for this radical. However, the spectra of some α-alkoxycarbonyl radicals $^{\bullet}CH_2CO_2R$ show[3] that a high α-proton splitting (*ca.* 2.1 mT) does not necessarily imply lack of delocalisation, since analysis of line-broadening in the α-proton splitting pattern indicates the existence of a considerable barrier to rotation (*ca.* 40 kJ mol^{-1}).

While for some benzyl radicals[4] and aminyl radicals[5] the extent of spin delocalisation claimed for SR, S(O)R, and S(O)$_2$R substituents parallels that discussed above, the sulphinyl substituent is claimed[6] to be the most effective at stabilizing the appropriate anion-radicals (**1**) [X = S, S(O), S(O)$_2$] and the SMe group is reported to be ineffective at delocalisation of the unpaired electron in substituted nitrobenzene anion-radicals and aryl alkoxy nitroxides.[7] Our finding[8] that the e.s.r. spectra of some 4-arylsulphenyl-substituted phenoxyl radicals (**2**; $R^1 = R^2$ = alkyl, R^3 = aryl) show an alternating line-width effect at low temperatures suggests that the extent of delocalisation in these and related radicals can be gauged by determination of the barrier to rotation about the C(4)–S bond. We have accordingly investigated further sulphenyl and related sulphinyl and sulphonyl substituents, in an attempt to determine whether similar line-width effects could be measured (to give unambiguous estimates of delocalisation onto the heteroatom) and to examine (*via* simple molecular orbital calculations) the dependence of splittings on mesomeric and inductive effects of substituents.



(**1**)



(**2**)

Results

(a) *Generation of Radicals and E.s.r. Spectra.*—Phenoxyl radicals were usually generated *in situ* by the photolysis of a solution of the phenol and di-t-butyl peroxide in either benzene or methylbenzene. For some phenoxyl radicals lacking a 4-substituent (which proved to be particularly short-lived), 4-methoxyacetophenone was also added as a photosensitizer,[9] and benzene employed as solvent (with methylbenzene, signals from the benzyl radical were detected); for phenols which were insufficiently soluble in both methylbenzene and benzene, a small amount of acetone was added to increase the solubility. An alternative method employed in some cases involved the generation of the phenoxyl radical *via* reaction of the parent phenol with Ce^{4+} in an aqueous flow system.[10]

(i) *Radicals with sulphenyl* (SR) *substituents.* Photolysis of a solution of 4-hydroxy-3,5-dimethylphenyl methyl sulphide and di-t-butyl peroxide in methylbenzene at 317 K gave a spectrum [Figure 1(a)] with parameters a(6H) 0.517, a(3H) 0.230, and a(2H) 0.120 mT (g 2.0052) assigned to the phenoxyl radical (**2**; $R^1 = R^2 = R^3$ = Me). The spectrum persisted for several hours after irradiation ceased. On lowering the temperature the spectrum changed considerably, until by 218 K it could be unambiguously analysed in terms of two non-equivalent ring methyl splittings (0.414 and 0.537 mT). The non-equivalence is interpreted as being due to attainment of the slow exchange limit for interchange of different methyl proton splittings [(**3**) $\rightleftharpoons$ (**4**)].[8]

Between these limits the spectra showed selective line-broadening, as well as movement in the position of the lines (characteristic of small variations in the magnitudes of individual splittings). Employing a two-jump model to account for the rotation about the C–S bond at varying frequencies and optimising both splittings and line-widths, spectra in the intermediate region were simulated.* Agreement between experimental and optimised computed spectra was excellent at all temperatures.

* At intermediate temperatures the individual ring methyl proton splittings were not directly measurable (because of the alternating line-widths) but their anticipated values were interpolated from the average value and the differences observed at low temperatures.

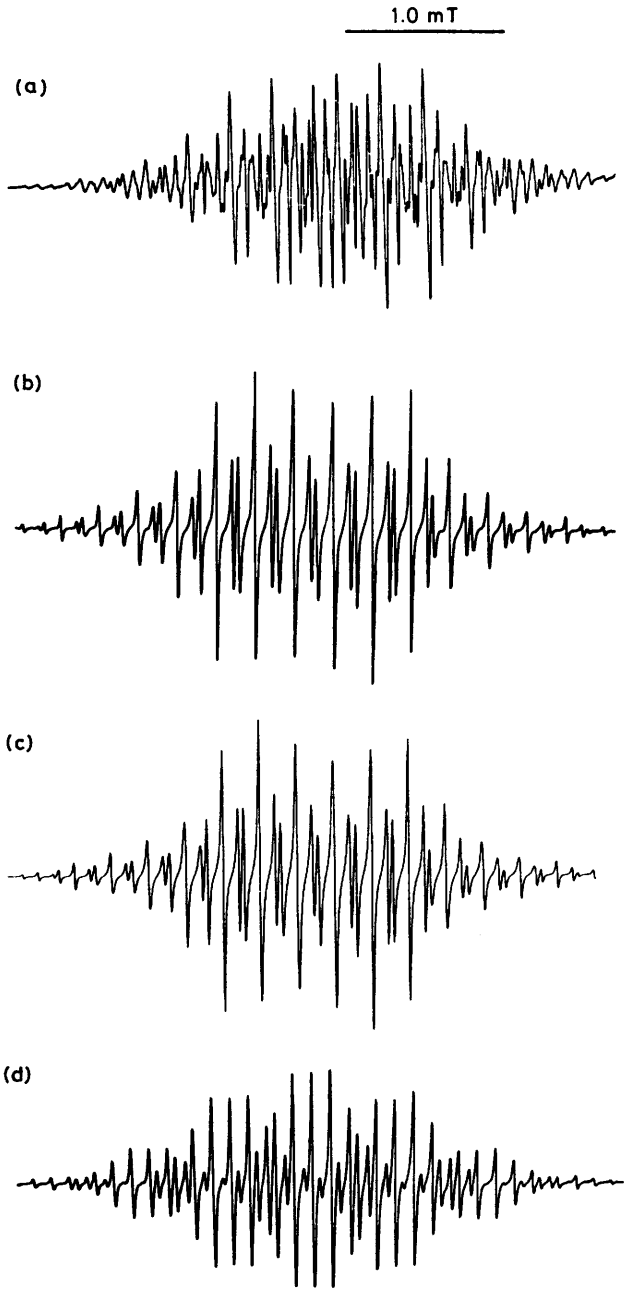
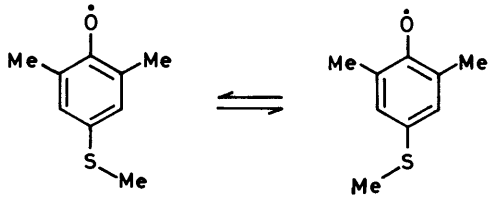


