Preparation and Characterisation of Thienonaphthoquinones and their Radical Ions

Joe A. Crayston,* Ahmed Iraqi, Philip Mallon and John C. Walton*
Department of Chemistry, University of St Andrews, St. Andrews, Fife, UK KY16 9ST

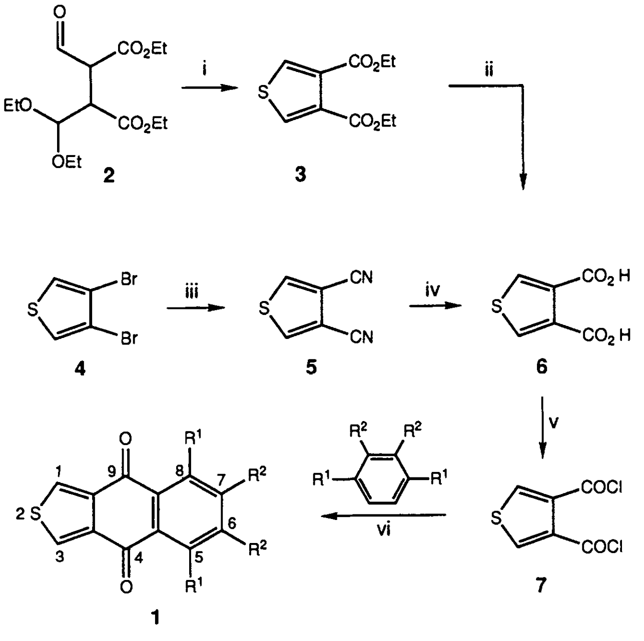
Three naphtho[2,3-*c*]thiophene-4,9-diones (thienonaphthoquinones) have been prepared and their redox properties studied by chemical, electrochemical and EPR spectroscopic methods. All three quinones were readily reduced electrochemically to the corresponding radical anions and subsequently to dianions. The cyclic voltammograms showed evidence of ion pairing of the dianions. All three quinones were also electrochemically oxidised to radical cations. The structures and thermodynamic properties of the quinones, the radical cations, radical anions and dianions were studied by the semi-empirical AM1 method. The experimental redox potentials were found to correlate with the computed energies of the appropriate frontier MOs. The electrochemically generated radical anions were observed by EPR spectroscopy and shown to decay with second-order kinetics. The rate constants increased as the electron-releasing character of the substituents in the benzene ring increased. The only EPR spectroscopically detectable radical cation was that from the 6,7-dimethoxynaphtho[2,3-*c*]thiophene-4,9-dione. Attempts by electrochemical and chemical methods to polymerise the thienonaphthoquinones were unsuccessful.

As part of a project designed to prepare paramagnetic polymers,[1] and in particular polymers based on thiophene and pyrrole, we sought to introduce stable free radical units into the 3- and/or 4-positions of the thiophene nucleus, while leaving the 2- and 5-positions open for subsequent oxidative coupling. Our initial target molecules were the thienonaphthoquinones (naphtho[2,3-*c*]thiophene-4,9-diones) (**1**), which, by analogy with the corresponding anthraquinones, ought to be readily reducible to stable radical anions, and possibly oxidisable to radical cations, either before or after oxidative coupling. The parent thienonaphthoquinone **1a** was previously synthesised in moderate yield by MacDowell and Wisowaty from the aluminium trichloride catalysed cyclic diacylation of benzene with thiophene-3,4-dicarbonyl chloride.[2] No other members of this class of heterocycle have been reported.

Results and Discussion

Synthesis of Thienonaphthoquinones.—We adopted the same basic method as MacDowell and Wisowaty in our investigation of the aluminium trichloride catalysed reaction of thiophene-3,4-dicarbonyl chloride with a series of aromatics (Scheme 1). Two methods of preparation were tried for the key intermediate in this synthesis *i.e.* thiophene-3,4-dicarboxylic acid (**6**). Ring closure of diethyl formyl-2-diethoxymethylsuccinate (**2**) with phosphorus pentasulfide, followed by hydrolysis of the diester **3** in ethanolic sodium hydroxide,[3] gave **6** in an overall yield of 24%. The second route involved conversion of 3,4-dibromothiophene (**4**) to the dicyanide **5** followed by hydrolysis to give **6**. We favoured this latter route because of the higher overall yield (59%) and better purity of the product. In an attempt to reduce this sequence by one step we examined the halogen–metal exchange of **4** with butyllithium, followed by carboxylation with carbon dioxide. However, only one bromine atom exchanged to yield 3-bromothiophene-4-carboxylic acid. Further treatment of this compound with more butyllithium and carbon dioxide produced no reaction.

