A Linear Dichroism and Cyclic Voltammetric Study of Substituted Naphthoquinones and an ESR Investigation of the Corresponding Anion and Cation Radicals

Giovanni Gottarelli, Marco Lucarini, Gian Franco Pedulli, and Gian Piero Spada
Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Via S. Donato 15, I-40127 Bologna, Italy
Sergio Roffia
Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy

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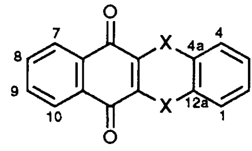
We have carried out an investigation on benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-dione (**1**) and benzo[*b*]naphtho[2,3-*e*][1,4]dithi-in-6,11-dione (**2**) by absorption and linear dichroism spectroscopy and cyclic voltammetry. The corresponding anion and cation radicals have been produced and studied by ESR. From these studies it has been concluded that the main contribution to the low-energy absorption for both compounds is an intramolecular charge-transfer transition which is polarized along the short molecular axis.

In a previous paper,[1] we showed that the long wavelength absorption for naphthoquinones bearing two methoxy substituents in positions 2 and 3, is polarized along the short molecular axis. This absorption band is likely to be due to an intramolecular charge-transfer (ICT) type transition from the donor methoxy groups to the quinoid moiety.

Dyes with short-axis polarized transitions are uncommon and might be used in liquid-crystal display technology as they produce two different colours depending on the dye molecule's orientation.[2]

In order to obtain low-energy CT transitions the molecule must show low-ionization potential and high electron affinity. We have, therefore, synthesized the two molecules benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-dione (**1**) and benzo[*b*]naphtho[2,3-*e*][1,4]dithi-in-6,11-dione (**2**). These compounds, as well as containing a donor–acceptor system, are considerably elongated, a property required in order to obtain a good alignment in liquid-crystalline matrices.



(**1**) ; X = O
(**2**) ; X = S

Furthermore, (**1**) and (**2**) not only contain the quinone moiety, which is known to give rise to very stable anion radicals, but a dioxine or dithi-ine group which is easily oxidized to give stable cation radicals. These compounds should, in principle, easily provide both types of radicals, a property which does not often occur in organic molecules.

We report here a spectroscopic, cyclic voltammetric, and ESR investigation of (**1**) and (**2**). The three techniques might at first sight seem unconnected, however, the absorption and linear dichroism spectra are determined by the energy difference of the HOMO and LUMO and by their symmetry properties; electrochemistry provides information on the energy properties of these two orbitals, and the ESR technique allows us to elucidate the spin distribution and, thus, the symmetry of the same orbitals.

Results and Discussion

Spectroscopic Studies.—The absorption spectra of (**1**) and (**2**) are shown in Figure 1 and the linear dichroism (LD) spectrum of (**2**) in the nematic phase ZLI1167 (a mixture of alkylcyanobicyclohexyl derivatives) is shown in Figure 2.

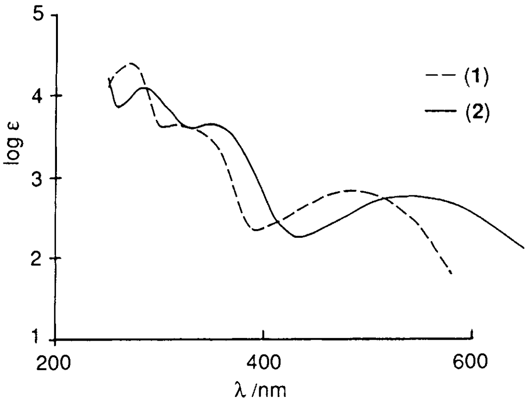


Figure 1. Absorption spectra of (**1**) and (**2**) in a 5 × 10^{-4} mol dm^{-3} chloroform solution.