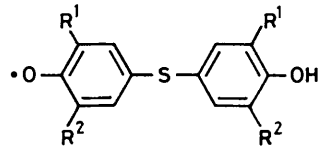
Figure 1. E.s.r. spectra of (**2**; $R^1 = R^2 = R^3 = Me$) in methylbenzene recorded at (a) 317 K, (b) 282 K, (d) 218 K. Figure 1(c) shows the spectrum simulated using hyperfine splittings and rate of exchange (for 282 K) shown in Table 1



(**3**) (**4**)

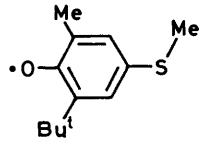
The splittings, their temperature dependences, and calculated rates of exchange (k) are given in Table 1. A plot of ln k *versus* T^{-1} gives a good straight line, from which the activation energy E_a for rotation about the C(4)–S bond is calculated as 36.6 kJ mol^{-1}, with A 2.5 × 10^{14} s^{-1} ($\Delta S^{\ddagger}$ of 28.4 J mol^{-1} K^{-1}), well within the range customarily found for conformational exchange.[11]

The phenoxyl radical (**5**; $R^1 = R^2 = Me$) from bis-(4-hydroxy-3,5-dimethylphenyl) sulphide shows[8] line-broadening similar to that described for (**2**; $R^1 = R^2 = R^3 = Me$), and the high barrier previously estimated for rotation about the C–S bond (54.5 kJ mol^{-1}) prompted reinvestigation. Particular care was taken over the measurement and control of temperature and the recording (and simulation) of spectra in the intermediate range; spectra obtained were considerably more intense than those detected previously and an improved set of simulations was achieved. The resulting splittings, their temperature dependences, and kinetic parameters for rotation about the C(4)–S bond are listed in Tables 1 and 2. The activation energy (46.6 kJ mol^{-1}) is significantly less than previously estimated but appears to be slightly greater than for the alkyl-substituted counterpart (**2**; $R^1 = R^2 = R^3 = Me$).



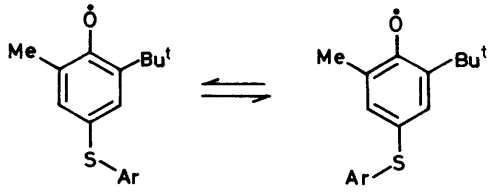
(**5**)

For some other sulphur-substituted phenoxyl radicals related line-width effects were observed. For example the radical (**2**; $R^1 = Me$, $R^2 = Bu^t$, $R^3 = Me$) gave a spectrum with two quartet splittings (at 294 K 0.557, 0.227 mT) and a small triplet (0.125 mT). On lowering the temperature, changes in position and line-width were observed and the low-temperature limit was reached by 208 K. The very complex spectrum which resulted defied complete analysis but it is clear that the major radical has a(3H) 0.590, a(3H) 0.241, a(1H) 0.122, a(1H) 0.095 mT (with g 2.0056). Whilst even in the fast-exchange limit the two ring protons will not be magnetically equivalent (because of their different environments with respect to the alkyl groups) it seems likely that any differences are enhanced (and hence observed at the low-temperature limit) as a result of the presence of the sulphenyl substituent. Although it is not clear which is the major conformer, structure (**6**) may be preferred on steric grounds.



(**6**)

For the radical (**5**; $R^1 = Me$, $R^2 = Bu^t$) the high-temperature spectrum comprised, as noted before,[5] a quartet of triplets; on lowering the temperature line-broadening occurred,



(**7**) (**8**)

Table 1. Temperature dependences of e.s.r. and kinetic parameters for some 4-substituted phenoxyl radicals

Radical	T/K	Hyperfine splittings/mT[a] a(Me)[c]	a(Me)[c]	a(SMe)	a(3,5-H)	k[b]/s^{-1}	g Value and d|a|/dT / μT K^{-1}
(**2**; R^1 = R^2 = R^3 = Me)	317	0.577[d]	0.457[d]	0.230	0.120	> 1.2 × 10^8	2.0052
	301	0.570[d]	0.450[d]	0.242	0.115	1.00 × 10^8	C–Me +0.46
	282	0.563[d]	0.443[d]	0.248	0.105	5.00 × 10^7	S–Me −0.42
	262	0.555[d]	0.435[d]	0.255	0.096	1.20 × 10^7	C–H +0.41
	251	0.548	0.428	0.260	0.095	7.00 × 10^6	
	240	0.545	0.425	0.267	0.090	3.00 × 10^6	
	226	0.537	0.423	0.265	0.090	8.00 × 10^5	
	218	0.537	0.414	0.272	0.085	< 7.00 × 10^5	
(**5**; R^1 = Me, R^2 = Me)	291	0.540[d]	0.490[d]	—	0.123	> 8.0 × 10^7	2.0056
	279	0.539[d]	0.489[d]	—	0.118	6.0 × 10^7	C–Me +0.27
	263	0.533[d]	0.483[d]	—	0.114	1.0 × 10^7	C–H +0.24
	255	0.529[d]	0.479[d]	—	0.112	5.0 × 10^6	
	239	0.524[d]	0.474[d]	—	0.108	2.0 × 10^6	
	235	0.522	0.472	—	0.107	< 4.0 × 10^5	
(**5**; R^1 = Me, R^2 = Bu^t)	296	0.580[d]	0.516[d]	—	0.127	> 8.0 × 10^7	2.0056
	273	0.573[d]	0.509[d]	—	0.115	1.0 × 10^7	C–Me +0.33
	266	0.570[d]	0.506[d]	—	0.112	8.0 × 10^6	C–H +0.45
	261	0.568[d]	0.504[d]	—	0.110	5.5 × 10^6	
	244	0.563	0.499	—	0.103	1.5 × 10^6	
	236	0.560	0.495	—	0.100	< 2.0 × 10^5	
(**13**)	241	0.709[d]	0.626[d]	—	0.219	> 5.0 × 10^7	2.0059
	229	0.711[d]	0.628[d]	—	0.219	2.7 × 10^7	2,6-H +0.08
	217	0.709[d]	0.626[d]	—	0.217	8.5 × 10^6	3,5-H +0.08
	205	0.707[d]	0.624[d]	—	0.216	7.5 × 10^6	
	199	0.706[d]	0.623[d]	—	0.215	4.0 × 10^6	
	193	0.705	0.622	—	0.215	< 1.0 × 10^6	
(**14**)	237	0.729[d]	0.628[d]	—	0.210	> 3.0 × 10^7	2.0051
	232	0.729[d]	0.628[d]	—	0.210	2.5 × 10^7	C–Me +0.10
	227	0.729[d]	0.628[d]	—	0.210	2.0 × 10^7	C–H +0.08
	222	0.729[d]	0.628[d]	—	0.210	1.4 × 10^7	
	217	0.729[d]	0.628[d]	—	0.210	7.5 × 10^6	
	212	0.729[d]	0.628[d]	—	0.210	5.0 × 10^6	
	207	0.729[d]	0.628[d]	—	0.210	3.0 × 10^6	
	202	0.729[d]	0.628[d]	—	0.210	2.0 × 10^6	
	197	0.729[d]	0.628[d]	—	0.210	1.2 × 10^6	
	192	0.729[d]	0.628[d]	—	0.210	< 1.0 × 10^6	

