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A Study of Some Quinones and their Anion Radicals with Vis-Near-IR Absorption

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ABSTRACT

The vis-near-IR spectra and synthesis of some quinones compounds such as 2,9-dichloropentacene-5,7,12,14-tetrone (2,9-dichloro-PDQ) and their semiquinone anion radicals were studied. The semiquinones of the diquinones show unusual shifts to the near-IR region (> 1·0 μm) compared to their precursors; these long-wavelength near-IR bands are assigned to π–π transitions from delocalized anion radicals.*

INTRODUCTION

Polyacenquinones, which are linearly annelated with 3–5 rings, thus having a 'rigid rod' configuration with extended length of conjugation, exhibit some unusual physical properties. For instance, they are quite stable to heat, insoluble in almost all organic solvents, and since the long delocalized π-system is interrupted by the cross-conjugated quinone moiety, they are almost electrical–insulators. Their anion radicals, especially semiquinones, show some interesting properties, e.g. their conductivities are about 10^7–10^9 higher than those of the precursors.[1] We report here the preparation of some new quinone compounds and their anion salts, and an evaluation of their vis-near-IR absorption spectra.

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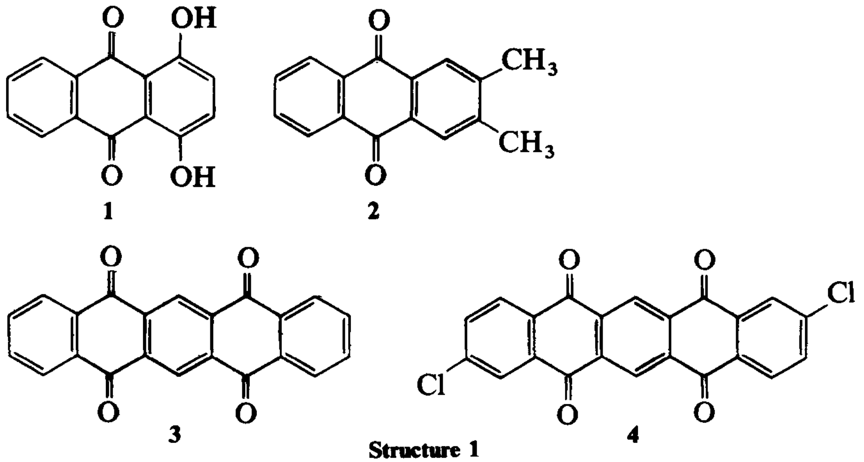
RESULTS AND DISCUSSION

Synthesis and electrochemistry

The compounds used in the investigation were quinizarin **1** (see Structure 1), 2,3-dimethylquinizarin **2**, pentacene diquinone (PDQ) **3**, and 2,9-dichloro PDQ **4**. Compounds **1**–**3** are known compounds; compound **4** was synthesized in 84% yield by the Friedel–Crafts reaction of chlorobenzene with pyromellitic dianhydride and subsequent dehydration with concentrated sulphuric acid.

The quinones can be reduced chemically or electrochemically to give the corresponding anion radicals. The reduction potentials for the compounds **1**, **2**, **3** and **4** were estimated at the mid point between the anodic and cathodic peak potentials from cyclic voltammetry (Table 1, Fig. 1).

The reduction of the quinones to the semiquinone anion radical was carried out using a 3–4 molar excess of 0·1 M tetrabutylammonium tetrafluoroborate in CH_3CN under a N_2 atmosphere (the anion solution being unstable in air); the results were verified using ESR of the solid anion salts which crystallized from the anion solution. These were stable, conductive and paramagnetic, and gave strong ESR signals (Fig. 2).



Structure 1

TABLE 1
Reduction Potentials of Quinones

	1^-	2^-	3^-	4^-
$-E°$ (V)	0·68	0·74	0·43	0·28

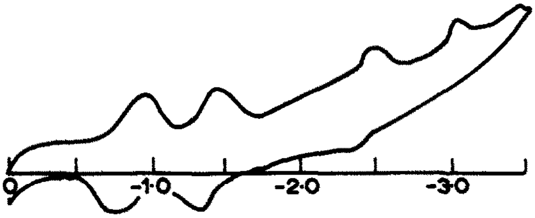


Fig. 1. Cyclic voltammogram of **3** (CH_3CN, 0·1 M $Bu_4N.BF_4$, 100 mV s^{-1}, 20°C).