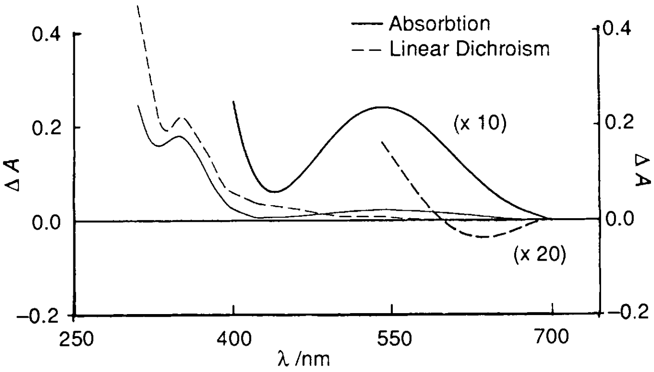


Figure 2. Absorption and LD spectra of (**2**) dissolved in the liquid crystalline matrix formed by the nematic phase ZLI1167. Spectra were recorded at 40 °C with path length 0.001 cm.

Linear dichroism is defined as the difference in absorbance for two perpendicularly polarized light beams due to the orientation of the molecule. The LD spectroscopic technique is useful in detecting and assigning the polarization of electronic transitions, provided that the orientation of the molecule with respect to a laboratory framework is known.[3] Here we use, as an

Table 1. Oxidation and reduction potentials of compounds (**1**) and (**2**) measured in ACN *vs.* SCE and ICT absorption maxima in eV.

	Compound	
	(**1**)	(**2**)
$E_{\frac{1}{2}}$(ox)/V	1.75	1.40
$E_{\frac{1}{2}}$(red,1)/V	−0.59	−0.48
$E_{\frac{1}{2}}$(red,2)/V	−1.22	−1.12
E_{ICT}	2.55	2.30

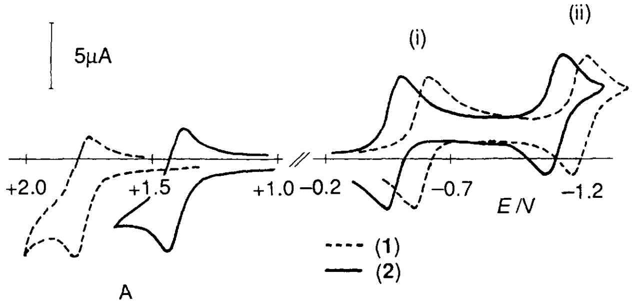


Figure 3. Cyclic voltammetric curves at 25 °C for 5 × 10^{-4} mol dm^{-3} ACN solutions of (**1**) and (**2**) in 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$. Working electrode: Pt; sweep rate: 0.2 Vs^{-1}.

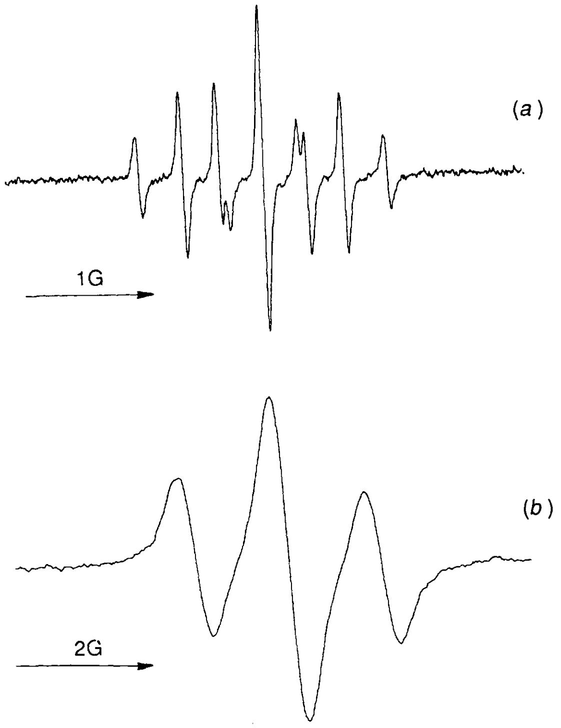


Figure 4. Room temperature ESR spectra of the radical anion (*a*) and cation (*b*) from (**2**) in DMSO and CF_3CO_2H respectively.

orientating matrix, a nematic liquid-crystalline phase whose orientation is controlled by surface effects.[1,4]

The band observed in unsubstituted 1,4-naphthoquinone between 280 and 400 nm has been analysed in terms of two main transitions: a 'benzenoid' one which is long-axis polarized and a 'quinoid' one which is short-axis polarized; the two transitions largely overlap but the 'benzenoid' one is at a slightly lower energy. Electron-donating substituents in positions 2 and 3 displace the 'quinoid' transition to lower energy while the 'benzenoid' transition is unaffected; when two methoxy groups in positions 2 and 3 are present, one observes a crossing of the two transitions which become well separated.[1]