[a] Splittings ±0.005 mT, g ± 0.0001. [b] Estimated rate constant for rotation about the C(4)–X bond. [c] Measured directly from spectra except where indicated. [d] Interpolated from the average (observed) value and the differences at low temperatures.

Table 2. Kinetic parameters for restricted rotation in 4-substituted phenoxyl radicals[a]

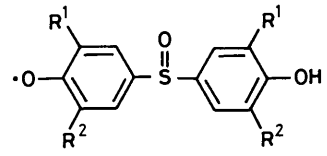
Radical	Substituent	E_a/kJ mol^{-1}	log (A/s^{-1})	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}[b]
(**2**; R^1 = R^2 = R^3 = Me)	SMe	36.6 ± 0.5	14.4 ± 0.2	28.4 ± 2.9
(**5**; R^1 = R^2 = Me)	SAr	46.6 ± 3.8	16.4 ± 1.1	61.5 ± 20.9
(**5**; R^1 = Me, R^2 = Bu^t)	SAr	37.6 ± 1.5	14.2 ± 0.4	20.5 ± 8.2
(**14**)	COMe	34.3 ± 0.4	15.2 ± 0.1	39.6 ± 2.3

[a] Standard errors quoted. [b] Calculated using the Eyring equation.

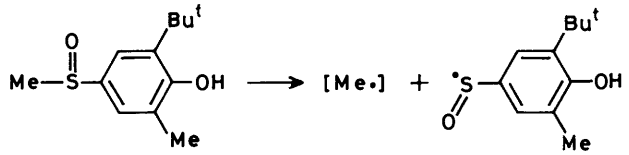
followed by resolution of two separate overlapping signals with different methyl proton splittings (and in a ratio of *ca.* 1:1). As with radical (**5**; R^1 = R^2 = Me), analysis and simulation of spectra obtained under improved conditions (see Tables 1 and 2) led to the determination of the barrier for interconversion [(**7**) ⇌ (**8**)] as 37.6 kJ mol^{-1}, which is not significantly different from that for the alkylthio counterpart (**2**; R^1 = R^2 = R^3 = Me). On this basis, there appears to be no significant enhancement of the torsional barrier associated with the arylthio groups examined.

Radical (**2**; R^1 = R^2 = Bu^t, R^3 = Me) showed an intense spectrum with (at 339 K) a(3H) 0.217 and a(2H) 0.145 mT (g 2.0056), as well as ^{13}C satellites [a(^{13}C) 0.850 mT, with an intensity as expected for interaction with two carbon atoms (probably the *ortho*-carbon atoms on the ring)]. On lowering the temperature, both splittings changed slightly [d|a|/dT − 0.21 μT K^{-1} for the methyl group, +0.21 μT K^{-1} for the ring protons] but even by 225 K there were no detectable line-width effects. While it is possible that conformational exchange is still in the fast region, it seems more likely that exchange is slow (but involving a species with indistinguishable ring proton splittings).

(ii) *Radicals with sulphinyl* [S(O)R] *and sulphonyl* [S(O)$_2$R] *substituents.* Reaction of bis-(4-hydroxy-3,5-dimethylphenyl) sulphoxide and bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphoxide with Bu^{t}O$^{\bullet}$ in methylbenzene over the temperature range 210—280 K gave transient spectra assigned to the radicals (**9**; R^1 = R^2 = Me) and (**9**; R^1 = Me, R^2 = Bu^t), respectively, with a(6H) 0.688, a(2H) 0.194 mT, g 2.0049, and a(3H) 0.700, a(2H) 0.188 mT, g 2.0049, respectively; no line-width effects were observed. The weakness of the spectra



(9)



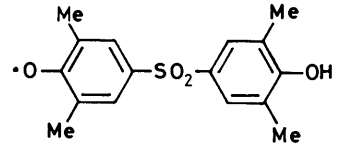
(10)

Scheme.

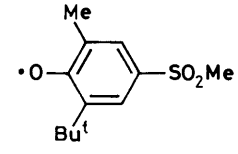
precluded the determination of meaningful temperature coefficients for the splittings. Closely similar spectra were recorded for these radicals in water at 293 K (generated with Ce^{4+} in a two-way flow system); 4-hydroxy-3,5-dimethylphenyl methyl sulphoxide behaved similarly under these conditions (see Table 3), though this phenoxyl radical could not be detected during photolysis. The small long-range methyl group splitting (0.047 mT) is notable.

Reaction of 4-hydroxy-3-methyl-5-t-butylphenyl methyl sulphoxide under photolytic conditions led to the detection of a radical assigned to the sulphinyl radical (**10**) [with a(2H) 0.226, a(3H) 0.069 mT, g 2.0095;[12] a separate experiment with the substrate alone in a benzene–acetone mixture led to the detection of the same species, evidently formed by direct photolysis (see Scheme).

The 4-sulphonyl-substituted phenoxyl radicals (**11**) and (**12**) were also generated as relatively short-lived species by the reaction of $Bu^tO^{\bullet}$ with the parent phenol in methylbenzene–acetone or benzene–acetone mixtures [with parameters a(6H) 0.719, a(2H) 0.220 mT, g 2.0050 and a(3H) 0.745, a(2H) 0.210, a(3H) 0.175 mT, g 2.0051, respectively]. The long-range methyl coupling in (**12**) is notable [and broadly as expected from parameters for[2] $^{\bullet}CH_2S(O)_2Me$]; there was no evidence of line-width alternation in the accessible temperature range (210—280 K). Radical (**11**) was also detected in aqueous conditions: no significant solvent effects were observed.