Using the route of Scheme 1, three thienonaphthoquinones **1a–c** were obtained in low yields from **7** and the appropriate aromatic. Cyclic diacylation of several other substrates, including 1,4-dicyanobenzene, pyrrole and cyclohexene was attempted, but only the starting materials were recovered in each case.



	R^1	R^2
a	H	H
b	Me	Me
c	H	OMe

Scheme 1 *Reagents:* i, P_2S_5–PhMe; ii, NaOH–aq. EtOH; iii, CuCN–DMF; iv, KOH–$(CH_2OH)_2$; v, $SOCl_2$; vi, $AlCl_3$–$(CH_2Cl)_2$

Electrochemical and Spectroscopic Study of the Redox Reactions of Thienonaphthoquinones.—The cyclic voltammograms of **1a–c** were examined in dimethylformamide (DMF) and MeCN. Those recorded in DMF are shown in Fig. 1, the data for all solvents are summarised in Table 1. Difficulties were encountered in finding a common solvent for these materials; for example, **1c** was poorly soluble in polar solvents such as DMF [see Fig. 1(*c*)]. In each case two one-electron reductions were observed, both chemically reversible (i_{pa}/i_{pc} close to unity), but only the first wave was electrochemically reversible with ΔE_p close to 50–80 mV, as observed for ferrocene oxidation in the

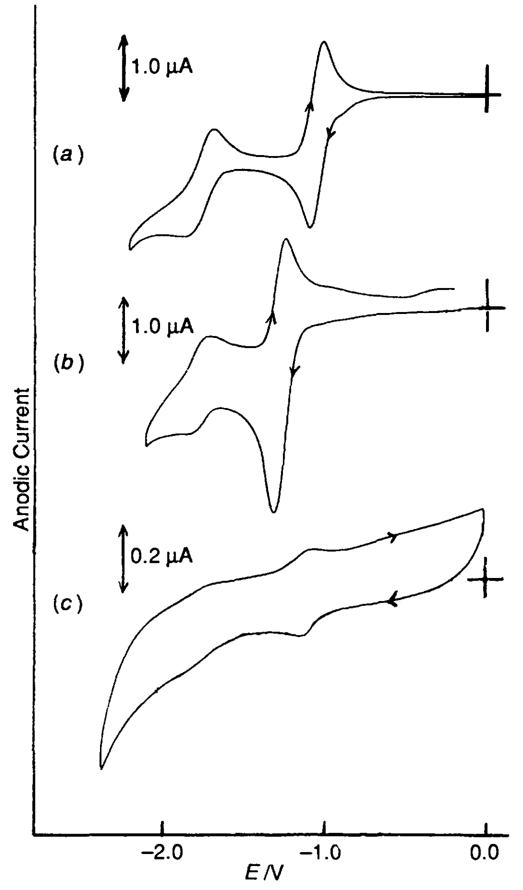


Fig. 1 Cyclic voltammetry (sweep rate 100 mV s^{-1}) of thienonaphthoquinones in DMF–0.1 mol dm^{-3} $TBAPF_6$ at 293 K: (*a*) **1a** (2 mmol dm^{-3}); (*b*) **1b** (2 mmol dm^{-3}); (*c*) **1c** (*ca.* 0.1 mmol dm^{-3}). Note the much lower solubility of **1c** in this medium.

Table 1 Cyclic voltammetric data for thienonaphthoquinones **1** and anthraquinone AQ[a]

	Solvent	E_{pc}/V	E_{pa}/V	$E^{\circ\prime}$/V	ΔE_p/mV
1a	DMF	−1.11	−1.05	−1.08	60
		−1.91	−1.72	−1.81	190
	MeCN	−1.26	−1.04	−1.14	220
		−2.16	−1.98	−2.07	180
	CH_2Cl_2[b]	—	+2.12	—	—
		—	+2.58	—	—
1b	DMF	−1.31	−1.25	−1.28	60
		−1.95	−1.78	−1.87	170
	MeCN	−1.68	−1.61	−1.65	70
		−2.10	−2.02	−2.06	80
	CH_2Cl_2[b]	—	+1.76	—	—
		—	+2.37	—	—
1c[c]	DMF	−1.15	−1.10	−1.13	50
		−1.82	−1.71	−1.77	110
	CH_2Cl_2[b]	+1.51	+1.59	+1.55	80
		—	+2.17	—	—
AQ	DMF	−0.91	−0.86	−0.89	50
		−1.76	−1.57	−1.67	190
	MeCN	−0.83	−0.88	−0.86	50
		−1.21	−1.41	−1.31	200
	CH_2Cl_2[b]	—	+2.90	—	—

