The Electron Spin Resonance Spectra of Naphthoxyl Radicals

By **William T. Dixon,*** **Wendy E. J. Foster,** and **David Murphy,** Department of Chemistry, Bedford College, Regent's Park, London NW1 4NS

The e.s.r. spectra of α- and of β-naphthoxyl radicals have been obtained and analysed. Unambiguous assignments of the coupling constants have been found by getting spectra from a number of substituted naphthols and these have been confirmed by generating radicals from the dihydroxynaphthalenes in acid solution and analysing the corresponding e.s.r. spectra.

THE e.s.r. parameters of α- and of β-naphthoxyl radicals are of intrinsic interest because they indicate features about the electronic structure of these species which are simple extensions of phenoxyl or, for that matter, of benzyl radicals. However the e.s.r. spectra of neither α- nor of β-naphthoxyl have until now been obtained in resolvable form so the two sets of proton coupling constants have not been available. The e.s.r. spectra of both radicals were obtained by Stone and Waters[1] in 1964 but the signal-to-noise ratio was unfavourable and analysis was not possible. Using essentially the same technique (*i.e.* the oxidation of naphthols by ceric ion) we have been able to increase the intensity of these two spectra by a factor of 10 or more and have thus been able to resolve and to analyse them. We achieved this by modifying the coaxial mixing device[2] so that the reactant

---

[1] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.

[2] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

solutions mixed virtually inside the cavity of our Varian E4 spectrometer. We estimate a ' dead time ' of *ca.* 1 ms. The signals were largest at the maximum flow rate we could achieve (*ca.* 15 ml s^{-1}) so it appears that naphthoxyl radicals are at least as unstable as phenoxyl radicals and the second ring contributes little towards their stability under the conditions used

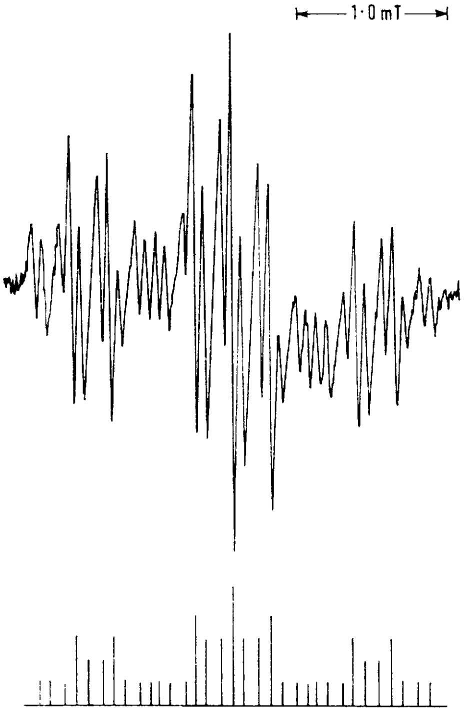


FIGURE 1 E.s.r. spectrum of 1-naphthoxyl

1-Naphthoxyl and Related Radicals.—The spectrum obtained for 1-naphthoxyl is shown in Figure 1 and was easily analysed to give the coupling constants shown in Table 1.

Of course, the assignments of these coupling constants to particular protons is ambiguous in the first instance, but can be tentatively made by comparison with the simple Huckel theory for the corresponding benzyl-type radical, or, since most of the odd electron density is on the rings and not on the oxygen (from the magnitude of the coupling constants) by comparison with the π electron radical formed by eliminating C-1. In either case the predicted odd electron densities are in the same ratios. A rough rule for getting negative spin densities which more or less inevitably appear when Huckel theory leads to predictions of zeros, is: the negative spin density at a position where the simple theory predicts zero, is approximately proportional to the adjacent positive spin density. By comparison then with the *meta*-splittings in phenoxyl we are led to the assignment shown, with some ambiguity in the 6- and 8-positions.

