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Electron transfer reactions of extended *o*-, *p*-quinones—voltammetric and EPR/ENDOR spectroscopic investigations

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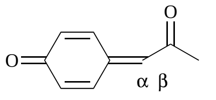
The electrochemical properties of four *ortho-*, *para*-extended quinones/quinonemethides † 1–4 have been investigated using cyclic voltammetry (CV) and normal pulse voltammetry (NPV). The species are reduced by addition of two, four or six electrons to form a dianion (1), tetraanions (2, 3) and a hexaanion (4), all of which can be re-oxidized to the corresponding quinonoid species. These compounds, thus, exhibit a multistep redox behaviour, acting as good (quasi)reversible electron acceptors with well separated potential steps, some of them corresponding to a formal two-electron transfer. The radical anions $1^{\bullet -}$–$4^{\bullet -}$ and the radical trianion $3^{\bullet 3-}$, prepared electrochemically in the first and third reduction steps, are persistent for several hours in the absence of air. They have been characterized by EPR and ENDOR spectroscopy, revealing a delocalization of the odd electron. The areas of preferential spin residing, however, are quite different in radical trianion $3^{\bullet 3-}$ as compared to radical monoanion $3^{\bullet -}$, indicating a strong influence of the charge state in these radical anions.

Introduction

Quinones are indispensable in organic electrochemistry due to their multistep redox properties[1] and they play a substantial role in biological electron transfer chains.[2] Like quinones, their anion radicals attract interest in biology, medicine and chemistry.[1,3] Extended quinones, on the other hand, have found increasing application as electron acceptors for the production of organic conducting materials.[4–8] Recently, we reported the electrochemical and spectroscopic properties of a series of extended *p*-quinones.[9] One important aspect of these investigations was to mark out the structural prerequisites for the use of *p*-phenylene units as ferromagnetic couplers. With a similar aim we investigated the *ortho-*, *para*-extended quinones/quinonemethides (**1**–**4**), where the internal steric strain and the s-*cis* β-keto group (structural element **I**) should provide further interesting properties. Such quinones are also of interest, because some of their partially reduced forerunners, *i.e.* hydroxyphenylquinones, are potential 5-lipoxygenase blockers.[10]



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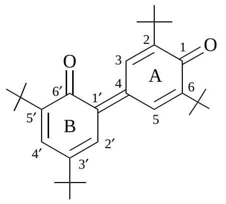
Here, we describe the voltammetric properties of these compounds using cyclic voltammetry (CV) and normal pulse voltammetry (NPV), as well as the EPR/ENDOR characterization of the radical species obtained on their reduction.

Experimental

Instrumentation

Elemental analyses were performed using a Carlo Erba Elemental Analyzer-1106. IR spectra were recorded on a Perkin-



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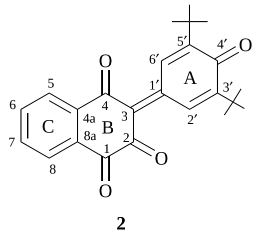

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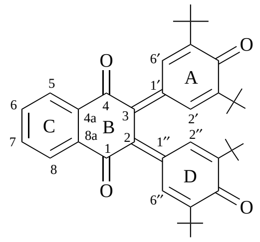

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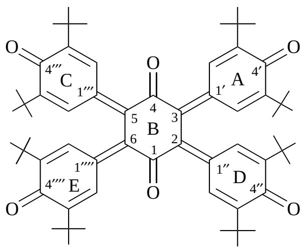

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† IUPAC names for *o-* and *p*-quinonemethide are 6-methylenecyclohexa-2,4-dien-1-one and 4-methylenecyclohexa-2,5-dien-1-one.

Elmer 281 spectrometer. NMR spectra were recorded on Bruker AC-250 and WM 400 spectrometers. All ^{1}H and ^{13}C NMR chemical shifts are given relative to $SiMe_4$ as internal standard and for $CDCl_3$ as solvent; the coupling constants (*J*) are reported in Hz. Mass spectra were recorded with Finigan MAT 711A or TSQ spectrometers. EPR and ENDOR spectra were obtained with a Bruker ESP 300E spectrometer. For *g*-factor measurements, the field gradients were corrected by replacing the sample with a reference compound (2,6-di-*tert*-butyl-4-*tert*-butoxyphenoxyl in benzene, $g = 2.004\,63$).

Computer simulations of EPR spectra were performed with 'programme PIP'. The EPR-analysis software was furnished by Illinois EPR-Research Center, NIH division of research resources grant No. RR 001811, by R. L. Belford, A. M. Maurice, M. J. Nilges, University of Illinois, Urbana.