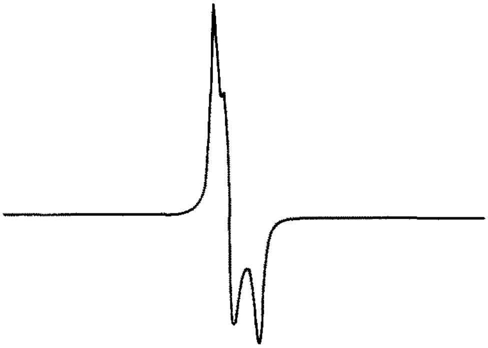


Fig. 2. ESR signals of powered sample 4^-. Bu_4N^- measured at 20°C.

Electronic spectra

The absorption spectra data of the quinones and of their radical anion semiquinones are shown in Table 2. Of primary interest are the electronic spectra of the **1**, **2**, **3** and **4** anions; for comparison, data for benquinone (**5**), 1,4-naphthoquinone (**6**) and 9,10-antraquinone (**7**)[2] are also listed. Because of the very low solubilities of compound **3** and **4**, their spectra were recorded in concentrated sulphuric acid.

From Table 2 it was observed[2] that the longest π-system on one side of the

TABLE 2
Absorption Spectral Data of Neutral and Semiquinones

	1	*2*	*3*	*4*	*5*	*6*	*7*
0	468 (CH_3CN)	485 (CH_3CN)	381 (H_2SO_4)	378 (H_2SO_4)	—	323[b]	327[b]
−1	586 (CH_3CN)	625 (CH_3CN)	1 335	1 410	450[a]	480[a]	552[a]

[a] Measured in DMF 0·1 M $Bu_4N.BF_4$.
[b] Ref. 1.

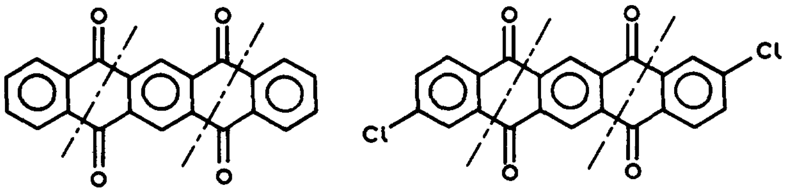


Fig. 3. 'Cross-conjugated' existing in quinones.

quinones determined the position of the long-wavelength band, because of the 'cross-conjugated' quinone moiety interrupting the delocalizing π-system (Fig. 3). The monoquinones **6** and **7** have a very similar long-wavelength π–π^* transition. For the same reason, the longest wavelengths of the diquinones **3** and **4** are in the same region as the monoquinones **6** and **7**. Additionally, because introduction of electron-donating groups enhances the delocalization, e.g. methyl and hydroxy, groups, as in compounds **1** and **2**, the absorption band show a red shift. This is readily apparent from a comparison of **7** (327 nm) with **1** (468 nm), or of **1** (468 nm) with **2** (485 nm).

From Table 2 it can also be seen that the long wavelength absorptions of neutral quinones and semiquinone anion radicals are quite different. For monoquinones, their anion radicals show strong bands ($\varepsilon = 4 \times$

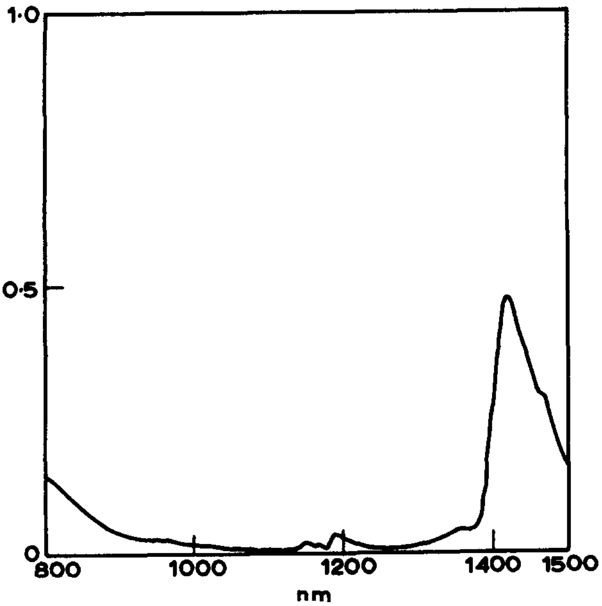


Fig. 4. The near-IR absorption spectra of compound **4**.