TABLE 1

Coupling constants (in mT) in α-naphthoxyl radicals

Substituents in starting material	1-OH	1-OH 2-CO_2H	1-OH 5-CO_2H [b]	1-OH 7-CO_2H [b]	1-OH 5-OMe [c]	1-OH 4-SO_3^-	1-OH 8-SO_3^- [d]	Assigned positions	Huckel MO spin density
Observed coupling constants	1·075	1·04	1·075	1·10	1·10		1·075	4	4*x*
	0·825		0·825	0·85	0·725	0·875	0·875	2	4*x*
	0·25	0·29	0·25		0·275	0·25	0·20	7	*x*
	0·25	0·29		0·25		0·25	0·20	5	*x*
	0·175	0·09	0·21	0·20	0·15	0·25	0·20	3	0
	0·065	0·09	0·09	0·05	0	0·075	0	6	0
	0 [a]	0	0·06	0·05	0	0		8	0

[a] Limit of resolution ~0·04 mT. [b] Ref. 4. [c] Ref. 5. [d] Ref. 6.

Although the agreement with such a simplified theory is in many ways very satisfactory, we felt it necessary to confirm the assignments empirically, the more so since the splittings bear almost no relationship with those observed in nitroxyl radicals containing naphthyl groups.[3] The results from a number of substituted 1-naphthols which gave rise to well resolved e.s.r. spectra are shown in Table 1 and evidently confirm the picture we have given.

A point of interest here is that the substituent groups do not seem to alter the general odd electron density very much.

2-Naphthoxyl and Related Radicals.—A similar exercise was undergone for 2-naphthoxyl and some of its derivatives, and though in general the spectra were not quite well resolved as in the 1-naphthoxyl, they could be analysed easily to give a consistent set of results leading to the assignments shown.

Once again the substituents did not seem to affect the odd electron density very much. The main deviations from what might be expected from a simplified molecular orbital model such as that used for 1-naphthoxyl are that the coupling constants of protons on 6- and 8-positions are rather large and the splitting of the 3-proton is rather small. We might attribute this to the relative fixation of double bonds across C-1 and -2 and across similar pairs of carbon atoms, in the naphthalene skeleton. The 6-position which is furthest from the oxygen atom has the highest spin density, apart from that on the 1-position, and this can be explained from simple molecular orbital theory in terms of the short C-7–C-8 bond (resonance integral β), *i.e.* in the non-bonding orbital $\beta C\text{-}8 + \beta' C\text{-}6 = 0$. But the C-7–C-8 bond is shorter

---

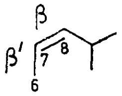
[3] J. L. Duncan, A. R. Forrester, G. McConnachie, and P. D. Mallinson, *J.C.S. Perkin II*, 1973, 718.

[4] F. A. Royle and J. A. Schedler, *J. Chem. Soc.*, 1923, 1641.

[5] C. A. Naylor and J. H. Gardner, *J. Amer. Chem. Soc.*, 1931, **53**, 4109.

[6] G. Heller, *Z. anorg. Chem.*, 1928, **41**, 171.

than the C-6–C-7 bond implying that β > β′ and hence that $(\text{C-6})^2 > (\text{C-8})^2$.



Radicals from Dihydroxynaphthalenes.—Some further interesting points come out of the study of radicals formed by the oxidation of dihydroxynaphthalenes by ceric ion. In most cases good e.s.r. spectra were obtained, but it is clear that the radicals are not particularly stabilised and that they were just as transient in the acidic oxidation conditions as were the naphthoxyl radicals themselves.

TABLE 2

Coupling constants (in mT) in β-naphthoxyl radicals

Substituents in starting material	2-OH	2-OH 1-CO_2H	2-OH 3-CO_2H	2-OH 3-OMe[a]	2-OH 6-OMe[b]	2-OH 7-OMe[a]	2-OH 1-SO_3^-	2-OH 6-SO_3^-	2-OH 7-SO_3^-	2-OH 6-SO_4^- 8-SO_3^-	Assigned positions	Huckel MO spin densities
Observed coupling constants	1·075		1·04	0·95	0·975	1·05		1·1	1·075	1·065	1	4*x*
	0·54	0·55	0·52	0·55		0·525	0·55		0·55		6	*x*
	0·43	0·425	0·44	0·45	0·375	0·4	0·45	0·425	0·425		8	*x*
	0·145	0·15			0·25	0·15	0·15	0·15	0·15	0·2	3	*x*
	0·145	0·15	0·16	0·10	0·125	0·125	0·15	0·15	0·125	0·15	5	0
	0·12	0·125	0·08	0·05	0·125		0·125	0·15		0·15	7	0
	0	0	0·08	0·05	0	0	0	0	0	0·05	4	0

[a] Ref. 7. [b] Ref. 8.