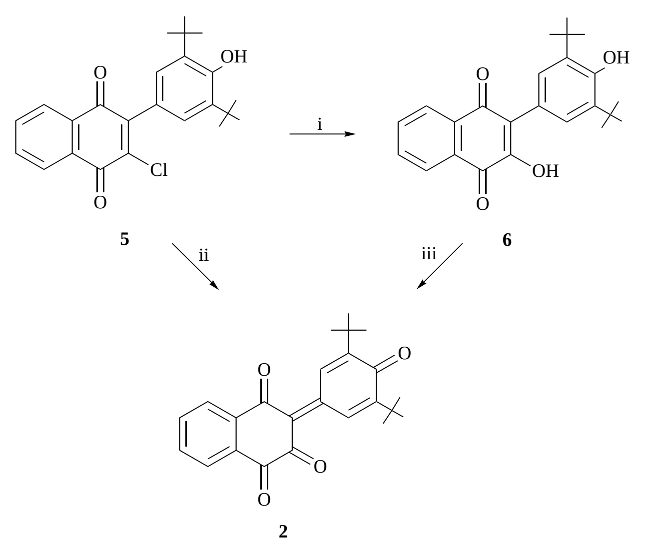
Electrochemical experiments were carried out at 25 °C under argon using a BAS CV-50W electrochemical analyzer (Bioanalytical Systems). For CV and NPV a glassy carbon disk electrode with an electroactive area of 0.07 cm^2 was used as working electrode. The auxiliary electrode consisted of a Pt wire. $Ag/AgClO_4$ (0.01 M in MeCN/0.1 M NBu_4PF_6) was used as reference electrode and separated by two glass frits from the Haber–Luggin capillary. All potentials given relate to this reference electrode. The supporting electrolyte consisted of a 0.1 M solution of NBu_4PF_6 in pyridine. Pyridine was purified by distilling it three times under argon after drying over KOH for several weeks, and was then kept over 4 Å molecular sieves. NBu_4PF_6 was prepared from NBu_4Br and NH_4PF_6, recrystallized four times from EtOH and dried *in vacuo* at 110 °C for 48 h. The number of electrons transferred per molecule was confirmed by controlled-potential electrolysis (CPE) at the relevant potentials, chosen from the corresponding CVs. For CPE, cylindrical Pt (10% iridium) gauze working and auxiliary electrodes, separated by a porous glass frit, were used.

The anion radicals were generated in *ca.* 0.5 mM solutions of the quinones **1**–**4** in a CPE cell (see above) under argon at 25 °C. Upon completion of the reduction (current drop at constant potential) they were transferred to the EPR tubes in an argon box. *Intra muros* generation (without potential control) gave almost identical spectra. During the ENDOR measurements, the electrolysis had to be interrupted.

Syntheses

2,6-Di-*tert*-butyl-4-(3,5-di-*tert*-butyl-6-oxocyclohexa-2,4-dien-1-ylidene)cyclohexa-2,5-dien-1-one 1.[12] Compound **1** was prepared by oxidation of the corresponding biphenol, 3,3′,5,5′-tetra-*tert*-butylbiphenyl-4,2′-diol,[11,12] with PbO_2 in toluene. δ_C(100.6 MHz) 29.17, 29.68, 29.72, 29.75 (12 Me), 35.28, 35.53, 35.78, 36.07 (4 Me_3*C*), 118.67, 128.67, 131.55, 131.74, 138.66, 140.31, 148.79, 148.90, 150.72, 151.36 (10 C_{arom}), 186.61 (C-1), 191.23 (C-6′); *m/z* (EI) 410 ($M^+ + 2$, 5%), 393 ($M^+ - Me$, 4), 351 ($M^+ - Bu^t$, 31), 337 ($M^+ - Me{-}Bu^t$, 30), 57 (Bu^t, 100), see also ref. 13.

3-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1,2,3,4-tetrahydronaphthalene-1,2,4-trione 2. Compound **2** had been synthesized by Wurm,[10] starting from 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-chloro-1,4-naphthoquinone **5** *via* 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-hydroxy-1,4-naphthoquinone **6** (Scheme 1) and oxidation of the latter with cerium(IV) ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$, CAN]. Although not quoted by Wurm,[10] **5** had already been synthesized earlier by Russkikh *et al.*[14] We found that **5** can be directly converted to **2** by hydrolysis and oxidation with sodium nitrite.



Scheme 1 *Reagents and conditions*: i, K_2CO_3, $MeOH{-}H_2O$; ii, $NaNO_2$, DMSO; iii, CAN

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3-chloro-1,4-naphthoquinone **5** (0.4 g, 1.0 mmol) and $NaNO_2$ (0.069 g, 1.0 mmol) in 3 ml of DMSO were stirred for 3 h at 25 °C. The brown precipitate of **2** was filtered, washed with water and recrystallized from hexane. Yield 0.27 g (71%), mp 224–226 °C (Found: C, 76.73; H, 6.33. Calc. for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43%); δ_H(250.1 MHz) 1.29 (9 H, s, Bu^t), 1.30 (9 H, s, Bu^t), 7.79 (1 H, d, ^4J 2.6, H-2′,6′), 7.84 (1 H, td, ^3J 7.5, ^4J 1.6, H-6), 7.92 (1 H, td, ^3J 7.5, ^4J 1.6, H-7), 8.04 (1 H, d, ^4J 2.6, H-2′,6′), 8.25 (1 H, dd, ^3J 7.6, ^4J 1.3, H-5), 8.30 (1 H, dd, ^3J 7.8, ^4J 1.3, H-8); δ_C(62.9 MHz) 29.69 (18 Me), 36.40 (2 Me_3*C*); 128.41, 128.82, 129.00, 134.97, 136.31 (C-5, C-6, C-7, C-8, C-2′, C-6′), 132.54, 137.01, 137.51 (C-3, C-4a, C-8a), 147.67 (C-1′), 154.86, 155.05 (C-3′, C-5′), 180.40, 184.86, 185.03, 187.11 (C-1, C-2, C-4, C-4′).