10^4 M^{-1} cm^{-1}) in the 400–600 nm region, and it was found that the long-wavelength absorption of compounds with more rings and more electron-donating groups showed the largest red shifts; the maximal shift is usually less than 200 nm (for **2** and **2**$^-$). For the diquinones, the anion radicals showed unusual absorption in the near-IR region. Thus, the semiquinones **3**$^-$ and **4**$^-$ exhibit sharp bands at 1335 nm[3] and 1410 nm ($\varepsilon = \times$ 10^2 M^{-1} cm^{-1}), respectively, shifted about 1000 nm to longer-wavelength compared with their precursors (Fig. 4). The difference between the spectra of neutral diquinones and that of the monoquinones is much less than that between the spectra of diquinone anions and monoquinone anions.

EXPERIMENTAL

Absorption spectra were recorded on a Shimadzu UV-265 Spectrophotometer and ^{1}H NMR on a Bruker Jeol-100 Spectrometer. Electron-impact mass spectra were recorded with a Hitachi M80 Mass Spectrometer. Cyclic voltammograms were recorded using an X-Y chart recorder. ESR spectra were recorded on an ER 2000-SRC ESR Spectrometer. Melting points are uncorrected.

SYNTHESIS

Compound **1** (quinizarin) was a commercial sample, recrystallized from toluene to give red needles, m.p. 198°C. Compound **2** (2,3-dimethylquinizarin) was prepared, with compound **1**, as previously reported.[4] The reaction mixture was initially recrystallized from chlorobenzene at first and the product thus obtained was chromatographed on silica gel (200–300 mesh), using CH_2Cl_2 as eluant. The highest R_f band was collected to give the desired product as red needles, m.p. 256°C (lit. 253°C). Compound **3**[5] (PDQ) was prepared from pyromellitic dianhydride and benzene, and recrystallized from nitrobenzene to give pale yellow needles, m.p. >300°C. Compound **4** (2,9-dichloro-PDQ) was prepared from the Friedel–Crafts reaction of pyromellitic dianhydride with chlorobenzene and dehydration with conc. H_2SO_4 (160–170°C). The crude product was recrystallized from nitrobenzene, washed with acetone to give silvery plate-like crystals in 84% yield, m.p. >350°C, ^{1}H NMR (90% D_2SO_4 + 10% D_2O, 100 MHz) δ 9·0 (s, 2H), 8·3 (s, 4H), 7·9 (s, 2H). IR(KBr) 1680, 1580, 1465, 1280, 710 cm^{-1}. MS m/e 409. Anal. calculated for $C_{22}H_8O_4Cl_2$: C, 64·86; H, 1·96; Cl, 17·44. Found: C, 64·53; H, 1·98; Cl, 17·11.

ELECTROCHEMISTRY

Typical procedure for the preparation of semiquinone anions

Reduction of 0·020 g samples of quinizarin (**1**) plus 0·1 M tetrabutylammonium tetrafluoroborate, with a carbon bar as cathode, Pt as anode and SCE as reference. The cell was divided, air was excluded from the system and the potentials were set about 200 mV more negative than E° ($-0{\cdot}180$). After passage of about 1·5 F mol^{-1}, the anion solution turned from red to blue; it was then transferred (via a syringe) to a Schlenk apparatus under a N_2 atmosphere. The UV/VIS/NIR spectra were measured immediately or under N_2. Insoluble salts were formed when the solution was syringed into $Bu_4N.BF_4$ (3–4 molar excess) in CH_3CN; these were filtered after 4–5 h, washed with CH_3CN, dried in vacuum and retained under an inert atmosphere.

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