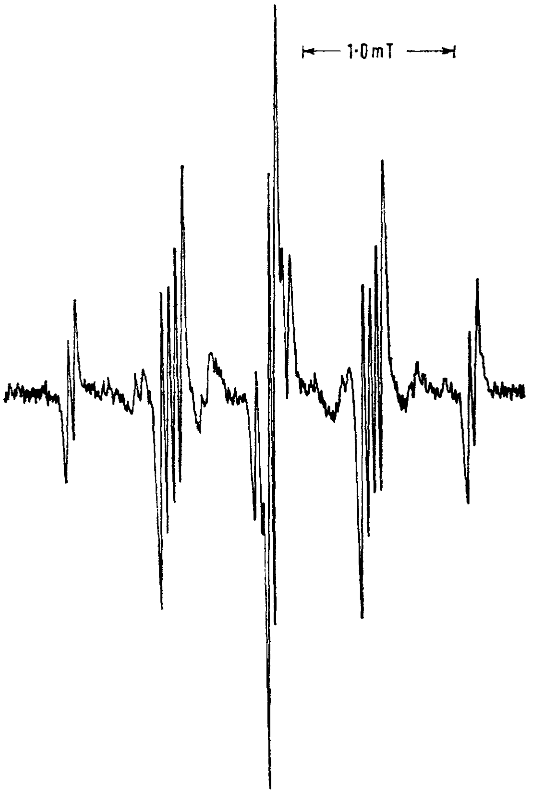


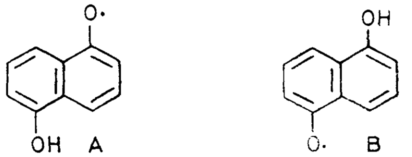
FIGURE 2 E.s.r. spectrum of radical from 4,5-dihydroxynaphthalene-2,7-disulphonic acid

In most cases spectra indicating a rather smoothed out odd electron density were obtained (see Figure 2) showing a change similar to that in going from phenoxyl to semiquinone.

In Table 3 we see that when the two hydroxy-groups are conjugated with each other (*i.e.* one can draw quinonoid structures) the coupling constants are relatively small whereas in the other cases larger couplings may appear.

In three cases the results appear to be anomalous, *i.e.* when starting from 2,3-, 1,6-, and 1,7-dihydroxynaphthalenes, in the sense that the coupling constants lack the expected symmetry. With the 1,6- and 1,7-isomers one can justify the result to some extent by suggesting that in each case there is competition between oxidations at a 1- or a 2-position and that the former is favoured. The second hydroxy-group can then be regarded as simply a perturbing substituent. We can rationalise the spectrum from the 2,3-isomer in an analogous way although here the oxygen atoms seem to be in identical positions.

Connection between Radicals from Mono- and Dihydroxynaphthalenes.—Tables 1—3 contain further information which throw light on the apparent anomalies just discussed. In the acidic conditions we would expect the hydroxy-groups to be protonated so that on oxidation say, of 1,5-dihydroxynaphthalene, the initial radical formed would be either A or B.



Once these naphthoxyl radicals are formed we would expect rapid proton exchange with the acidic medium, leading to rapid equilibration of the two isomers. The result of this is that an average coupling constant would be observed for each proton (see Figure 3). This type of

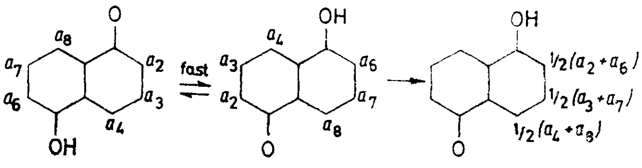


FIGURE 3 Averaging of coupling constants due to rapid proton exchange

---

[7] P. Friedlaender, *Monatsh.*, 1902, **23**, 513.

[8] D. F. Downing and D. Woodcock, *J. Chem. Soc.*, 1958, 531.

situation has been observed in the case of *ortho*- and *para*-semiquinones.[12]

As we have seen from Tables 1 and 2, substituents have but little effect on coupling constants so we might use the coupling constants in the two parent naphthoxyl radicals to estimate the average. These are compared with the splittings observed in Table 4 and the agreement is very convincing.