2,3-Bis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1,2,3,4-tetrahydronaphthalene-1,4-dione 3. Cerium(IV) ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$] (1.10 g, 2.0 mmol) in a mixture of 5 ml of acetonitrile and 5 ml of water was added to 2,3-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,4-naphthoquinone[14] (0.57 g, 1.0 mmol) in 6 ml of acetonitrile. After 5 min of stirring the precipitate was filtered off and washed with 5 ml of methanol. Yield 63%, mp 190–191 °C (Found: C, 81.12; H, 7.93. Calc. for $C_{38}H_{44}O_4$: C, 80.85; H, 7.80%); δ_H(250.1 MHz) 1.16 (18 H, s, Bu^t), 1.32 (18 H, s, Bu^t), 6.85 (2 H, d, ^4J 2.6, H_{quin}), 8.11 (2 H, d, ^4J 2.6, H_{quin}), 7.80–7.85 (2 H, m, H_{arom}), 8.18–8.23 (2 H, m, H_{arom}); δ_C(100.6 MHz) 29.33, 29.63 (12 Me), 35.71, 35.90 (4 Me_3*C*), 127.29, 129.04, 134.90, 135.12, 137.84, 140.06, 151.78, 151.93 (18 C_{arom} and $C_{olefinic}$), 186.67, 186.75 (4 *C*O); ν_{max}/cm^{-1} (KBr) 1676, 1616 (C=O); *m/z* (FD) 564 (M^+).

2,3,5,6-Tetrakis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)cyclohexane-1,4-dione 4. Compound **4** was prepared in a two step synthesis starting with the substitution of chlorine in tetrachloro-1,4-benzoquinone by 2,6-di-*tert*-butylphenol to give **7**, followed by oxidation of **7** with PbO_2 in toluene (Scheme 2) as described below.

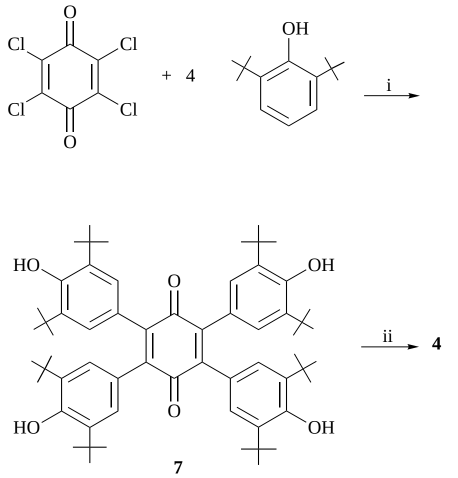
2,3,5,6-*Tetrakis*(3,5-*di*-tert-*butyl*-4-*hydroxyphenyl*)-1,4-*benzoquinone* **7**.—Tetrachloro-1,4-benzoquinone (0.25 g, 1.0 mmol), 2,6-di-*tert*-butylphenol (0.82 g, 4.0 mmol) and potassium carbonate (0.56 g, 5.0 mmol) were dissolved in 10 ml of DMSO and heated to 100 °C for 2 h. The solution was diluted with 50 ml of water and extracted three times with chloroform. The organic layers were separated and dried over potassium carbonate. After filtration and evaporation *in vacuo*, the residue was chromatographed on silica gel with toluene. Yield 0.37 g (40%), deep red crystals, mp >300 °C (Found: C, 79.99; H, 9.32. Calc. for $C_{62}H_{84}O_6$: C, 80.47; H, 9.15%); δ_H(400.1 MHz) 1.27 (72 H, s, Bu^t), 5.16 (4 H, br s, OH), 6.84 (8 H, s, H_{arom}); δ_C(100.6 MHz) 30.33 (24 Me), 34.18 (8 Me_3*C*), 125.19, 128.30, 134.98, 143.95, 153.58 (28 C_{arom} and C_{quin}), 187.61 (2 *C*O); ν_{max}/cm^{-1} (KBr) 3645 (OH), 1657 (C=O); *m/z* (FD) 924 (M^+).

