In situ Electrochemical Reduction of Some Naphthazarin Derivatives. An Electron Spin Resonance and INDO Study

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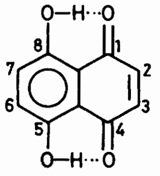
Twelve naphthazarin derivatives were reduced electrochemically giving rise to the corresponding semiquinone anion radicals. Their e.s.r. spectra were recorded *in situ* and their hyperfine coupling constants and *g* factor were evaluated. For this purpose, SCF INDO MO calculations were performed in order to obtain an approximate value of the different coupling constants. The structure of these radicals was also deduced from these calculations, showing a strong linear O–H–O hydrogen bond, free rotation of the methyl group, and the absence of hyperfine interactions in the methoxy-group.

SEVERAL papers have been devoted to an e.s.r. study of naphthazarin radical anion.[1-5] To our knowledge, however, only a paper by Piette *et al.*[6] is concerned with the radical anions of chloro- and methoxy-derivatives of naphthazarin. Piette *et al.* obtained the corresponding radical anions by electrochemical reduction of the parent quinone, but their assignments of the hyperfine splitting constants in the more complex cases were purely speculative.

In the present work, we have carried out the electrolysis of various chloro, methoxy, and methyl derivatives (1)—(12) of naphthazarin at controlled potentials inside a resonance cavity. When assignments were not obvious we used the INDO SCF MO method to obtain the electron spin density distribution for each proton and the corresponding hyperfine splitting constants.

The e.s.r. signals obtained after degassing the solution of the naphthazarin derivatives in *NN*-dimethylformamide, before and after electrolysis, are analysed and the corresponding hyperfine splitting constants reported.



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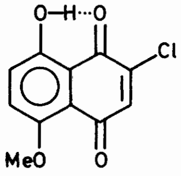

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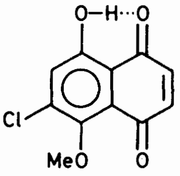

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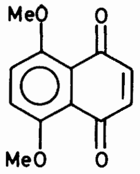

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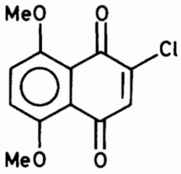

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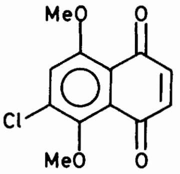

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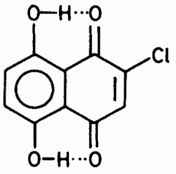

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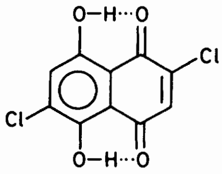

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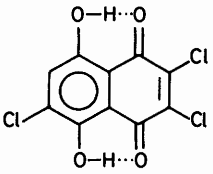

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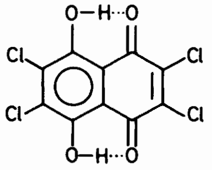

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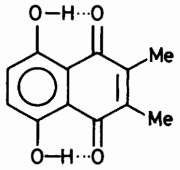

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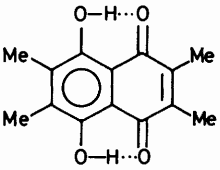

(12)

EXPERIMENTAL

Materials.—Compounds (2) and (3) were obtained by selective methylation of 2-chloronaphthazarin with MeI, according to the previously described procedure.[7] Compound (4) was obtained by complete methylation of naphthazarin with MeI.[7] Compounds (5) and (6) were obtained by complete methylation of 2-chloronaphthazarin. The chlorine and methyl derivatives were synthesised using the reported procedure described in refs. 8 and 9, respectively. The compounds were purified by sublimation under vacuum; their physical constants were checked and agree with those given in the literature.

Electrolysis.—Electrochemical reduction was carried out by means of an electrochemical flat quartz cell placed inside the microwave cavity of an *X*-band spectrometer as described in ref. 10. The complete description of this cell can be obtained in ref. 11. The following experimental conditions were used for electrochemical reductions: *NN*-dimethylformamide was the solvent, tetraethylammonium perchlorate (100 mM) the supporting electrolyte, gold the cathode, and a platinum wire gauze the anode.