[a] Volts *vs.* $Ag^{+/0}$ calibrated against the ferrocene couple in the same medium at 293 K (+440 mV *vs.* $Ag^{+/0}$). [b] Contains also 5% v/v CF_3COOH and 5% v/v $(CF_3CO)_2O$. [c] Insoluble in MeCN.

same solvent. The second wave was broader, indicating electrochemical irreversibility. In addition to being broad, the second wave had a smaller peak height compared with that of the first wave. The redox properties are typical of quinone reductions in non-aqueous dipolar aprotic solvents.[4,5] The two reduction processes correspond to reactions (1) and (2).

$$Q + e^- \longrightarrow Q^{\bullet -} \qquad (1)$$

$$Q^{\bullet -} + e^- \longrightarrow Q^{2-} \qquad (2)$$

Cyclic voltammetry of anthraquinone (AQ) was carried out under our conditions and the data is supplied in Table 1 for comparison purposes. Clearly, our new quinones were reduced less readily than AQ; the E° values for the first wave (E°_1) became more negative in the order AQ > **1a** > **1c** > **1b**, a reflection of the progressive introduction of electron-releasing groups into the molecules. This is expressed more quantitatively by a plot of E°_1 *vs.* the energy of the LUMO of the neutral quinone calculated by the AM1 method[6] (Fig. 2). The regression line was $E^\circ_1/\mathrm{V} = -2.19\text{–}0.94E(\mathrm{LUMO})/\mathrm{eV}$ ($r^2 = 0.980$) the gradient of this line can be compared with the gradient of −0.412 reported recently by Sasaki *et al.*[7] who, however, used the older and less sophisticated CNDO/2 calculation method.

The electrogenerated radical anion $AQ^{\bullet -}$ is chemically stable on the cyclic voltammetric time-scale, and indeed no decay for $AQ^{\bullet -}$ in 50% H_2O–DMF was observed by Umemoto after several minutes,[8] although recent papers have reported evidence for the disproportionation of $AQ^{\bullet -}$ over the longer timescales associated with controlled potential electrolysis.[9–11] In contrast, the electrogenerated radicals $\mathbf{1}^{\bullet -}$ decayed slowly when monitored by EPR spectroscopy (see below).

The lower observed currents for the E_2 process compared with the first wave can also be related to ion-pairing between the Q^{2-} anion and the cation of the supporting electrolyte, which causes the quasi-reversible nature of the second reduction process and leads to a positive shift in E_2 (as Q^{2-} becomes more stable)[12,13] [eqn. (3)]. Presumably, since the cation is present

$$Q^{2-} + M^+ \rightleftharpoons [Q^{2-}\cdots M^+]^- \qquad (3)$$

in vast excess, an ion-pair forms rather than an ion triple as sometimes observed in EPR spectra.[14] The extent of ion-pair formation is greater for less well solvated Q^{2-} species or if Q^{2-} is generated in a less polar solvent. Ion-pair formation is believed to cause the opposite dependence of the redox potential E_2 on the redox orbital ($Q^{\bullet -}$ LUMO) energy and this was indeed observed (Fig. 2) the regression line being $E^\circ_2/\mathrm{V} = -2.36 + 0.21E(\mathrm{LUMO})/\mathrm{eV}$ where LUMO energies were computed for the radical anion ($r^2 = 0.860$). Again, similar correlations were observed by Sasaki *et al.*[7] Other effects of ion-pairing are manifested in the data in Table 1: (1) the separation between the redox potentials ($E_1 - E_2$) is larger for **1a** in the more polar solvent DMF where there is less ion-pairing, and (2) the increasingly more 'hydrophobic' quinones (in the order AQ < **1a** < **1c** < **1b**) exhibit more ion-pairing in DMF since they are less well solvated by this solvent, and this leads to a larger ($E_1 - E_2$) separation. To a small extent also the reduced wave heights for the $Q^{2-/-}$ reductions are attributed to the reduced diffusion coefficients for the $[Q^{2-}\cdots M^+]^-$ ion pairs.

