861. *Electron Spin Resonance Spectra of Some Iminoxybenzoquinone Radicals*

By W. M. Fox and William A. Waters

Benzoquinone monoximes can easily be oxidised to oximino free radicals which give well-defined e.s.r. spectra. The analyses of a number of these are reported and discussed: the radical obtained from 4-nitrosoresorcinol corresponds to that from a 1,2- and not a 1,4-benzoquinone.

OUR study of radicals obtained by the one-electron oxidation of benzoquinone monoximes arose from the observation [1] that oxidation of *p*-nitrosodimethylaniline gave rise to a radical of quinonoid type, decidedly more stable than other dimethylamino-radical-cations and giving an e.s.r. spectrum showing a wide triplet splitting due to one nitrogen. Under some conditions (see below) the observed spectrum is actually that of the radical of 4-iminoxy-1,4-benzoquinone (I).

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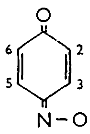
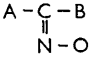
[1] W. M. Fox and W. A. Waters, *J.*, 1964, 6010.

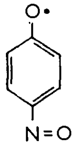
E.s.r. spectra of iminoxy free radicals (II) together with that of (I) were first reported by Thomas [2] after the present work had commenced. More recently several new radicals of type (II) have been reported from this laboratory;[3] all of them characteristically show a very wide triplet splitting (a_N *ca.* 30 œrsted) indicating that the odd electron



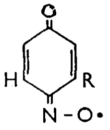
(I)



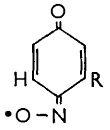
(II)



(III)



(IV)



(V)

is to a high degree localised in the region of the N–O group. The same wide triplet splitting (see Figures 1—5) can be seen in the spectra of iminoxy-benzoquinone radicals and this alone indicates that formulation as nitrosoaryloxy-radicals (III) can be disregarded.

Moreover just as radicals (II) can exist in geometrically isomeric forms, corresponding to those of the oximes from which they have been prepared, so the e.s.r. spectrum (Figure 1) of the 4-iminoxy-1,4-benzoquinone radical (I) shows hyperfine splitting into two duplets, because the hydrogen atoms attached to the nuclear carbon atoms 3 and 5 are not symmetrically placed with respect to the oximino-group; in structure (III) positions 3 and 5 are indistinguishable. Again in all iminoxy-1,4-benzoquinone radicals as yet examined hyperfine splitting indicative of hydrogen atoms at the carbon atoms 2 and 6, adjacent to the C=O group, is too minute to have been detected; in (III) this splitting would be large (*ca.* 6 œrsted [4]). Correspondingly, the spectrum of the radical of 4-iminoxy-3,5-dimethyl-1,4-benzoquinone shows splitting due to two distinguishable but overlapping methyl groups (Figure 2) whilst those of the radicals from 4-iminoxy-2,6-dimethyl-1,4-benzoquinone, 4-iminoxy-2-methyl-1,4-benzoquinone, and 2-chloro-4-iminoxy-1,4-benzoquinone are very like that of radical (I).

Mono-3-substituted 4-iminoxy-1,4-benzoquinone can exist in geometrically isomeric forms and consequently isomeric free radicals of types (IV) and (V) can exist provided that the substituent R is not so large that the *cis*-structure (IV) cannot be a stable molecule. An indication of the existence of geometrically isomeric radicals (IV) and (V) is afforded by their e.s.r. spectra, which prove to be unsymmetrical, and correspond to a mixture of radicals having slightly different median g values. This lack of symmetry is shown in the spectrum (Figure 3) from 3-chloro-4-iminoxy-1,4-benzoquinone and also in those of the 3-fluoro and 3-methyl analogues, but is not so evident in that (Figure 4) from the 3-bromo-compound, for which the *cis*-isomer (IV; R = Br) could not have a stable planar structure on account of steric hindrance.

We suggest that the spectrum of Figure 4 consists of three groups of quintets and can rationally be ascribed to the splitting of a quartet of lines, owing to interaction with a bromine atom (nuclear spin $I = 3/2$) into doublets, due to one hydrogen, for the intensity distribution is *ca.* 1,2,2,2,1. Thus if (V; R = Br) is the true structure of the radical that gives the e.s.r. spectrum of Figure 4 the splitting constant for the *cis*-hydrogen (at 5) and for the bromine at 3 are both about 3·7 œrsteds. This appears to be the first instance in which hyperfine splitting due to a bromine atom has possibly been recognised in the e.s.r. spectrum of an aromatic radical.

The splitting constant for the hydrogen atom corresponds to the larger doublet splitting of Figure 1, in accordance with the conclusions of Gilbert, Norman, and Price [3] who assign the largest proton splitting in rigid iminoxy radicals to hydrogens spatially close to the oxygen of the iminoxy-group.