To obtain e.s.r. spectra with high resolution, we prepared dilute solutions of the studied compounds (1mM) and used very low microwave power (2—5 mW). The solutions were degassed for 30 min to avoid the scavenging effect of dissolved oxygen, the solubility of which in this solvent gives rise to concentrations similar to those used for quinones. During electrolysis an inert atmosphere was maintained.

Cyclic voltammetry was previously carried out in order to apply a suitable potential.

Spectra.—Spectra were recorded with a Varian E-3 spectrometer provided with a 100 kHz field modulation. The g factor was obtained by means of relation (1) where the

$$g = 0.714\,484\ \nu\ (\mathrm{MHz})/H(\mathrm{G}) \qquad (1)$$

magnetic field H (in Gauss) at the sample was calibrated with the e.s.r. signal of Fremy's salt (5mM) whose magnetic parameters, at room temperature in an aqueous sodium carbonate (100mM) solution, are g_{iso} 2.005 590 [12] and a_{N} 13.0 G.[13]

The microwave frequency ν (in MHz) was measured with a high-precision frequency-meter. For complex spectra the hyperfine coupling constants were assigned by comparing the experimental spectra with those simulated by a computer, assuming a Lorentzian line shape. The ERSPEC program was used.[14]

THEORY

Theoretical calculations were performed to obtain the electron spin density distribution and the corresponding theoretical coupling constants in order to make an unambiguous assignment of the hyperfine coupling constants of the experimental spectra.

Method.—In the present calculations we have used the SCF INDO MO method in the unrestricted Hartree–Fock scheme. In this UHF scheme, the isotropic hyperfine coupling constant a_I, due to a magnetic nucleus I, is related to the electron spin density ρ_{sIsI} by the expression (2) [15]

$$a_I = \left\{\frac{4\pi}{3} g\beta\gamma_I\hbar(S_z)^{-1}|\phi_{sI}(R_I)|^2\right\}\rho_{sIsI} \qquad (2)$$

where g is the electron g factor, β is the Bohr magneton, γ_I is the gyromagnetic ratio of the nucleus I, $|\phi_{sI}(R_I)|^2$ is the density of the valence s orbital of the atom I evaluated at the nucleus and ρ_{sIsI} is the unpaired electronic population of the valence s orbital of atom I.

We have used the INDO method in its original parametrisation [16] for the elements C, H, and O. For the chlorine atom the inclusion of the d orbitals has been considered following the suggestion that the role of these orbitals could be important.[17-19] The program GEOMO [20] was used. The constant term in the bracket, for each type of magnetic nucleus, was obtained by Pople [16] choosing $\phi|_{sI}(R_I)|^2$ so that it gives a best fit between the observed a_I and calculated ρ_{sIsI} in a least-squares sense. Spin annihilation is not included in the unrestricted wave function and does not introduce any serious errors.[21]

Geometrical Input Data.—The standard C–C ring bond length was considered to be 1.397 Å. The bond length for the methoxy-group was taken from electron diffraction data for anisole.[22] For the C–O bond, an optimisation of the C–O distance was performed, by looking for the minimum in the energy–distance curve in order to avoid the deficiencies of INDO hyperfine splitting in the case of semiquinones.[23] The C–Cl bond length was taken from ref. 24. The different bond lengths used are given in Table 1.

In the case of methoxy-derivatives, we previously made a conformational analysis of the torsional barrier of the methoxy-group.[25] In this study the calculation shows the important role of the d orbitals in the chlorine orbital basis set. The results indicate a planar configuration of the methoxy-group with respect to the naphthalene skeleton.

TABLE 1

Bond lengths (Å) of the naphthazarin derivatives

C–C (ring)	1.397
C–O	1.360 *
C–H (ring)	1.090
O–H	0.90
C–Cl	1.68
$C-CH_3$	1.52
$C-OCH_3$	1.363
$O-CH_3$	1.419
C–H (MeO)	1.100

* Optimised for naphthazarin.