The quinone containing two methoxy groups, **1c**, also has a chemically reversible, quasi-reversible oxidation at +1.38 V; this potential and the extreme anodic potentials of the other quinones were found roughly to correlate with the AM1 calculated energies of the neutral quinone HOMOs *i.e.* $E^a_p/\mathrm{V} =$

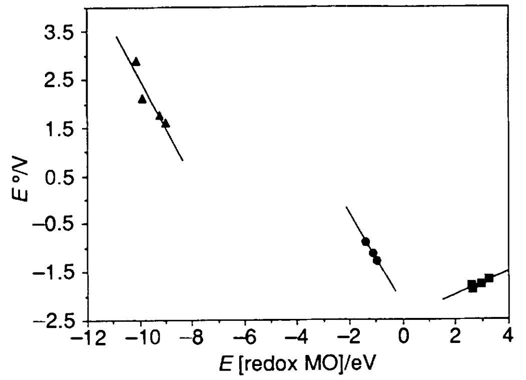


Fig. 2 Correlation of the redox potentials of anthraquinone and **1a–c** with AM1 computed frontier orbital energies: ▲, $E_p{}^a$ *vs.* E(HOMO) of quinones; ●, E_1° *vs.* E(LUMO) of quinones; ■, E_2° *vs.* E(LUMO) of radical anions

Table 2 AM1 computed thermodynamic parameters for thienonaphthoquinones **1** and anthraquinone AQ[a]

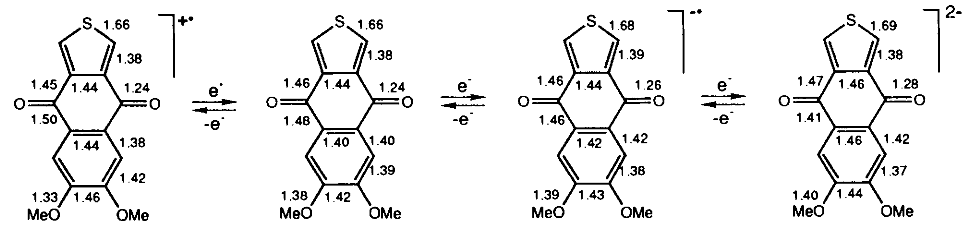
	Radical cation	Neutral quinone	Radical anion	Dianion
AQ				
ΔH_f°	210.3	−5.9	−51.4	9.3
E(HOMO)	−13.263	−10.126	−2.626	2.056
E(LUMO)	−8.576	−1.389	3.270	7.401
1a				
ΔH_f°	206.3	−2.4	−36.5	24.8
E(HOMO)	−13.334	−9.893	−2.393	2.261
E(LUMO)	−8.202	−1.123	2.577	6.887
1b				
ΔH_f°	174.7	22.5	−51.5	5.5
E(HOMO)	−12.919	−9.253	−2.355	2.060
E(LUMO)	−7.519	−0.990	2.633	6.713
1c				
ΔH_f°	110.3	−73.4	−117.4	−58.6
E(HOMO)	−12.795	−9.008	−2.643	1.858
E(LUMO)	−7.081	−1.092	2.950	6.522

[a] ΔH_f° in kcal mol^{-1} (1 cal = 4.18 J), orbital energies in eV.

−7.66–1.02E(HOMO)/eV with $r^2 = 0.845$ (Fig. 2). Evidence was sought for electropolymerisation of the thiophene groups during both potential sweep and potentiostatic experiments, however, no characteristic build-up in background current or polymer nucleation loops was observed. This clearly related to the very high potentials for formation of the thiophene cations and the deactivating effect of the electron-withdrawing quinone carbonyl groups on the thiophene ring. Even in the CH_2Cl_2–CF_3COOH–$(CF_3CO)_2O$ (20 : 1 : 1) medium (which is known to stabilise cations) there was evidence only for adsorption in the case of **1c**. Chemical methods of polymerisation employing sulfuric acid or iron(III) chloride also failed, as did an attempt to couple **1b** with 2-bromothiophene catalysed by tetrakis(triphenylphosphine)palladium(0).