2,3,5,6-*Tetrakis*(3,5-*di*-tert-*butyl*-4-*oxocyclohexa*-2,5-*dien*-1-*ylidene*)*cyclohexane*-1,4-*dione* **4**.—Compound **4** was prepared by oxidation of **7** (92 mg, 0.10 mmol) with a four-fold excess

Table 1 Formal potentials (E^{o}/mV)[a] and potential separation (ΔE/mV)

Comp.	E^{o1}	ΔE^1	E^{o2}	ΔE^2	E^{o3}	ΔE^3	E^{o4}	ΔE^4
1	−830	82	−1365	84				
2	−425	82	−1065	83	-1955^b	130		
3	−650	88	−1110	89	−1700	90	−2100	160
4	−405	79	−763	77	-1180^b	85	-2190^b	180

[a] Potentials *vs.* Ag/(0.01 M) $AgClO_4$ electrode; E^o, the mean value of E_p^r (reduction peak potential) and E_p^o (oxidation peak potential); $\Delta E = E_p^r - E_p^o$. [b] Formal two-electron transfer.



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Scheme 2 *Reagents and conditions*: i, K_2CO_3–DMSO; ii, PbO_2–Toluene

of PbO_2 in toluene. After 30 min of stirring, PbO_2 was filtered off and the solvent removed *in vacuo*. Yield 77 mg (84%), deep red crystals, mp 294 °C (Found: C, 80.80; H, 8.87. Calc. for $C_{62}H_{80}O_6$: C, 80.83; H, 8.75%); δ_H(400.1 MHz) 1.17 (36 H, s, Bu^t), 1.36 (36 H, s, Bu^t), 6.74 (4 H, d, ^4J 2.5, H_{quin}), 8.35 (4 H, d, ^4J 2.5, H_{quin}); δ_C(100.6 MHz) 29.47, 29.71 (24 Me), 35.85, 36.17 (8 Me_3C), 127.71, 129.12, 137.05, 140.50, 152.67, 152.68 (24 $C_{olefinic}$), 186.51 (4 CO), 187.01 (2 CO); ν_{max}/cm^{-1} (KBr) 1684 (sh), 1631, 1620 (C=O); *m/z* (EI) 920 (M^+).

Results and discussion

Electrochemical investigation

Cyclic (CV) and normal pulse (NPV) voltammograms of **1**–**4** are shown in Figs. 1 and 2; the electrochemical data are listed in Table 1.

The *o*-, *p*-diphenoquinone **1** shows two well separated reduction (Pr_1, Pr_2) and re-oxidation peaks (Po_1, Po_2) in CV [Fig. 1(*a*)]. NPV [Fig. 2(*a*)] reveals equal currents of the first (Pr_1) and the second peak (Pr_2), indicating that the same number of electrons are exchanged during each electron-transfer process. The combined results from CV, NPV and CPE confirm that **1** is reduced in the first step by one-electron transfer to a radical anion (which can further be characterized by EPR and ENDOR spectroscopy, see below). This may be re-oxidized to the quinone state or further reduced by a second electron-transfer to a dianion. The latter is re-oxidizable to **1** in two successive one-electron transfers.

The CV of **2** [Fig. 1(*b*)] shows three peak couples of reduction (Pr_1–Pr_3) and re-oxidation (Po_1–Po_3). The currents of Pr_1 and Pr_2 are approximately equal, but they are much smaller than that of Pr_3. The NPV of **2** is shown in Fig. 2(*b*). Here, the currents of the first peak (Pr_1) and the second peak (Pr_2) are equal, as in the case of **1**, and their sum is approximately equal to the current of the third peak (Pr_3), indicating that in the first and second reduction step **2** is reduced *via* the anion radical (which gives an EPR signal, see below) to the dianion in two consecutive one-electron transfers. The dianion is further reduced by incorporation of two more electrons to give the tetraanion, which can be oxidized back to the neutral state in the corresponding re-oxidation peaks. Because the third and the fourth reduction step apparently occur at potentials very close together, the two peaks overlap, and only one peak is observed for both reduction steps.

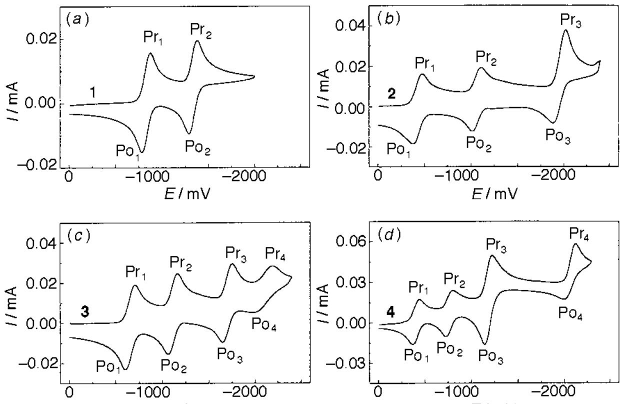

Fig. 1 Cyclic voltammograms of **1**–**4** in pyridine solution; potential, *vs.* Ag/$AgClO_4$ (0.01 M in MeCN/0.1 M NBu_4PF_6); scan rate, 100 mV s^{-1}; (*a*) **1**, (*b*) **2**, (*c*) **3**, (*d*) **4**