RESULTS AND DISCUSSION

The mechanism of the electrochemical reduction of the studied compounds is the well known redox process (3).

$$Q + e^- \rightleftharpoons Q^{-\cdot} \qquad (3)$$

The radical anions so obtained are extremely stable compared to the corresponding radicals obtained by chemical methods. We have obtained the same radicals by chemical methods, but the spectra change with time in several cases, due to spurious reactions.

Some representative experimental spectra of the radical anions obtained are given in Figures 1—3 for compounds (2), (8), and (12), respectively.

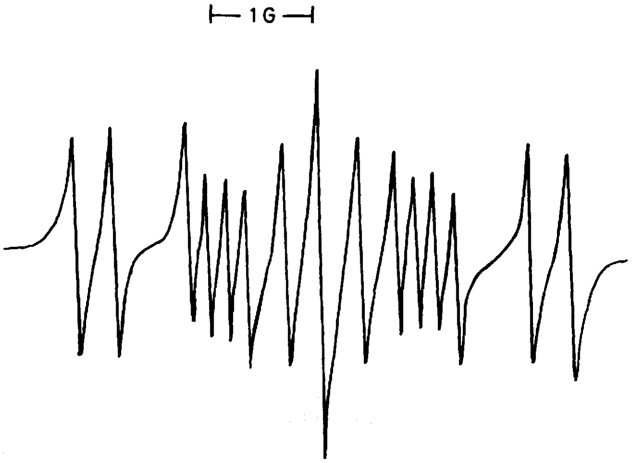

FIGURE 1 E.s.r. spectrum of radical (2)

In those cases where it was difficult to assign hyperfine splitting constants, namely for radicals derived from compounds (2), (3), (5), and (6), theoretical calculations were performed according to the method of Pople *et al.* previously discussed. The theoretical coupling constants obtained are given in Table 2. Although the agreement between calculated and experimental values is not as good, these calculations allow a reasonable assignment to be made of the experimental hyperfine splitting constants.

For all the semiquinone radical anions studied in this work, Table 3 shows the experimental hyperfine coupling constants a_I and the g factors. For the discussion, the different radical anions may be classified into three groups: (a) chloronaphthazarin methyl ether derivatives; (b) chloronaphthazarin derivatives; and (c) methylnaphthazarin derivatives.

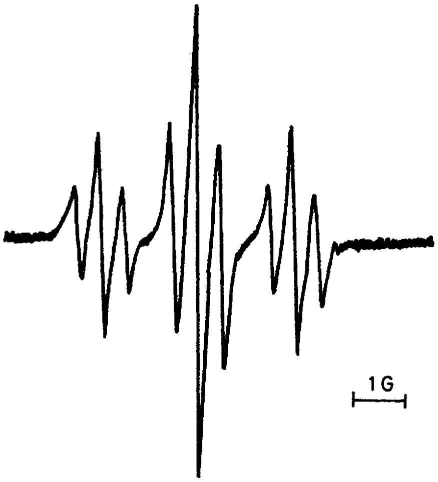

FIGURE 2 E.s.r. spectrum of radical (8)

(a) *Chloronaphthazarin Methyl Ether Derivatives*.—Analysis of the spectra indicates a hyperfine splitting for the protons of the methoxy-group. This result is not in complete agreement with that reported by Piette *et al.*[6] for several methoxynaphthazarins. An explanation for this nil spin density at the proton methoxy-group could be a lack in the planarity of this group. However, INDO calculations (with *s*, *p*, and *d* orbitals for chlorine)[25] indicate a strong Cl/MeO stabilising energy which gives rise to a coplanar conformation of the methoxy-group with respect to both rings. A recent paper by Anderson *et al.*[26] confirms this result for other methoxy-derivatives. On the other hand, the hyperfine coupling constants of hydroxy protons attached to the 5- and 8-positions indicate a low spin density, whereas the other ring positions present much greater hyperfine splitting. This fact explains why for non-hindered methoxy-derivatives, Piette *et al.* obtained an appreciable hyperfine splitting for the methoxy-protons in the 2-, 6-, and 7-positions of naphthazarin and why we do not obtain hyperfine splittings for the methoxy-protons in the 5- and 8-positions.