Also for (**1**) and (**2**) two distinct broad absorptions are present down to 300 nm. In derivative (**2**) the low energy one (at *ca.* 540 nm) has a negative LD and that at *ca.* 350 nm a positive LD.* As this elongated molecule is likely to be aligned with its major axis parallel to the nematic director, transitions polarized along this axis display positive LD, and transitions polarized perpendicularly to this axis, negative LD.[4] The low-energy band, therefore, corresponds to a short-axis polarized transition and the one at *ca.* 350 nm to a long-axis polarized one.

This trend is similar to that recorded for 2,3-dimethoxy-naphthoquinone, the only relevant difference being the strong bathochromic shift due to the sulphurated substituents. It therefore seems clear that for derivative (**1**), whose LD spectrum could not be recorded owing to its very low solubility in the nematic matrix, the first absorption corresponds to the 'quinoid' transition and the second to the 'benzenoid' one. It will be clear from the discussion below that the 'quinoid' transition has a large intramolecular charge-transfer character.

Electrochemical Results.—Figure 3 shows the cyclic voltammetric curves recorded for (**1**) and (**2**). In the potential range examined, both compounds exhibit one oxidation (A) and two reduction peaks (i and ii) which, according to the usual criteria, appear to be due to one-electron diffusion controlled reversible processes.

These can be described in terms of reactions (1–3).

$$\mathbf{(1)}\ [\mathbf{(2)}] \rightleftharpoons \mathbf{(1)}^{+\bullet}[\mathbf{(2)}^{+\bullet}] + \mathrm{e} \tag{1}$$

$$\mathbf{(2)}\ [\mathbf{(2)}] + \mathrm{e} \rightleftharpoons \mathbf{(1)}^{-\bullet}[\mathbf{(2)}^{-\bullet}] \tag{2}$$

$$\mathbf{(1)}^{-\bullet}[\mathbf{(2)}^{-\bullet}] + \mathrm{e} \rightleftharpoons \mathbf{(1)}^{2-}[\mathbf{(2)}^{2-}] \tag{3}$$

The half-wave potentials $E_{\frac{1}{2}}$ for the various processes are reported in Table 1 as the average between the anodic and the cathodic peak potentials.

ESR Results.—The electrochemical studies show that compounds (**1**) and (**2**) can be reversibly reduced and oxidized at low potentials to the corresponding radical anions and cations respectively, this suggests that these paramagnetic species should be easily detectable by ESR spectroscopy, thus allowing the determination of the spin-density distribution in the highest occupied and lowest unoccupied MOs. These data, together with MO calculations, may provide the shape and symmetry of the two molecular orbitals involved in the charge-transfer transition.

The radical anions were obtained by treatment of these compounds with potassium t-butoxide in DMSO solutions, and gave rise to intense ESR spectra consisting of a triplet of triplets (see Figure 4), which, as will be discussed later, are due to the two couples of equivalent protons of the naphthoquinone moiety. In the case of the radical from (**1**), each line shows an additional hyperfine structure from the protons of the

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* Owing to the low solubility of compound (**2**) and, hence, to the low absorbance in the spectroscopic region of interest, it is impossible to obtain a decomposition of the absorption spectrum into the two components, long- and short-axis polarized, with the treatment described in ref. 3. Only a qualitative analysis of the LD spectrum is then possible. The fact that the negative maximum is considerably displaced to lower energy with respect to the absorption spectrum is likely to be due to the overlap with the stronger positive dichroism corresponding to the second absorption.

Table 2. ESR parameters (hfs constants in Gauss = 10^{-4} Tesla) for the cation and anion radicals of (**1**) and (**2**).[a]

	Radical			
	$(\mathbf{1})^{+\bullet}$	$(\mathbf{2})^{+\bullet b}$	$(\mathbf{1})^{-\bullet}$	$(\mathbf{2})^{-\bullet}$
$a(H_{1,4})$	0.48	<0.3	0.036	—
	(−0.42)	(−0.16)	(0.028)	(0.015)
$a(H_{2,3})$	1.33	1.57	0.095	—
	(−1.21)	(−0.78)	(−0.063)	(−0.032)
$a(H_{7,10})$	—	—	0.38	0.34
	(0.017)	(0.035)	(−0.28)	(−0.29)
$a(H_{8,9})$	—	—	0.77	0.62
	(−0.065)	(−0.032)	(−0.94)	(−0.87)
g	2.0040	2.0085	2.0048	2.0047
Solvent	H_2SO_4	H_2SO_4	DMSO	DMSO

[a] Hfs constants calculated from computed spin densities (Q = −25) are reported in parenthesis. [b] In CF_3CO_2H, $a(H_{2,3})$ 1.43 G and g 2.0086.