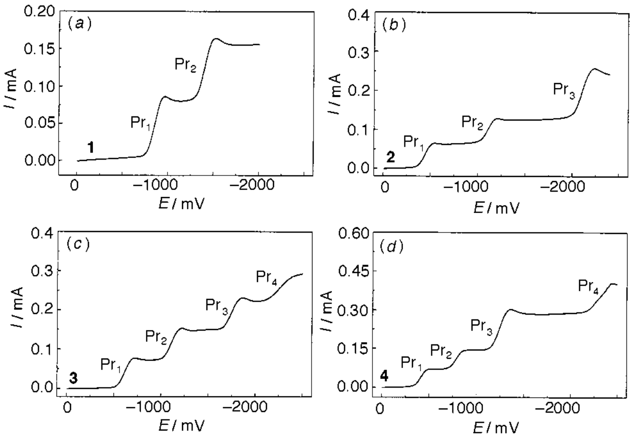

Fig. 2 Normal pulse voltammograms of **1**–**4** in pyridine solution; potential, *vs.* Ag/$AgClO_4$ (0.01 M in MeCN/0.1 M NBu_4PF_6); scan rate, 20 mV s^{-1}; pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; (*a*) **1**, (*b*) **2**, (*c*) **3**, (*d*) **4**

The two-fold extended **3** exhibits CV [Fig. 1(*c*)] and NPV [Fig. 2(*c*)] curves different from those of **2** in that the fourth peak couple of reduction (Pr_4) and re-oxidation (Po_4) can be observed due to the larger difference between the third and fourth reduction potentials than in the case of **2**. Interestingly, the average of the E^o values for the third and fourth electron-transfer in **3** is close to the E^o value for the third peak couple of **2**. The peak currents of the fourth couple of **3** are smaller than those of the other couples, and the potential separation between the reduction and re-oxidation peak is here much larger than in the case of the other couples[15,16] (Table 1). Such effects are known,[17–19] and we have discussed[9a] the first effect in terms of a lower electron-transfer rate ‡ and a high repellent effect of the multiply charged anions towards the cathode.[17] The second effect, and especially the lower re-oxidation peak of the fourth couple, might be due to a reversible chemical reaction. In similar cases, dimerization of radical anions[16] or a combination of radical anion and parent quinone[20] have been postulated. In the present case, reversible protonation–deprotonation reactions involving the highly negatively charged anions, even in pyridine (containing trace of water) seem to be more reasonable.

CV and NPV spectra of **4** are shown in Figs. 1(*d*) and 2(*d*). They resemble the voltammograms of **2**, as far as regards the reduction peaks Pr_1–Pr_3. The currents of Pr_1 and Pr_2 are approximately the same, and each of them is only half of the current of Pr_3, indicating that **4** undergoes two successive one-electron reductions up to the dianion *via* a monoanion (which is EPR-active, see below). Obviously, the dianion is further reduced in a two-electron step to the tetraanion. A fourth two-electron transfer peak couple, although less reversible, reveals that the tetraanion is further reducible to a hexaanion. All anion species can be re-oxidized to the neutral **4**. The potential separations between the third and fourth, and between the fifth and sixth reduction step are very small, or even inverted,[21] so that each pair of processes exhibits only one peak. The current of Pr_4 is smaller than that of Pr_3, the reasons for this may be the same as for the case of the fourth reduction peak of **3**, discussed above. Probably, there are again proton-transfer equilibria coupled to the fifth and sixth electron-transfers, because the fourth re-oxidation peak is relatively small when compared with the corresponding reduction peak. This is reasonable since the polyanions involved certainly are strong protophilic (basic) species. Nevertheless, **4** displays six-step redox behaviour and is, thus, capable of acting as an excellent electron acceptor.

The positions of the CV peak potentials of **1**–**4** depend on the scan rate. With increasing scan rate, the reduction peaks ($E_p{}^r$) are shifted towards more negative potentials, whereas the re-oxidation peaks ($E_p{}^o$) move towards more positive potentials. The resulting increase in the potential separations ΔE_p ($=E_p{}^o - E_p{}^r$) indicates that the reduction of **1**–**4** is quasi-reversible.[15] From the structures of **1**–**4** and the experimental results of CV and CPE measurements it can be derived that **1**, **2**/**3** and **4** are reducible with an overall two, four and six electron transfer to form a dianion, tetraanions and a hexaanion, resepectively. Since all anion species can be re-oxidized up to their neutral quinonoidal states, the electrochemical behaviour of **1**, **2**/**3** and **4** can be formally denoted as quasi-reversible EE, EE(EE) and EE(EE)(EE) processes, respectively.

As can be seen from Table 1, the enlargement of the π-system with an increasing number of keto groups changes the redox potentials. The first reduction potentials become less negative in the order **1** < **3** < **2** < **4**, indicating that **2**–**4** possess a much higher electron-accepting ability than **1**, and **4** is the strongest electron acceptor.