TABLE 2

Theoretical hyperfine coupling constants (G)

Compd.	H(2)	H(3)	H(6)	H(7)	H(OH)	H(OMe)
(2)		5.17	1.47	−0.76	0.73	0.01
(3)	−2.06	4.84		−0.94	0.69	0.01
(5) [a]		−0.75	0.65	−0.28		0.02
(6) [a]	−0.99	−1.12		−0.21		0.02

[a] In these radicals the INDO calculation was realised with the fluorine atom. In the case of chlorine the basis set required would have exceeded our computer availability. The results are quantitatively very poor, although the relative hyperfine splitting values are consistent with those of similar radicals.

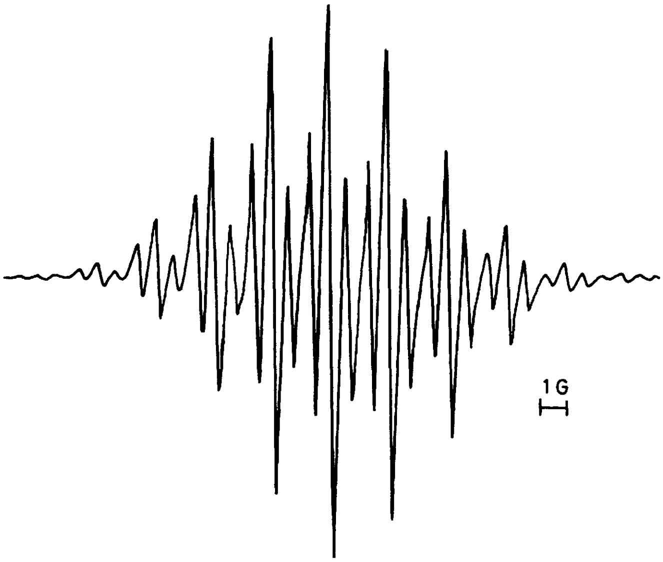

FIGURE 3 E.s.r. spectrum of radical (12)

In all chloro-methoxy-derivatives studied, the radical anions were also obtained after degassing the solution without any electrolysis. We suspect that this fact is due to the formation of a charge transfer complex with the solvent. The other radical is not observed in our experimental conditions, because the concentration of the parent molecule (DMF) is several times greater than that of the radical cation, thus leading to exchange broadening.[27] The methoxy-group and the chlorine

TABLE 3

Experimental hyperfine coupling constants (G) and *g* factors

Compound	$-E$/mV [a]	H(2)	H(3)	H(6)	H(7)	H(OH)	H(CH_3)	*g*
(1) [b]	290	2.39	2.39	2.39	2.39	0.52		2.004 10
(2) [c]	700		2.11	1.35	1.14	0.41		2.004 62
(3) [c,f]	345	1.93	4.07		1.27	0.49		2.004 60
(4) [c]	740	2.85	2.85	1.09	1.09			2.004 78
(5) [c]	670		3.15	1.12	0.92			2.004 80
(6) [c]	680	2.49	2.90		1.20			2.004 43
(7) [b,c]	150		3.00	1.88	1.61	0.53		2.004 18
(8) [c]	50		2.18		2.18	0.53		2.004 37
(9) [c,d]	50				1.70	0.40		2.004 35
(10) [b,c,e]	250							2.004 83
(11) [f]	400			2.60	2.60	0.61	1.90	2.004 26
(12)	800					0.64	2.10	2.004 03

[a] *versus* Saturated calomel electrode. [b] E.s.r. spectrum reported previously: radical (1) in refs. 1—6; radicals (7) and (10) in ref. 6. [c] Before electrolysis, the degassed solution gives an e.s.r. signal. [d] The simulated spectrum is not in complete agreement with the experimental one. Speculative assignment of hyperfine splittings and *g* factor has therefore been made. [e] No hyperfine interaction observed; a single very broad line obtained. [f] The corresponding spectra were previously obtained and have been published elsewhere: radical (3) in ref. 25; radical (11) in ref. 29.

atom withdraw electrons from the ring, giving rise to an electron acceptor whilst the *NN*-dimethylformamide, which possesses a lone pair, can act as an electron donor. The e.s.r. signals thus obtained are not very intense and an incompletely resolved hyperfine structure is always recorded. Completely resolved spectra were obtained after electrolysis.