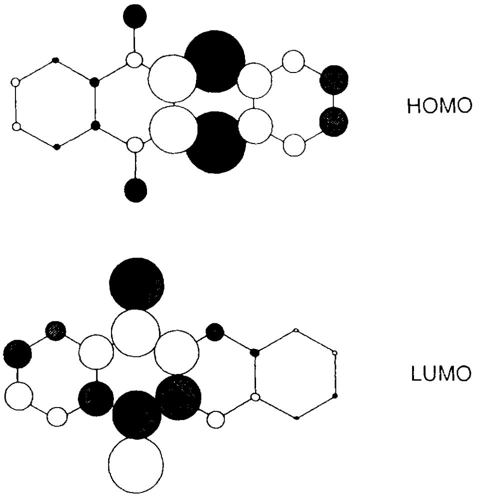

Figure 5.

benzodioxine group, which could be resolved by numerical differentiation of the recorded second derivative spectrum. The measured spectroscopic parameters are reported in Table 2.

The radical cations were produced by reacting (**1**) and (**2**) with sulphuric acid (98%) or by photolyzing inside the ESR cavity degassed solutions of the substrates in trifluoroacetic acid containing mercury(II) trifluoroacetate.[5] Also on oxidation we obtained intense ESR spectra consisting of a triplet of triplets for the radical cation from (**1**) and of a broad triplet for the radical cation from (**2**) (see Figure 4). The large linewidth of the latter spectrum is probably due to the combined effect of unresolved hyperfine structure and random modulation of the g-tensor by the molecular tumbling in solution. The line broadening due to the latter effect is expected to be quite significant given the large deviation of the g-factor from the free-spin value, which is usually associated with a strong anisotropy of the g-tensor.[6]

The assignment of the proton splittings was made on the basis of McLachlan[7] spin-density calculations. The coupling constants obtained from the computed spin densities, ρ, by means of the McConnell relation,[8] $a_H = -25\rho$, reported in parentheses in Table 2, are in good agreement with the experimental values. We may then be confident that these calculations also correctly predict the spin densities on the molecular positions which are not directly bonded to hydrogen atoms. Figure 5 graphically shows the shapes of the highest occupied and lowest unoccupied Hückel orbitals of compound (**2**), with radii proportional to the coefficients of the p_z atomic orbitals, the solid and open circles referring to coefficients having opposite sign.

From these data it is inferred that the unpaired electron is essentially delocalized on the naphthoquinone moiety in the radical anions and in the benzodioxine or benzodithi-ine moieties in the radical cations of (**1**) and (**2**), *i.e.* in the LUMO and HOMO of the parent compounds. In fact the spectral parameters of both $(\mathbf{1})^{-\bullet}$ and $(\mathbf{2})^{-\bullet}$ closely resemble those of the naphthoquinone radical anion $(NQ)^{-\bullet}$ produced under the same conditions; thus $a(H_{7,10})$ 0.38, 0.34 (0.31), $a(H_{8,9})$ 0.77, 0.62 (0.63 G), and g 2.0048, 2.0047 (2.0047) for $(\mathbf{1})^{-\bullet}$, $(\mathbf{2})^{-\bullet}$, and $(NQ)^{-\bullet}$, respectively. However, the hyperfine splittings of $(\mathbf{2})^{+\bullet}$ are similar to those of the cation radical of 1,4-benzodithi-ine, *i.e.* $a(H_{1,4}) < 0.3$ (0.20) and $a(H_{2,3})$ 1.57 (1.06 G).[9]

Hence, (**1**) and (**2**) are rather peculiar derivatives since they are made by two moieties one being a good electron acceptor and the other a good electron donor which, although sharing the two carbon atoms 4a and 12a, behave almost independently from each other.