The structures and thermodynamic properties of the thienonaphthoquinones and anthraquinone were investigated by the semiempirical AM1 method.[6] Structures were fully optimised using the UHF version for the open-shell radical cations and radical anions and the RHF version for the neutral quinones and the dianions. For each series all members were computed to be essentially planar, partial structures are given in Scheme 2 for the species based on the dimethoxy quinone skeleton. The calculated bond lengths in the parent quinone were appropriate for 'aromatic' benzene and thiophene rings. Structural adjustments were not large on oxidation or reduction; the main changes were small increases in the benzene ring bond lengths on either oxidation or reduction, progressive increase in the C=O bond length with each reduction and a significant decrease in the MeO–C bond length on oxidation. The computed enthalpies of formation of each species and the energies of the frontier MOs are given in Table 2. The good correlations of these quantities with the redox potentials of the quinones have been referred to above. The doublet MOs of the radical cations and radical anions were seriously contaminated with higher multiplicity states. Not surprisingly therefore the computed spin densities did not correlate well with the experimental hyperfine splittings (see below). The computed enthalpies of formation predict that the first reduction will be exothermic for all three quinones but that the second reduction, and the oxidation steps will be strongly endothermic. However, the computed ΔH_f for AQ was disappointingly far from the experimental value (−23 kcal mol^{-1})[15] so that no reliance can be placed on the enthalpies of the other species.

EPR spectra of the radical anions derived from **1** were obtained by means of a flat quartz cell fitted with a platinum gauze working electrode and a tungsten loop, sometimes platinum, counter electrode. The thienonaphthoquinone and tetrabutylammonium tetrafluoroborate (TBAT) or tetrabutylammonium hexafluorophosphonate ($TBAPF_6$) were dissolved in acetonitrile or DMF and electrolysed at various constant potentials in the cavity of an EPR spectrometer. Electrolysis of **1a** in the −1.3 to −2.0 V range gave rise to a strong quintet signal which we attribute to the radical anion **1a**$^{\bullet -}$. Two of the three pairs of equivalent hydrogens couple with the unpaired electron and the hyperfine splittings (hfs) (see Table 3) were comparable in magnitude to those of the anthraquinone radical anion [$a(H^{1,4,5,8}) = 0.065$, $a(H^{2,3,6,7}) = 0.104$ mT].[16] The tetramethyl derivative, **1b**, gave a rather weaker septet of triplets spectrum on electrolysis at −2.3 V in either solvent. The hfs (Table 3) indicated that the unpaired electron coupled with the thienyl hydrogens ($H^{1,3}$) and one pair of methyl hydrogens from the benzene ring. Electrolysis of the 6,7-dimethoxy derivative, **1c**, in the −1.0 to −3.0 V range gave rise to a triplet of triplets spectrum (Fig. 3). Thus, there was no coupling of the unpaired electron with the methoxy hydrogens. The tentative assignments of the hfs to particular hydrogens in Table 3 were made on the assumption that spin density is small at the 6- and 7-positions of the benzene rings of all three anions so that hfs from hydrogens,



Scheme 2

Table 3 EPR hfs of radical ions derived from thienonaphthoquinones[a]

	Solvent	hfs		
		$a(H^{1,3})$	$a(R^1)$	$a(R^2)$
Radical anion				
$R^1 = R^2 = H$, **1a**$^{\bullet -}$	DMF[b]	0.141 (2 H)	0.141 (2 H)	—
$R^1 = R^2 = Me$, **1b**$^{\bullet -}$	CH_3CN	0.05 (2 H)	0.15 (6 H)	—
$R^1 = H$, $R^2 = OMe$, **1c**$^{\bullet -}$	CH_3CN	0.06 (2 H)	0.16 (2 H)	—
Radical cation				
$R^1 = H$, $R^2 = OMe$, **1c**$^{\bullet +}$	CH_3CN	—	0.053 (2 H)[c]	0.341 (6 H)

[a] hfs in mT; measured at 20 °C. [b] Identical hfs in CH_3CN. [c] Speculative assignment; could be $H^{1,3}$ (see the text).