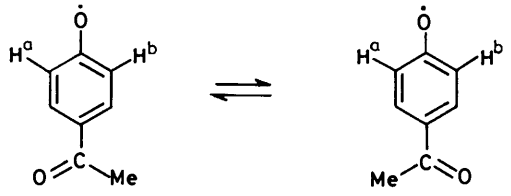


(11)

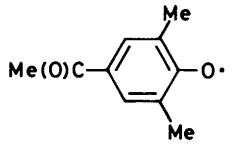


(12)

(iii) *Acetyl substituent.* The phenoxyl radical (**13**), generated in methylbenzene by reaction with $Bu^tO^{\bullet}$, was also found to exhibit e.s.r. signals which show line-width alternation [parallel to those for *e.g.* (**2**; $R^1 = R^2 = R^3 = Me$)] at low temperature. At 241 K the *ortho*-protons appeared equivalent [a(2H) 0.668 mT, with a(2H) 0.219 mT and g 2.0059] whereas different (*ortho*) ring proton splittings of 0.705 and 0.622 mT were detected at 193 K. Analogous effects were observed for the corresponding phenoxyl radical (**14**) from 4-acetyl-2,6-dimethylphenol. Simulation of line-broadening effects for (**14**) over the intermediate temperature range leads to the spectroscopic and kinetic parameters for interconversion of the rotamers given in Tables 1 and 2; for radical (**13**) the quality of the spectra precluded the estimation of reliable activation parameters.



(13a) (13b)



(14)

(iv) *Radicals lacking a 4-substituent.* Some 2,6-dialkylphenols were also oxidised (in both hydrocarbon and aqueous solution) in order to compare splittings of the derived phenoxyl radicals with those for the 4-substituted radicals discussed above (Table 3).

(b) *Molecular Orbital Calculations.*—Hückel–McLachlan molecular orbital calculations were carried out in order first to determine the optimum parameters for the unsubstituted phenoxyl radical and then to vary the Coulomb integral for the carbon atom at the 4-position ($h_{C\text{-}4}$) as an inductive model of the substituent effect.[13]

The parameters which give optimum agreement between calculated and experimental splittings for the phenoxyl radical itself were found to be h_O 1.6 and k_{CO} 1.0 (similar to those reported previously for phenoxyl radicals whose spectra were obtained in aqueous solution[14]). Examination of the spin densities calculated employing an inductive model (Table 4) shows that inductively electron-donating substituents (with $h_{C\text{-}4}$ negative) decrease the spin density on oxygen and at C-2 and C-6, effectively decrease that at C-3 and C-5 (positions of negative spin density) and increase that at C-1. The similarity between changes at C-2 (and -6) and C-3 (and -5) is notable (see later). Positive $h_{C\text{-}4}$ values, appropriate for inductively electron-withdrawing groups, have the opposite effect and significantly increase the spin densities at the *ortho*- and *meta*-carbons. It can be seen that there is a significant redistribution of spin density between the oxygen and the ring. The importance of this finding is that the observation in a substituted radical of a reduced ring proton splitting (compared with the unsubstituted parent) while possibly being due to spin withdrawal by the substituent may also result from redistribution of spin density within the phenoxyl moiety if the substituent exerts a significant $+I$ effect; conversely, relatively high ring splittings may reflect the operation of a significant $-I$ effect rather than simply the lack of mesomeric electron withdrawal. As explained below, we believe that such effects have previously been overlooked.

Discussion

(a) *Kinetic Parameters for Restricted Rotation.*—The observed barriers to rotation about the bonds between the 4-substituents [SMe, SAr, and C(O)Me] and the aromatic ring (see Table 2) suggest both that these bonds possess significant double-bond character and that there is effective delocalisation of the unpaired electron onto the substituent. The barriers to rotation observed are broadly comparable with those for related aliphatic radicals, *e.g.* $^{\bullet}CH_2SMe$ (>30 kJ mol^{-1}),[15] $^{\bullet}CH_2COMe$ (37 kJ mol^{-1}),[16] and $^{\bullet}CH_2CO_2R$ (40 kJ mol^{-1})[3]

Table 3. E.s.r. parameters for substituted phenoxyl radicals[a]

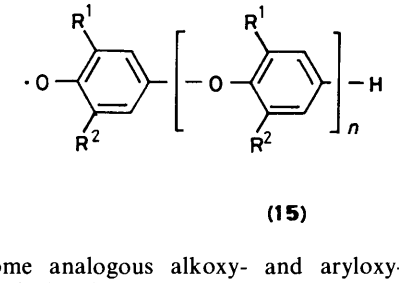
R^1	R^2	R^3	$a(R^1)$	$a(R^2)$	a(3,5-H)	$a(R^3)$	g	$\delta_{2,6}$[b]	$\delta_{3,5}$[b]
Me	Me	SMe	(−)0.517	(−)0.517	0.120	0.230(3H)	2.0056	−150	−70
Me	Me	SAr[c]	(−)0.515	(−)0.515	0.123	0.015[d]	2.0056	−152	−67
Me	Bu^t	SMe	(−)0.557	—	0.125	0.227(3H)	2.0056	−144	−69
Me	Bu^t	SAr[e]	(−)0.548	—	0.127	—	2.0056	−153	−67
Me	Me	S(O)Me	(−)0.695	(−)0.695	0.193	0.047(3H)	2.0049	28	3
Me	Me	S(O)Ar[c]	(−)0.680	(−)0.680	0.193	—	2.0049	13	3
Me	Bu^t	S(O)Me	(−)0.712	—	0.188	—	2.0049	11	−6
Me	Bu^t	S(O)Ar[e]	(−)0.714	—	0.191	—	2.0049	13	−3
Me	Me	$S(O)_2Ar$[c]	(−)0.719	(−)0.719	0.220	—	2.0050	52	30
Me	Bu^t	$S(O)_2Me$	(−)0.745	—	0.210	0.175(3H)	2.0051	44	16
Me	Bu^t	$S(O)_2Ar$[e]	(−)0.725	—	0.208	—	2.0050	24	14
H	H	C(O)Me	(−)0.668	(−)0.668	0.219	—	2.0059	3	39
Me	Me	C(O)Me	(−)0.678	(−)0.678	0.210	—	2.0051	11	20
H	H	H	(−)0.665	(−)0.665	0.180	1.010	—	0	0
Me	Me	H	(−)0.667	(−)0.667	0.190	0.937	2.0046	0	0
Me	Bu^t	H	(−)0.701	—	0.194	0.962	2.0047	0	0

[a] Proton splittings in mT (±0.005); g-values ±0.0001. Values refer to ambient temperature except where the temperature dependence was explored (in which case the splittings refer to the highest temperature achieved: see Table 1); substituents R^1, R^2, and R^3 are situated at ring positions 2, 6, and 4, respectively. For solvents, see text. [b] Difference in absolute magnitudes between the splittings from protons at the 2,6-positions and the 3,5-positions and those of the unsubstituted phenoxyl radical (μT). See text. [c] Ar = 4-hydroxy-3,5-dimethylphenyl. [d] Small extra splittings: see text. [e] Ar = 4-hydroxy-3-methyl-5-t-butylphenyl.