(b) *Chloronaphthazarin Derivatives.*—The spectra of the compounds (7) and (8) are completely resolved. However, the trichloro-derivative (9) gives a partially resolved spectrum and for the tetrachloronaphthazarin (10) only a single broad line is observed. In this last case, Piette *et al.*[6] obtained the same result.

As in the case of compounds (2)—(6) the four chloronaphthazarins give rise to the corresponding radical anion after degassing their solutions in DMF, with an e.s.r. signal intensity which increases with the number of chlorine substituents. The e.s.r. signal is, however, as in the case of the chloro-methoxy-derivatives, less intense than that obtained by electrochemical reduction and no well defined hyperfine structure can be recorded.

(c) *Methylnaphthazarin Derivatives.*—In the two cases studied, (11) and (12), the equivalence of all the methyl protons and of the two hydroxy protons is observed, indicating free rotation of the methyl protons and a symmetric O · · · H · · · O hydrogen bond. This last result is also observed in compounds (1) and (7)—(10). By chemical reduction of compounds (8), (11), and (12), in strong alkaline medium, the same e.s.r. spectra are obtained, which fact indicates that this hydrogen bond is very strong. These results are analogous with those observed for naphthazarin (1) and 1,4-dihydroxy-9,10-anthrasemiquinone radical anion.[28] Figure 4 shows the INDO potential energy curves corresponding to the O · · · H · · · O and Cl · · · O · · · H interactions. The calculations were performed for the complete molecule with the molecular geometry fixed except for the hydrogen atom, for which both the distance $d(\mathrm{H{-}O_1})$, and the angle θ were varied. The curve displays a 'minimum of minima ' when the distances, $d(\mathrm{H{-}O_1})$ and $d(\mathrm{H{-}O_2})$, between hydrogen and the two oxygen atoms are equal (d 1.21 Å). The calculations also indicate, as observed experimentally, a strong O · · · H · · · O hydrogen bond with a linear OHO arrangement, the H atom being in the middle of the O · · · O segment. The result is a static view of the problem and is not in contradiction with the dynamic point of view in which the tunnel effect was invoked.

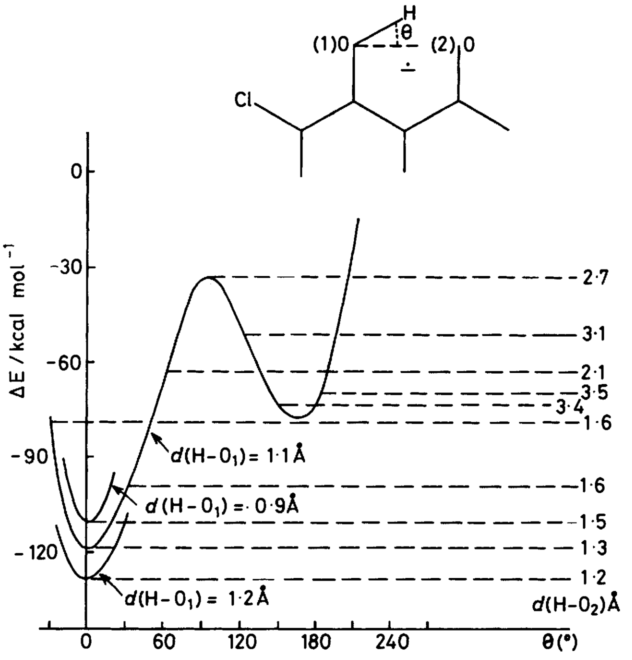

FIGURE 4 Theoretical potential energy as a function of the angle θ for different O · · · H distances of the O · · · H · · · O hydrogen bond

The free rotation of the methyl group is an interesting point because, in both radicals, the methyl groups are sufficiently close together so that they hinder each other's free rotation. We have previously made a study of this restricted rotation [29] and the large residual energy of the lowest hindered states and the large population of the coupled rotation states are invoked to explain the proton equivalence observed.

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