The so-called anomalous cases can now be seen in a different light. An obvious possibility is that the proton exchange is relatively slow in these cases and that the β-oxygen atoms are effectively protonated for a long time, on the scale of the e.s.r. experiment. What factors are involved here we cannot say exactly at the moment but in the case of the 2,3-isomer it is likely that some sort of complexing takes place with the metal ion present influencing the proton exchange rate. In the other cases, the radicals from 1,6- or 1,7-dihydroxynaphthalene, it appears that an α-naphthoxyl type of radical is preferred. The presence of a 3-sulphonate group does not change this tendency.

TABLE 3

Coupling constants (in mT) in spectra from dihydroxynaphthalenes

1-OH [a] 2-OH	1-OH 2-OH 4-SO$_3^-$	1-OH 3-OH	2-OH 3-OH	1-OH 4-OH	1-OH 5-OH	1-OH 6-OH	1-OH 7-OH [b]	1-OH 7-OH 3-SO$_3^-$ [c]	1-OH 8-OH	1-OH, 8-OH 3-SO$_3^-$ 6-SO$_3^-$	2-OH 6-OH	2-OH 7-OH
	0·20	1·19	0·95	0·325	0·54	1·075	0·95	0·925	0·70	0·70	0·41	0·74
	0·125	0·47	0·475	0·325	0·54	0·875	0·675	0·70	0·70	0·70	0·41	0·74
	0·125	0·36	0·525	0·081	0·35	0·30	0·225	0·25	0·575	0·613	0·24	0·32
	0·05	0·36	0·125	0·081	0·35	0·20	0·10		0·575	0·613	0·24	0·32
		0·11	0·125		0·06	0·20	0·10	0·10	0·125			0·07
			0·125		0·06		0·10	0·10	0·125			0·07
									0·05 [d]	0·05 [d]		

[a] Spectrum very poor. [b] Ref. 9. [c] Ref. 10. [d] Coupling with H-bonded proton characteristic of 1,8-derivatives.[11]

TABLE 4

Comparison of observed and calculated spectra for radicals from some dihydroxynaphthalenes (in mT)

1,3			1,4			1,5		
Calc.	Obs.	Position	Calc.	Obs.	Position	Calc.	Obs.	Position
0·49	0·47	2	0·323	0·325	2	0·38	0·35	2
1·07	1·19	4	0·125	0·08	5	0·035	0·06	3
0·34	0·36	5	0·09	0·08	6	0·54	0·54	4
−0·09	0·11	6						
0·39	0·36	7						
−0·07	0	8						

2,6			2,7			1,8		
Calc.	Obs.	Position	Calc.	Obs.	Position	Calc.	Obs.	Position
0·46	0·41	1	0·75	0·74	1	0·54	0·575	2
0	0	3	0·34	0·32	3	−0·125	0·125	3
0·215	0·24	4	−0·07	0·07	4	0·67	0·70	4

The excellent agreement between calculated and observed splittings shown in Table 4 reinforces our confidence in the assignments of the coupling constants in α- and β-naphthoxyl both from the point of view of their magnitudes and of their signs.

EXPERIMENTAL

E.s.r. Spectra.—The spectra were observed using a Varian E4 spectrometer. The naphthoxyl radicals were obtained using a flow system modified so that the mixing took place virtually in the cavity of the spectrometer. Naphthols were dissolved if possible in a small amount of hot water or, if insoluble, in the minimum amount of ethanol, and the solution diluted with water to a concentration of *ca.* 10^{-3}M. These solutions were run against ceric sulphate (BDH reagent grade) at a concentration of 2×10^{-3}M in 0·5M-sulphuric acid.

Materials.—All naphthols and substituted naphthols used were purified by the usual methods. Their physical constituents agreed well with those of the literature.

[3/1542 *Received, 23rd July,* 1973]

---

[9] H. T. Bucherer and K. Seyde, *J. prakt. Chem.*, 1907, **75**, 249.

[10] J. Boeseken, *Rec. Trav. chim.*, 1939, **58**, 3.

[11] L. H. Piette, M. Okamura, G. P. Rabold, R. T. Ogata, R. E. Moore, and P. J. Scheuer, *J. Phys. Chem.*, 1967, **71**, 29.

[12] I. C. P. Smith and A. Carrington, *Mol. Phys.*, 1967, **12**, 439.