Table 4. Calculated π-spin densities in 4-substituted phenoxyl radicals[a]

h_{C4}	ρ_O	ρ_{C1}	$\rho_{C2,6}$	$\rho_{C3,5}$	ρ_{C4}
0.5	0.32	0.13	0.22	−0.08	0.27
0.4	0.30	0.14	0.22	−0.08	0.28
0.3	0.29	0.15	0.21	−0.07	0.28
0.2	0.27	0.16	0.20	−0.06	0.29
0.1	0.26	0.17	0.19	−0.05	0.29
0.0[b]	0.24	0.18	0.18	−0.04	0.30
−0.1	0.23	0.19	0.16	−0.02	0.29
−0.2	0.22	0.19	0.16	−0.01	0.29
−0.3	0.21	0.20	0.15	0.00	0.28
−0.4	0.20	0.21	0.14	0.02	0.28

[a] Hückel–McLachlan calculations, with $h_O = 1.6$, $k_{CO} = 1.0$ *cf.* ref. 12. [b] Spin densities for the phenoxyl radical in aqueous solution calculated from the observed splittings are $\rho_{C2,6} = 0.24$, $\rho_{C3,5} = 0.06$, and $\rho_{C4} = 0.36$.



(15)

and for some analogous alkoxy- and aryloxy-substituted phenoxyl radicals [the barrier to rotation about the C(4)–O bond in 4-methoxy-2,6-dimethylphenoxyl is 32.6 kJ mol^{-1};[17] the phenoxyl radicals (**15**; $R^1 = R^2 = Me$) and (**15**; $R^1 = Me$, $R^2 = Bu^t$) have barriers of 39.3 and 41.8 kJ mol^{-1}, respectively[18]]. The calculated A values are typically in the range normally associated with unimolecular processes (10^{12}—10^{14} s^{-1}).[11]

It is particularly instructive to compare the barriers to rotation of the substituent in phenoxyl radicals having 4-SMe and 4-COMe substituents with those in the precursor phenols. For example, the barrier to torsion of the substituent in thioanisole has been estimated as 5.4 kJ mol^{-1} for benzene solution; this barrier is reduced by electron donor functions in the *para* position.[19] Consequently the barrier to torsion of the SMe group in 4-hydroxythioanisole is expected to be <5 kJ mol^{-1}. Oxidation of 4-sulphenylated phenols to the corresponding phenoxyls thus increases the torsional barrier approximately eight-fold (Table 2). By contrast, the barrier to rotation of the acetyl group in acetophenone is 22.4 kJ mol^{-1}, increasing to 28 kJ mol^{-1} in 4-methoxyacetophenone.[20] A barrier of similar height is expected for 4-hydroxyacetophenone. Oxidation of 4-acetylated phenols to the corresponding phenoxyls, at least as judged by the value of E_a for (**14**), thus produces no significant change in barrier for torsion of the acetyl group (Table 2). This contrasting behaviour is explained in frontier orbital terms by reference to Figure 2.

The low barrier to rotation of SMe in 4-hydroxythioanisole arises from interaction ($n - \pi^*$) of the sulphur lone-pair with the LUMO of the phenol, which affords it only a small stabilisation [Figure 2(a)]. Assuming no perturbation of orbital energies on oxidation, the corresponding orbital interaction will make a similar small contribution to the rotational barrier in the phenoxyl radical. In addition, however, the phenoxyl SOMO now may interact with the substituent lone-pair orbital ($n - \pi$) [Figure 2(b)]. If, as we expect,[21] the phenoxyl SOMO and the sulphur lone-pair orbitals are of similar energy, this interaction at once accounts for a significantly increased rotational barrier (due to the electron pair stabilisation) and the observation of significant spin density on sulphur; the new SOMO is strongly influenced by its sulphur-centred component orbital.

The barrier to rotation of the acetyl group in 4-hydroxyacetophenone is accounted for by the significant stabilisation of the electron pair in the HOMO of the phenol by interaction of this orbital with the LUMO of the substituent [Figure 2(c)]. The contribution of the analogous orbital interaction to the barrier in the 4-acetylphenoxyl radical is expected to be approximately halved due to the halving of the number of stabilised electrons. The observation of a torsional barrier of the same magnitude in the radical (**14**) as in the phenol implies that this relative loss of stabilisation is compensated in some way; we believe that this occurs by the interaction of the SOMO with the substituent HOMO [Figure 2(d)]. The stabilisation of acetyl-substituted phenoxyls is thus the result of an approximately equal combination of phenoxyl SOMO/acetyl LUMO and

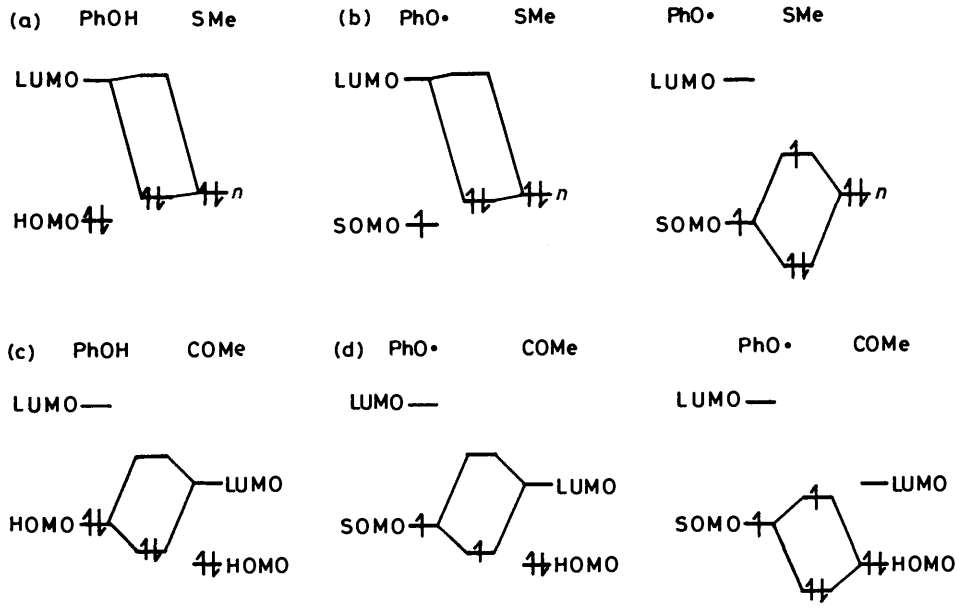


Figure 2. Frontier orbital diagrams showing the interaction between 4-SMe and 4-COMe substituents and the aromatic ring in both phenols and the corresponding phenoxyl radicals