Conclusions

Compounds (**1**) and (**2**) constitute new examples of molecules able to originate easily both cation and anion radicals. They also show a first absorption band which is polarized perpendicularly to the molecular long axis. The ICT nature of this transition is supported by the HOMO–LUMO analysis: in fact, the symmetry of these orbitals predicts short-axis polarization and the charge distribution in the HOMO is localized mainly on the heterocyclic sulphur and oxygen atoms, while in the LUMO mainly on the carbonylic oxygens. The correctness of the HOMO–LUMO description is supported by the excellent agreement between experimental and the calculated ESR hyperfine splitting constant. The finding that, on passing from derivative (**1**) to derivative (**2**), there is a parallel decrease of ν_{max} of the low-energy transition and of the difference between the oxidation and the first reduction potential further supports the ICT nature of the transition.

Unfortunately, the low solubility in the liquid-crystal matrices prevents possible application of the two dyes in liquid-crystal display technology. We are currently trying to synthesize derivatives from (**1**) and (**2**) containing hydrocarbon chains in order to increase the solubility as well as the orientational order in liquid-crystal matrices.

Experimental

Synthesis.—Compound (**1**) was synthesized as reported in ref. 8, m.p. 287–289 °C (from toluene) (lit.,[10] 280 °C). Compound (**2**) was prepared: to a solution of 2,3-dichloro-1,4-naphthoquinone (0.76 g, 3.3 mmol) in ethanol (5 cm^3), 1,2-benzenedithiol (0.5 g, 3.3 mmol), dissolved in ethanol (5 cm^3), was added dropwise in an argon atmosphere. The mixture was then refluxed for 4 h. At room temperature a reddish precipitate was obtained, which, recrystallized from chloroform, gave violet needles (0.25 g, 25%), m.p. 290–291 °C; m/z 296 (M^+, 100%), 268 (M^+ − CO, 41), 240 (M^+ − 2CO, 63), 208 (M^+ − 2CS, 18), 164 (18), 152 (11), 120 (34), and 76 (37); ν_{max}(KBr) 1 670 (quinonic C=O) and 1 585 (quinonic C=C) cm^{-1}.

Optical Spectroscopy.—Absorption spectra were recorded with a Jasco Uvidec 510 spectrophotometer. The LD spectrum of (**2**) was recorded with a Jasco J500A spectropolarimeter equipped with an LD attachment. The experimental details and the procedure for the conversion of the instrumental signal into the linear dichroism are reported in ref. 3.

Electrochemistry.—Electrochemical measurements were made in acetonitrile (ACN, Merck Uvasol reagent grade), used as received, by utilizing 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$ as supporting electrolyte. Experiments were performed at 25 ± 0.1 °C, by using a conventional three-electrode cell. A platinum electrode was used as working electrode. A saturated calomel electrode (SCE), separated from the test solution by 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$ solution in ACN sandwiched between two fritted disks, was used as reference electrode, and all potentials were referred to it. A platinum electrode, immersed into a 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$ solution, separated from the main compartment by a glass frit, was the counter-electrode.

Cyclic voltammetric measurements were carried out with an AMEL 552 potentiostat, a 568 programmable function generator, a 731 integrator, a 836 *x*/*y* recorder and a Nicolet 3091 digital oscilloscope.

The minimization of the effect of uncompensated resistance was achieved with a positive feedback network of the potentiostat.

ESR Spectra.—The ESR spectra were recorded at room temperature with a Bruker ESP 300 spectrometer equipped with standard devices for field calibration and *g*-factor determination. Photolysis was carried out focussing the light from a 500 W high pressure mercury lamp into the ESR cavity.

McLachlan spin density calculations were performed by using the following parameters: $h_O(C{=}O)$ 1.2, $k_{C=O}$ 1.56,[11] h_O 2.0, k_{C-O} 1.0,[12] h_S 1.2, k_{C-S} 0.65,[9] and λ 1.2.

Acknowledgements

Financial support from Consiglio Nazionale delle Ricerche (Progetto Finalizzato 'Chimica Fine II') is gratefully acknowledged.

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Paper 0/00869I
Received 26th *February* 1990
Accepted 21*st May* 1990