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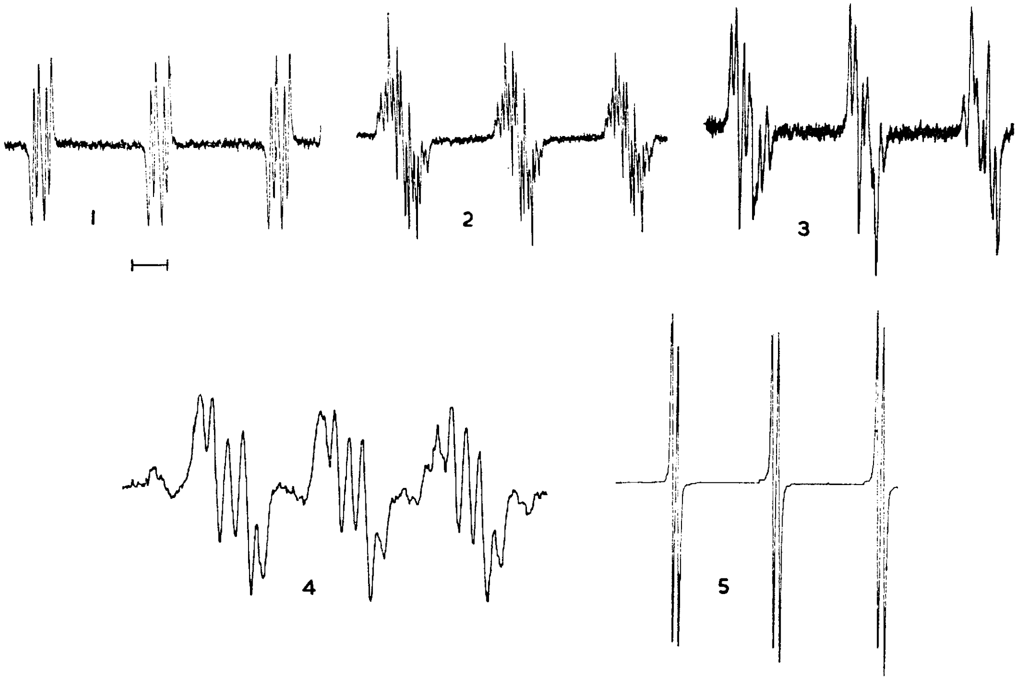
[2] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 1446.
[3] B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 1964, 234.
[4] T. J. Stone and W. A. Waters, *J.*, 1964, 213.

Some support for our view that in 4-iminoxy-1,4-benzoquinone radicals *cis*-hydrogen atoms [*i.e.*, 3 in (I) and 5 in (V)] give hyperfine splittings of 3·5—4 œ. is afforded by a tentative analysis of the spectrum (Figure 3) given by 3-chloro-4-iminoxy-1,4-benzoquinone. A big doublet, of about 4 œ. splitting can be noticed in each of the triplicated groups of lines, together with groups of weaker lines with about half this degree of splitting. We suggest that the big doublet is due to the *cis*-hydrogen atom in the more stable isomer (V; R = Cl) in which the chlorine is so far away from the N–O• oxygen that its interaction is extremely small, and that the group of weak lines is due to the presence of a smaller amount of the isomer (IV; R = Cl), for which the hydrogen splitting could be 1·5—2 œ. and the chlorine splitting ($I = 3/2$) of corresponding magnitude owing to its proximity to the N–O• oxygen. A chlorine splitting constant of this magnitude has been observed for the 4-chloro-*m*-benzosemiquinone radical.[5] For the poorly resolved spectrum of 3-fluoro-4-iminoxy-1,4-benzoquinone tentative splitting values are given in the Table and accord with the general finding that the splitting constant for fluorine is 2—3 times that for a similarly placed hydrogen.



Electron spin resonance spectra of iminoxy-benzoquinone radicals
(The marked distance on each spectrum = 10 œrsteds.)

1. Radical from 4-iminoxy-1,4-benzoquinone
2. Radical from 3,5-dimethyl-4-iminoxy-1,4-benzoquinone
3. Radicals from 3-chloro-4-iminoxy-1,4-benzoquinone
4. Radical from 3-bromo-4-iminoxy-1,4-benzoquinone
5. Radical from 1-iminoxy-4-methoxy-1,2-benzoquinone

1,2-*Benzoquinone Monoximes*.—4-Nitrosoresorcinol (VI) can be written in either 1,4- or 1,2-quinonoid forms. Thomas[2] assigned to the corresponding iminoxy-radical, which gives an e.s.r. spectrum showing a well-defined triplet of doublets corresponding to a_N = 28 œ. and a_{C-H} = 1·7 œ, the 1,4-quinonoid structure (VII), but we consider that the true structure is (VIII) since (i) the a_{C-H} splitting corresponds to one *ortho trans* and not an *ortho cis* hydrogen as in (VIII) (see above), (ii) an almost identical e.s.r. spectrum (Figure

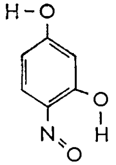
[5] T. J. Stone and W. A. Waters, *J.*, 1964, 4302.