Table 5. Table of hyperfine splittings for some 4-substituted phenoxyl radicals ($^{\bullet}OC_6H_4R$)

R	$a_{2,6}$ [a]	$a_{3,5}$ [a]	$\delta_{2,6}$ [a]	$\delta_{3,5}$ [a]	Reference
H	(−)665	180	0	0	This work
SO_3H	(−)725	210	60	30	24
CF_3	(−)720	220	55	40	25
Bu^t	(−)625	165	−40	−15	26
NO_2	(−)700	240	35	60	14
CN	(−)675	225	10	45	27
CO_2H	(−)675	220	10	40	14
COMe	(−)668	219	3	39	This work
CO_2^-	(−)653	193	−12	13	28
Cl	(−)640	175	−25	−5	25
F	(−)650	145	−15	−35	25
OH	(−)510	30	−155	−150	29
OMe	(−)505	35	−160	−145	30
OMe	(−)505	20	−160	−160	29
NH_2	(−)275	−175	−390	−355	29
O^-	(−)237	−237	−428	−417	29
NMe_2	(−)214	−214	−451	−394	31

[a] In μT.

phenoxyl SOMO/acetyl HOMO interactions. In both of these, however, the new SOMO is more influenced by its phenoxyl-centred component orbital than by the substituent-centred component. This, in part, would explain our observation of significant torsional barriers in acetylated radicals with little apparent concomitant withdrawal of spin density by the substituent (see later).

Since no alternating line-width effects are detectable for any of the aromatic radicals containing 4-sulphinyl or 4-sulphonyl substituents, we conclude that, in these radicals, the rotation about the C–S bond is much less hindered at all temperatures studied (there is a very low barrier to rotation, with little or no delocalisation of the unpaired electron density onto the substituent).

(b) *Hyperfine Splittings.*—An estimate of unpaired electron density withdrawn by a substituent is customarily obtained from the decrease in ring proton (*ortho* and *meta*) and methyl group hyperfine splittings on substitution (see *e.g.*, ref. 22). This approach (using values in Table 3) leads to a value of *ca.* 16% spin withdrawal by the methylsulphenyl substituent and *ca.* 17% by the arylsulphenyl substituent (spin withdrawal amounting to *ca.* 22% has previously been estimated[2] for carbon-centred radicals of the type $^{\bullet}CR^1R^2SMe$). Further evidence for spin withdrawal, in addition to the existence of a barrier to rotation, is provided by the substantial proton splitting from the methylthio group in (**2**; $R^1 = R^2 = R^3 =$ Me) (which presumably arises *via* hyperconjugation from the spin density on sulphur), the marked temperature dependence of the ring and alkylthio groups splittings in *e.g.* (**2**; $R^1 = R^2 = R^3 =$ Me) (which reflects the increased contribution of the out-of-plane rotation of the –SR group at higher temperatures) and the elevated *g*-value for radicals of the type (**2**).

However, the ring splittings exhibited by the carbonyl-substituted radicals (**13**) and (**14**) suggest at first sight that the substituent has little, if any, effect on the spin density in the π-orbital on the ring (indeed, increased splittings are observed). This appears to be inconsistent with the significant barrier to rotation about C(4)–C(O), which would be expected to reflect the existence of some spin delocalisation (*cf.* also $^{\bullet}CH_2COMe$, in which the substituent withdraws *ca.* 16% of the spin density).[23] We believe that this apparent contradiction stems from the inductive ($-I$) effect exerted on the C-4 position and the consequent redistribution of spin, within the phenoxyl moiety, as suggested by the HMO calculations described earlier.

Recognition of this phenomenon also allows us to rationalise the experimental observations for a variety of phenoxyl radicals with oxidised sulphur substituents in the 4-position. Firstly, there is no evidence for hindered rotation about the C(4)–S bond in the sulphinyl-and sulphonyl-substituted radicals, which suggests that spin delocalisation *via* π–π overlap is very small, or, at best, considerably reduced compared with their thio-substituted counterparts (exactly as found for their aliphatic analogues). Secondly, we note the significant increases in the ring proton and methyl group splittings when these are compared with splittings from the corresponding unsubstituted radicals (see Tables 3 and 5); the continuation of this trend with the parameters for (**16**) and (**17**), for which no π–π delocalisation

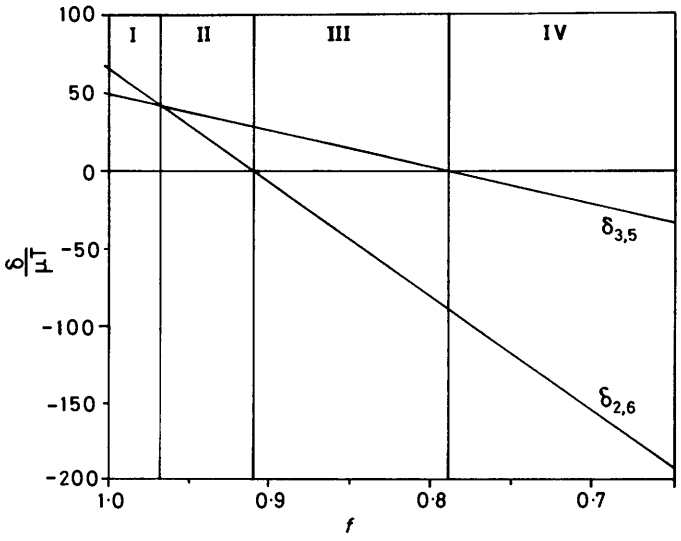
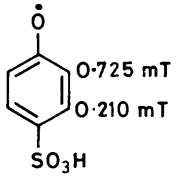


Figure 3. Variation of $\delta_{2,6}$ and $\delta_{3,5}$ with f (the fraction of spin remaining on the aromatic ring) in a hypothetical series of phenoxyl radicals with the different domains indicated (see text)

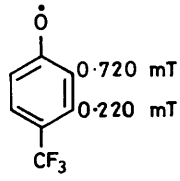
Table 6. Classification of 4-substituents in phenoxyl radicals