The ease of electron-uptake (expressed in E^o) of the different species of one extended quinone as well as of species with the same charge but derived from different parent quinones reflects the structural features of the respective compounds. This information, although not complete, can be derived from the magnetic resonance studies of the radical anions of **1**–**4**.

EPR and ENDOR spectroscopy

The radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ and radical trianion $\mathbf{3}^{\bullet 3-}$ should be able to be electrochemically generated in the first and third reduction steps. In pyridine solution at room temperature, the species obtained proved to be persistent for several hours in the absence of air, as shown by EPR investigation. The EPR spectra (Fig. 3) appeared in the $g = 2.004$ region, where the signals of radical anions of quinones are usually observed. The interaction of the odd electron with the protons of the Bu^t groups could not be resolved by EPR spectroscopy. In addition, ENDOR spectroscopy was used to characterize further the radicals $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ and $\mathbf{3}^{\bullet 3-}$. As shown in Fig. 4, the ENDOR spectra at 233 K allow the resolution of the different proton couplings. Even the interaction of the odd electron with the protons of the Bu^t groups is resolvable by ENDOR spectroscopy. The hyperfine splitting constants (hfs) a_H and g tensor values are listed in Table 2. The coupling constants (a_H) obtained at 233 K with ENDOR are approximately equal to those obtained at room temperature with EPR spectroscopy. In order to get further verification of the experimental results, a

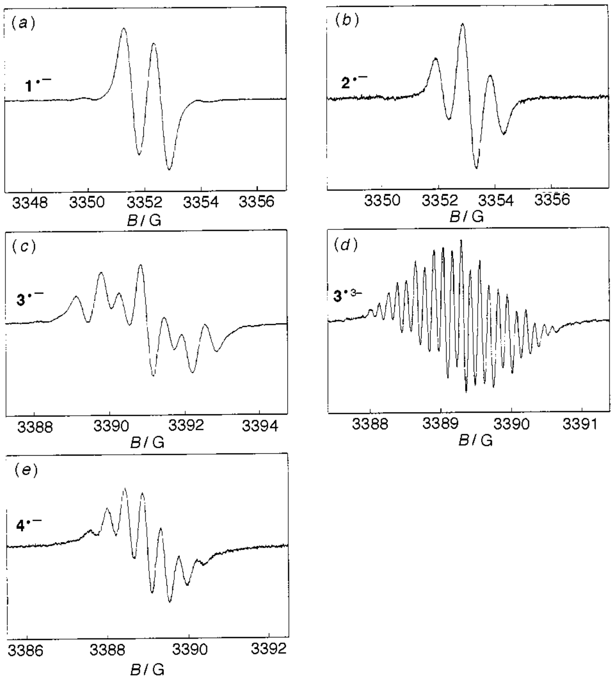

Fig. 3 EPR spectra of the radical anions in pyridine solution at 298 K; (*a*) $\mathbf{1}^{\bullet-}$, (*b*) $\mathbf{2}^{\bullet-}$, (*c*) $\mathbf{3}^{\bullet-}$, (*d*) $\mathbf{3}^{\bullet 3-}$, (*e*) $\mathbf{4}^{\bullet-}$

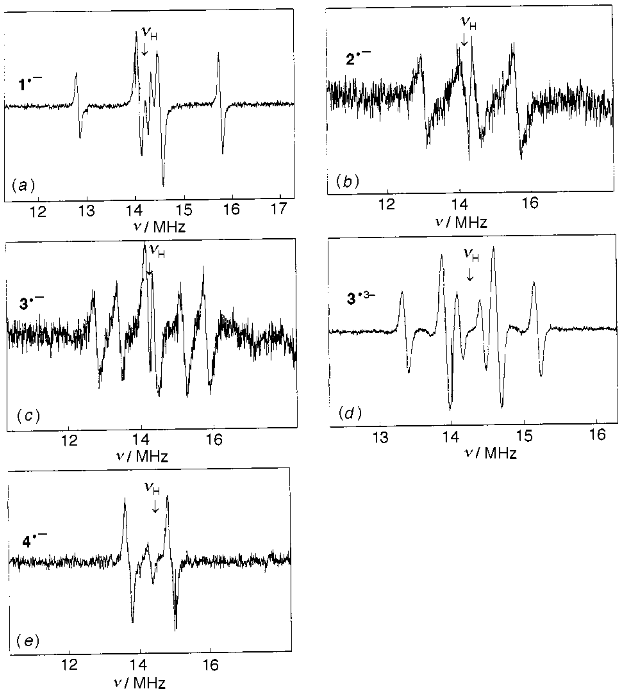

Fig. 4 ENDOR spectra of the radical anions in pyridine solution at 233 K; (*a*) $\mathbf{1}^{\bullet-}$, (*b*) $\mathbf{2}^{\bullet-}$, (*c*) $\mathbf{3}^{\bullet-}$, (*d*) $\mathbf{3}^{\bullet 3-}$, (*e*) $\mathbf{4}^{\bullet-}$

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‡ As stated correctly on p. 933 of ref. 9*a*; on p. 934, left column, in the last sentence of the second paragraph, however, k_{s1} and k_{s2} should be exchanged.