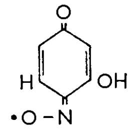
Splitting constants for iminoxy-benzoquinone radicals

Radical source		Splitting constants (œrsteds ±0·4)			
		$a_{\text{C-H}}$ (3,5)		$a_{\text{C-R}}$ (3,5)	
	a_N	*cis*	*trans*	*cis*	*trans*
4-Iminoxy-1,4-benzoquinone	33·3	3·9	1·4	—	—
	(33·0)	3·7	(1·2)		
3, 5-Dimethyl- ,, ...	32	—	—	3	1
2,6-Dimethyl- ,, ...	32·4	(Low-stability radical)			
2-Methyl- ,, ...	32·2	4	2	—	—
3-Methyl- ,, ...	31·5	4	—	—	2?
(2 isomers)	31·5	—	2?	2?	
2-Chloro- ,, ...	32·3	3·3	1·4	—	—
3-Chloro- ,, ...	32	4?			
(2 isomers)	34?		1·5?	2	
3-Bromo- ,, ...	33·5	3·7	—	3·7?	—
3-Fluoro- ,, ...	33—34	3·9?	—		3—4?
(2-isomers)		—	1·4?	8—10?	
1-Iminoxy-1,2-benzoquinone					
4-Hydroxy- ,, ...	28·4		1·8		—
	(27·9)		(1·7)		
4-Methoxy- ,, ...	28·3		1·7		

The queried assignments are tentative suggestions only.
[The figures in parentheses are those of Thomas (ref. 2).]

5) is given by the radical obtained from 5-methoxy-2-nitrosophenol (IX), the main nitrosation product of resorcinol monomethyl ether, and (iii) the Table shows that all the iminoxy-1,4-benzoquinone radicals have larger a_N splitting constants (32—34 œ.). The orientation of the starting product (IX) follows from the successive work of Henrich and Rhodius [6] who reduced it to an amine from which by acylation and subsequent heating they obtained


(VI)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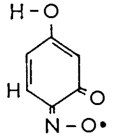
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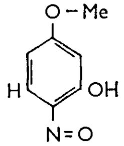
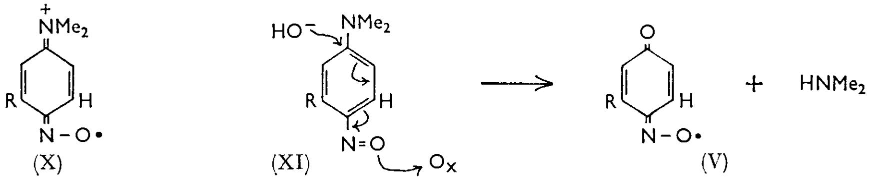

(IX)

both methyl and phenyl methoxybenzoxazoles, and of Hodgson and Clay [7] who oxidised it to 5-methoxy-2-nitrophenol which they also made from 3-chloro-4-nitroanisole. The solubility of (IX) in benzene was noted as indicative of internal hydrogen bonding.

Radicals from NN-*Dimethyl*-p-*nitrosoaniline and its Analogues*.—When *p*-nitrosodimethylaniline, *p*-nitrosodiethylaniline, or their 3-halogenated analogues were oxidised by ceric sulphate in the presence of an excess of either hydrochloric or sulphuric acid then only e.s.r. spectra showing triplets (a_N = 33·5 œ.) about 20 œ. broad could be obtained. The resolution of the spectrum from dimethyl-*p*-nitrosoaniline was not improved by buffering the oxidation mixture to pH 6 with sodium acetate in the hope of increasing the rate of oxidation in dilute solution, but a sharp spectrum was obtained by oxidising dimethyl-*p*-nitrosoaniline in an excess of alkali with ceric sulphate and this was identical with that (Figure 1) of the 4-oximino-1,4-benzoquinone radical (I).


(X) (XI) (V)

We suggest that the broad triplet spectra are those of radical-cations (X) in which the multiplet fine structure that could be associated with the dimethylamino-group leads to

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[6] F. Henrich and O. Rhodius, *Ber.*, 1902, **35**, 1475.
[7] H. H. Hodgson and M. Clay, *J.*, 1929, 2775.

the line broadening. The free bases (XI) are known to be hydrolysed easily by warm alkali, and it is probable that electron removal from the nitroso-group by the oxidant accelerates this reaction.

EXPERIMENTAL

Materials.—The substituted quinone monoximes were all prepared from the corresponding phenols, or tertiary amines, by the general methods of nitrosation described by Hodgson and his colleagues [8] and were then crystallised from aqueous ethanol, acetone, or benzene to satisfactory melting point.[9] The decomposition to oximino-quinone radicals of the radicals obtained from the *p*-nitroso-derivative of tertiary amines was, in alkali, so rapid that these nitrosated amines often provided the most convenient materials from which to obtain particular oximino-quinone radicals.

The radicals were obtained by oxidising aqueous methanolic solutions (10^{-2}—10^{-3}M) of the quinone monoximes by a slight excess of ceric sulphate in dilute sulphuric acid using the standard flow technique developed in this laboratory.[1,3,4] The radicals were in general so stable that slow rates of flow could be used.

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[8] H. H. Hodgson and D. E. Nicholson, *J.*, **1939**, 1808 (and earlier references therein).

[9] Beilstein, " Handbuch," Vol. VII (and supplements).