Domain		Substituents
I	$\delta_{2,6}$ + ve, $\delta_{3,5}$ + ve; $\delta_{2,6} > \delta_{3,5}$	CF_3, SO_3H, SO_nR (n = 1, 2)
II	$\delta_{2,6}$ + ve, $\delta_{3,5}$ + ve; $\delta_{2,6} < \delta_{3,5}$	NO_2, CN, COMe, CO_2H
III	$\delta_{2,6}$ − ve, $\delta_{3,5}$ + ve	CO_2^-
IV	$\delta_{2,6}$ − ve, $\delta_{3,5}$ − ve	Cl, OMe, SR, F

would be expected, indicates the important role played by the inductive effect of the substituent in redistributing spin density between phenoxyl oxygen and the ring.*



(16)



(17)

We have attempted to rationalise, *via* a semi-quantitative model, the observed changes in *ortho*- and *meta*-proton splittings (both the directions of change and their relative magnitudes) consequent upon introduction of a wide variety of substituents into phenoxyl itself (Tables 3 and 5). As can be seen, for some substituents both splittings increase (SO_3H, CF_3), for others both decrease (SMe), for the COMe substituent the increase in 3,5-splitting is much greater than that for the 2,6-positions and for one substituent (CO_2^-) the directions of change are different. These trends can be understood if it is considered that mesomeric effects will remove spin density from the 2- and 6-position (and hence proportionately from the 3,5-positions too) whereas the inductive effect can redistribute spin density between C-2 (and C-6) and C-3 (and C-5) (as well as between carbon and oxygen); for example, negative spin density is increased at C-3 for inductively electron-withdrawing substituents and inductively electron-donating groups lead to a build-up of positive spin density at this position (counteracting negative spin density: *cf.* Table 4). These effects are both incorporated in the following approach.

Equation (1) expresses a ring proton hyperfine splitting a^X for a 4-X-substituted phenoxyl radical in terms of a^H, the corresponding splitting in the unsubstituted radical, an increment i, representing the redistribution of spin within the phenoxyl moiety as a consequence of the inductive effect of the substituent, and f, the fraction of spin density which remains on the phenoxyl moiety after (mesomeric) spin withdrawal by the substituent.

$$a^X = (a^H + i)f \qquad (1)$$

The difference, δ, between corresponding ring hyperfine splittings in the substituted and parent radicals is thus given by equation (2).

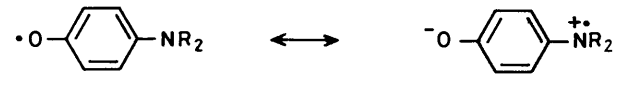
$$\delta = a^X - a^H = [(a^H + i)f - a^H] \qquad (2)$$

Thus for a hypothetical family of phenoxyl radicals having 4-substituents with a common value of i, δ is a linear function of f.

In Figure 3 the difference δ is plotted as a function of f for hypothetical radicals in which $i_{2,6} = 0.1|a^H_{2,6}|$ and $i_{3,5} = 0.075|a^H_{2,6}|$. The relationship of the two lines in Figure 3 with one another and with the abscissa allows division of Figure 3 into domains **I**—**IV**, which differ in the extent of spin withdrawal. In reality, both i and f will vary from substituent to substituent with the consequence that the intercepts and boundaries of Figure 3 are not precisely defined for real radicals. Nevertheless, actual radicals falling into each domain are known (Table 6).

Radicals which fall in the first and second domains include those which have been discussed earlier (*e.g.*, SO_3H and COMe, respectively). The phenoxyl radical derived from 4-hydroxybenzoate anion appears to lie just inside domain **III**; by contrast, the acid form of this radical lies in domain **II**. In the fourth domain the mesomeric effect of the 4-substituent is more important than the inductive effect. This is characterised by both $\delta_{2,6}$ and $\delta_{3,5}$ being negative and radicals falling into this domain include those with Cl, OMe, and F substituents, as well as SR as discussed above.

There are, however, some radicals which do not fall into any of the domains (X = O^-, NR_2). In these the spin withdrawal onto the substituent is so great that they can no longer be regarded as typical phenoxyl radicals. The 3,5-splitting is now negative (due to the spin density at these positions having become positive) and is similar in size to that at the 2,6-positions with structures (**18a**) and (**18b**) of approximately equal importance.



(18a) (18b)

* Failure to recognize this effect may lead to erroneous deductions. For example, it has been concluded[32] from comparison of the methyl group proton splittings in 4-$CH_3C_6H_4\dot{C}H_2$ (0.653 mT), 4-$CH_3C_6H_4$-$\dot{C}$HOMe (0.590 mT), and 4-$CH_3C_6H_4\dot{C}(OMe)_2$ (0.640 mT) that the second methoxy group is 'antagonistic' rather than additive in its electron-withdrawing effect and that there is very little delocalisation (3%) in the disubstituted radical. However, as we have shown[33] *via* analysis of e.s.r. spectra and by M.O. calculations for some related species that there is significant spin withdrawal onto each oxygen (*ca.* 6% each) together with redistribution of the spin density between the radical centre and C-4 (thus raising the splitting from groups in the latter position), as a result of the oxygens' inductive effect.

Conclusions

For the sulphinyl [S(O)R] and sulphonyl [$S(O)_2R$] substituents there is little evidence for mesomeric interaction of the substituent with the unpaired electron; molecular orbital calculations suggest that it is their inductive effects which influence ring splittings. The lack of a significant temperature dependence of the spectra of these radicals suggests that there is relatively free rotation about the C–S bonds. In contrast, evidence from the barriers to rotation about the C–S bond, hyperfine splittings, and *g*-values for radicals with sulphenyl (–SR) substituents shows that these groups interact strongly with the unpaired electron and withdraw nearly 20% of the spin density from the ring. Acetyl-substituted phenoxyls exhibit a barrier to rotation yet the hyperfine splittings suggest that there is little unpaired electron delocalisation by the substituent, a conclusion supported by the small temperature dependence of the hyperfine splittings.

Several factors contribute to this behaviour. The withdrawal of spin density from phenoxyl radicals by 4-acetyl substituents may not be substantial; and in any case, the spin withdrawal that does occur is camouflaged by redistribution of spin density within the phenoxyl moiety which arises from the inductive effect of the substituent (the barrier to torsion of the substituent contains a significant contribution from the stabilisation of orbitals containing paired electrons).

The extent of spin delocalisation onto COMe in the appropriate 4-substituted phenoxyl can be obtained by comparison of the differences between splittings for 2,6- and 3,5-positions compared with those of the parent. On the assumption that a nominal 10% increase in $a_{2,6}$ is associated with the carbonyl's $-I$ effect (see Figure 3), then the δ values of +3 and +39 μT are consistent with the occurrence of spin delocalisation of *ca.* 8% onto the carbonyl group (*cf.* 16% for $^{\bullet}CH_2COMe$ [23]).