Table 2 a_H values

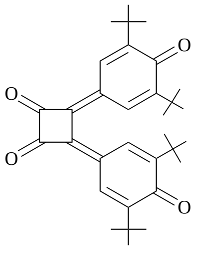
Radical	a_H/G
1$^{\bullet -}$	1.05,[a] 0.05,[c] 0.16,[c] 1.04[c]
2$^{\bullet -}$	0.95,[a] 0.10,[c] 0.93[c]
3$^{\bullet -}$	0.64,[a] 1.05,[a] 0.65 (2 H),[b] 1.05 (2 H),[b] 0.06,[c] 0.64,[c] 1.10[c]
3$^{\bullet 3-}$	0.12 (2 H),[b] 0.25 (4 H),[b] 0.65 (2 H),[b] 0.12,[c] 0.26,[c] 0.65[c]
4$^{\bullet -}$	0.43,[a] 0.44 (8 H),[b] 0.02,[c] 0.43[c]

[a] Obtained by EPR at room temperature. [b] Obtained by simulation. [c] Obtained by ENDOR at 233 K.

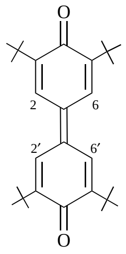
computer simulation of the more complicated EPR spectra of the anion radicals **3**$^{\bullet -}$/**4**$^{\bullet -}$ and **3**$^{\bullet 3-}$ was carried out, furnishing very good agreement between experimental and simulated curves. However, some assignments remain equivocal, since a specific deuteriation was not undertaken. To make the discussion easier, the rings in the species **1**–**4** are marked with the letters A–E.

Let us start with the monoanions. The most straightforward EPR spectrum seems to be that of radical anion **2**$^{\bullet -}$ [Fig. 3(*b*)], consisting of a triplet hfs with $a_H = 0.95$ G, which should be assigned to the quinonoid ring protons H-2′,6′ in moiety A. This means that the two quinonoidal protons are equivalent either accidentally or by rapid rotation (relative to the EPR timescale) around the weakened exocyclic double bond. This coupling can be found again in the ENDOR spectrum [Fig. 4(*b*)], which reveals an additional small coupling expected for the Bu^t protons. The value of *ca.* 0.10 G is however too large for Bu^t in the *ortho*-position to the quinonoid keto group. For the anion radicals of *para*-extended quinones[9a] and the other species of Table 1 the corresponding values are <0.06 G. Thus, the splitting of 0.10 G may be due to a small coupling of the free electron to protons in the naphthalene ring superimposed by an even smaller coupling caused by the Bu^t protons. Anyway, the observed pattern shows that the free electron in **2**$^{\bullet -}$ is mainly delocalized into moiety A and (presumably) B.

A simple EPR spectrum [Fig. 3(*e*)] is also observed for radical anion **4**$^{\bullet -}$: seven equidistant lines with $a_H = 0.43$ G. This indicates a coupling of the free electron with six equivalent protons. Since there is no reason to assume that two ring protons should be different from six others and since the ENDOR spectrum shows only one line pair ($a_H = 0.43$ G) in addition to the line pair due to the Bu^t protons ($a_H = 0.02$ G), it is more reasonable to assume equal coupling to all eight quinonoidal ring protons. In principle, nine lines would then be expected, however, the two lines at both wings are apparently so weak that they cannot be observed. This was further verified by computer simulation (eight equivalent protons) also showing only seven lines on the same intensity scale. This means that the free electron is delocalized over all rings A–E. The relatively small coupling constants for ring and Bu^t protons are in agreement with this assumption. Again, we are unsure, whether the eight ring protons are either accidentally equivalent or whether the rotation around the exocyclic double bonds is rapid. Similar observations have been reported by West and co-workers[22] in the case of the radical anion of the 1,2-diquinocyclobutanedione **8**.



8



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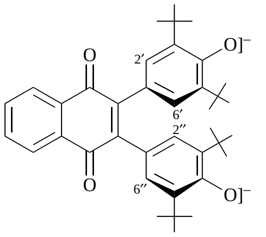

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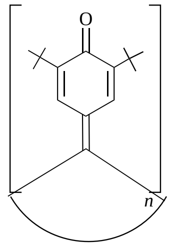

11

The EPR spectrum of radical anion **3**$^{\bullet -}$ [Fig. 3(*c*)] exhibits seven non-equidistant lines, the ENDOR spectrum [Fig. 4(*c*)] shows three line pairs, indicating that the odd electron is coupled to two types of ring protons ($a_H = 1.10$ and 0.64 G) and also interacts with the protons of the Bu^t groups ($a_H = 0.06$ G). The simulation of the EPR spectrum reveals a multiplicity of two for each of the two coupling proton types. At first glance, this pattern would suggest a coupling of the free electron with the 2 × 2 protons of the naphthalene ring. However, the coupling constants seem to be too large for a 1,4-naphthosemiquinone[23] and, moreover, a usual coupling with the Bu^t protons ($a_H = 0.06$ G) is observed. Therefore, it is more reasonable to assume a delocalization of the free electron only to rings A, B and D on a first-order treatment. Then, $a_H = 1.10$ and 0.64 G should be assigned to the quinonoid protons H-2′,2″,6′,6″. Why these protons are magnetically non-equivalent in contrast to the situation with **2**$^{\bullet -}$ and **4**$^{\bullet -}$ is not evident; presumably, **3** is more rigid than **2** or **4**. Interestingly, the average of the two coupling constants, $a_{AV} = 0.87$ G, is just twice the *a*-value (0.43 G) for the quinonoidal ring protons of **4**$^{\bullet -}$ with a delocalization area of about twice that of **3**$^{\bullet -}$, a fact which strongly supports the above conclusions.

The EPR spectrum of **1**$^{\bullet -}$ [Fig. 3(*a*)] surprisingly consists of two broad lines ($\Delta H = 1.14$ G) with relative intensities 1 : 1, suggesting a strong coupling of the odd electron to one ring proton ($a_H = 1.05$ G) and relatively small couplings to other protons. Smaller signals at both wings may be due to ^{13}C coupling. The corresponding ENDOR [Fig. 4(*a*)] exhibits three line pairs, indicating an interaction with the protons of the Bu^t groups ($a_H = 0.05$ G) and two types of aromatic protons. In analogy to *o*-quinones[24] it is reasonable to assign the largest coupling to H-4′ of the *o*-quinonoid part of **1**$^{\bullet -}$. The coupling constant $a_H = 0.16$ G would then correspond to one or more of the remaining quinonoidal protons in both rings, which might be accidentally magnetically equivalent. Since in the radical anion of 3,3′,5,5′-tetra-*tert*-butyl-*p*-diphenoquinone **9** the ring protons show $a_H = 0.45$ G,[9a] the above results, although being compatible with a delocalization of the free spin over the whole π-system, suggest that the free electron is located mainly in the *o*-quinonoidal moiety B of the molecule.

The only EPR-active multianion species is the trianion **3**$^{\bullet 3-}$. Its EPR spectrum [Fig. 3(*d*)] with 21 lines is much more complicated than that of **3**$^{\bullet -}$. The hfs constants a_H obtained by simulation (Table 2) are 0.12 (2 H), 0.25 (4 H) and 0.65 (2 H) G. The ENDOR spectrum [Fig. 4(*d*)] also exhibits three line pairs, confirming further the simulation results. In this case, the coupling of the protons of the *tert*-butyl groups is too weak to be observed. This is reasonable, if we assume a structure like **10** for the dianion **3**$^{2-}$, in which the steric strain between the two quinonoidal rings present in **3** is relieved due to the twisting around the single bonds which now connect the phenolate (A,D) and the quinone (B) rings. In **3**$^{\bullet 3-}$g, which can be regarded as the semiquinone of **10**, the coupling of the free electron with the now equivalent protons H-2′,2″,6′,6″ seems to occur by π–σ interaction and is therefore small. For the same reason, a coupling with the Bu^t protons is no longer possible. Thus, we see the dramatic effect of the charge state which strongly influences the spin density distributions and hence the

EPR spectra mainly *via* conformational changes; an additional direct influence on the spin density can, however, not be excluded.

Conclusions

The *ortho*-, *para*-extended quinones **2**–**4** are better electron acceptors than the corresponding *para*-, *para*-extended compounds[9a] or simple quinones. This is reflected in their more positive redox potentials. In the series **1**–**4** the potential increases roughly with the number of keto groups, where the non-extended groups, as expected, exert a stronger effect. The positions of the individual peak-couples in CV seem to be mainly determined by structural, especially conformational, features responsible for electron conjugation and free spin delocalization. This is nicely demonstrated by the EPR/ENDOR spectra of the monoanion $\mathbf{3}^{\bullet -}$ and the trianion $\mathbf{3}^{\bullet 3-}$. Presumably, the effect of formal two-electron transfers observed in some cases, should also be attributed to such changes (for a summary see ref. 25). Generally, the spectra disclose the complex structure of the radical anions. The species are obviously not planar, and some protons maintain very low spin densities with unresolvable hfs. More detailed discussions will only be possible if structural determinations of at least some of the involved compounds are known; we are currently investigating this possibility. If we compare the highest reduction potentials for **2**, **3** and **4**, we see that they are never lower than about $-2.0 - -2.2$ V. This shows that **4** especially is a good electron acceptor, which can be used, if such a substance is needed, to allow successive (reversible) electron uptake at different potentials, as in the case of constructing polynary chips. Finally, to our knowledge, **4** is the first example of a quinoradialene derived from a [6]-radialene system **11** ($n = 6$). The corresponding [3]- and [4]-radialene systems (**11**, $n = 3$ and $n = 4$, respectively) are known and their redox activities well investigated by West and coworkers[22,26] (for a related compound see ref. 27).

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