Experimental

E.s.r. spectra were recorded on Varian E-104 and Bruker ESP 300 X-band spectrometers, each with 100 kHz modulation. The hyperfine splittings and *g*-values were determined directly from the spectrometers' field scans, these having been calibrated with the signal from Fremy's salt [a_N 1.3091 mT,[34] *g* 2.0055 [35]]. For variable-temperature work we employed either a Varian Variable Temperature accessory (the temperature being measured with a Comark 3015 Cr/Al digital thermometer) or with the Bruker ER-4111 VT attachment. Photolysis was carried out on static samples with the unfiltered radiation from a Hanovia 977B-1 1 kW mercury–xenon compact arc. Solutions in methylbenzene with phenol (typically *ca.* 0.25 mol dm^{-3}) and di-t-butyl peroxide (typically *ca.* 2 mol dm^{-3} were deoxygenated with nitrogen before photolysis. Oxidation of phenols with Ce^{4+} was carried out with a two-stream rapid-mixing system in which reagents were mixed *ca.* 30 ms before passage through the cavity of the spectrometer: the two solutions typically contained, respectively, ammonium ceric nitrate (0.001 mol dm^{-3}) in distilled water with sulphuric acid (pH 1) and the appropriate phenol (0.002 mol dm^{-3}) either in water or aqueous acetone. Both solutions were deoxygenated with nitrogen before use. Flow was maintained by a Watson-Marlow 502S flow-inducer positioned on the inlet tubing of the mixing chamber.

Spectral simulations were carried out using a program (kindly provided by Dr. M. F. Chiu) in which exchange and second-order effects were incorporated: it was executed on either a DEC-10 mainframe computer or (with a modified version) on a BBC microcomputer. For the Hückel–McLachlan calculations we employed a program, originally written in Fortran IV by Dr. D. R. Burnham, modified for use on a BBC microcomputer.

Chemicals and solvents except where stated otherwise were commercially available and used without further purification. 4-Hydroxy-3,5-dimethylphenyl methyl sulphide,[36] bis-(4-hydroxy-3,5-dimethylphenyl) sulphide,[37] bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide,[37] bis-(4-hydroxy-3,5-dimethylphenyl) sulphoxide,[38] 4-hydroxy-3,5-dimethylphenyl methyl sulphoxide,[39] 4-hydroxy-3-methyl-5-t-butylphenyl methyl sulphoxide,[39] bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphoxide,[37] 4-hydroxy-3-methyl-5-t-butylphenyl methyl sulphone,[39] bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphone,[40] and bis-(4-hydroxy-3,5-dimethylphenyl) sulphone[40] were prepared using literature procedures. 4-Hydroxy-3-methyl-5-t-butylphenyl methyl sulphide was prepared using the literature procedure for the 3,5-dimethyl analogue[36] and gave satisfactory elemental analysis.

Acknowledgements

We thank the S.E.R.C. for a studentship (W. J. I.).

References

1 See *e.g.* J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1043.
2 P. M. Carton, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1245.
3 W. Lung-min and H. Fischer, *Helv. Chim. Acta*, 1983, **66**, 138.
4 D. D. M. Wayner and D. R. Arnold, *Can. J. Chem.*, 1984, **62**, 1164.
5 Y. Miura, H. Asada, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 720; Y. Miura, Y. Nakamura, and M. Kinoshita, *Chem. Lett.*, 1978, 521; *Bull. Chem. Soc. Jpn.*, 1978, **51**, 947.
6 R. Leardini and G. Placucci, *J. Heterocycl. Chem.*, 1976, **13**, 277.
7 A. Alberti, G. Martell, and G. F. Pedulli, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1252.
8 B. C. Gilbert and B. Gill, *J. Chem. Soc., Perkin Trans. 2*, 1979, 776.
9 D. Griller, K. U. Ingold, and J. C. Scaiano, *J. Magn. Reson.*, 1980, **38**, 169.
10 T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.
11 S. W. Benson and W. B. de More, *Annu. Rev. Phys. Chem.*, 1965, **16**, 397.
12 B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. H. Laue, *J. Chem. Soc., Perkin Trans. 2*, 1977, 497.
13 A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.
14 W. T. Dixon, M. Moghimi, and D. Murphy, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1713.
15 I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.
16 G. Golde, K. Mobius, and W. Kaminski, *Z. Naturforsch.*, 1969, **24a**, 1214.
17 W. J. van den Hoek, W. G. B. Huysmans, and M. J. C. van Gemert, *J. Magn. Reson.*, 1970, **3**, 137.
18 W. J. van den Hoek, J. F. Th. de Winter, and J. Smidt, *J. Magn. Reson.*, 1972, **6**, 15.
19 T. Schaefer and J. D. Baleja, *Can. J. Chem.*, 1986, **64**, 1376.
20 T. Drakenberg, J. Sommer, and R. Jost, *J. Chem. Soc., Perkin Trans. 2*, 1980, 363.
21 D. J. Pasto, R. Krasnansky, and C. Zercher, *J. Org. Chem.*, 1987, **52**, 3062.
22 H. Fischer, *Z. Naturforsch.*, 1964, **19a**, 866; 1965, **20a**, 428.
23 D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Am. Chem. Soc.*, 1973, **95**, 7978.
24 W. T. Dixon and D. Murphy, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1630.
25 D. M. Holton and D. Murphy, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1637.
26 S. A. Weiner, *J. Am. Chem. Soc.*, 1972, **94**, 581.
27 W. T. Dixon, M. Moghimi, and D. Murphy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1189.
28 P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.
29 W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1221.
30 W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 432.
31 P. J. Zandstra and E. M. Evleth, *J. Am. Chem. Soc.*, 1964, **86**, 2664.
32 L. Sylvander, L. Stella, H.-G. Korth, and R. Sustmann, *Tetrahedron Lett.*, 1985, **26**, 749.

33 C. Gaze and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1979, 763.
34 R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.
35 J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.
36 E. Goethals and P. De Radzitzky, *Bull. Soc. Chim. Belg.*, 1964, **73**, 546.
37 G. Brunton, B. C. Gilbert, and R. J. Mawby, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1267.
38 H. H. Takimoto and G. C. Denault, *J. Org. Chem.*, 1964, **29**, 759.
39 M. Fujio, M. Mishima, Y. Tsuno, Y. Yukawa, and Y. Takai, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2127; F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, 1957, **79**, 717.
40 *Chem. Abstr.*, 1968, **69**, 76927c (U.S.P.).

Received 10*th February* 1988; *Paper* 8/00483