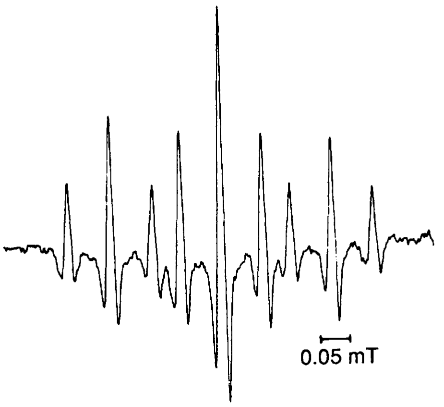


Fig. 3 9.7 GHz EPR spectrum of **1c**$^{\bullet -}$ in CH_3CN at 20 °C, applied potential −2.0 V, second derivative presentation

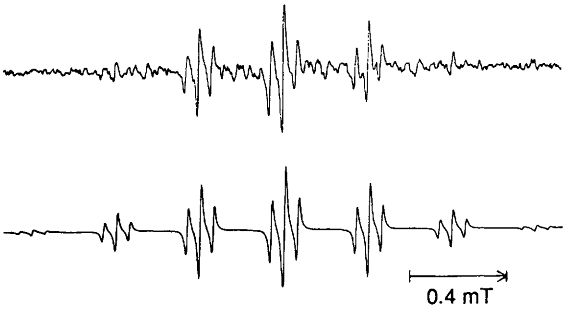


Fig. 4 9.7 GHz EPR spectrum attributed to **1c**$^{\bullet +}$ in CH_3CN at 20 °C, applied potential +1.5 V: (*a*) upper spectrum experimental, (*b*) lower spectrum computer simulation with hfs of Table 3

Table 4 Second-order kinetic decay parameters for thienonaphthoquinone radical anions[a]

Radical anion	$2k/dm^3\ mol^{-1}\ s^{-1}$	$t_{\frac{1}{2}}/s$
1a$^{\bullet -}$	1.2	91
1b$^{\bullet -}$	8.5	23
1c$^{\bullet -}$	86	8.8

[a] In CH_3CN at 20 °C.

methyl, or methoxy groups at these sites will be small and unresolved. The overall small magnitude of the hydrogen hfs indicated that, as expected, most spin density was associated with the oxygen atoms. However, it is interesting to note that unpaired spin is delocalised into both the thiophene and benzene rings adjacent to the central quinone structural unit. Spin densities calculated by the AM1-UHF method showed no correlation with the experimental hfs.

The CVs indicated that each thienonaphthoquinone was readily oxidised to the corresponding radical cation (see above). Attempts were made to observe these cations by EPR spectroscopy using the same electrochemical cell. For **1a**, **b** no radical cations could be detected in acetonitrile or dichloromethane with applied potentials in the range +0.5 to +3.0 V. However, for the **1c** spectrum a second species, additional to that of the radical anion, began to appear after several minutes electrolysis at −0.50 V in CH_3CN and became the sole paramagnetic intermediate for potentials in the range +0.5 to +1.5 V (Fig. 4). This spectrum was readily analysed as a septet of triplets [Fig. 4(*b*)] and we attribute it to the radical cation **1c**$^{\bullet +}$. The fact that it began to appear on the EPR spectra at negative applied potentials can probably be explained by migration of radical cations formed at the loop counter electrode into the sensitive area of the EPR cavity. The hfs (Table 3) are comparable in magnitude to those of radical cations derived from methoxybenzenes, *e.g.*, for the cation of 1,4-dimethoxybenzene values of $a(OCH_3) = 0.330$ and $a(H^{1,2,4,5}) = 0.156$ were obtained, and for the cation of 1,2,4,5-tetramethoxybenzene hfs of $a(OCH_3) = 0.221$, $a(H^{3,6}) = 0.089$ mT were obtained.[17–19] It is probable that the electron donor methoxy substituents of **1c**$^{\bullet +}$ stabilise it in comparison with **1a**, **b**$^{\bullet +}$. The lifetimes of the last two cations are therefore too short for their concentrations to build up sufficiently for EPR detection. We have tentatively assigned the observed hfs to hydrogens of the benzene rings by analogy with the cations of methoxybenzenes; a consequence of this is that the spin density in the thiophene ring is undetectably small. The AM1-UHF calculations showed very small and virtually indistinguishable spin densities for the thiophene and benzene hydrogens.

The EPR signals of the radical anions **1**$^{\bullet -}$ decayed sufficiently slowly for the kinetics of their disappearance to be determined by repeated scanning over a period of several minutes. Using this method the radical anion concentrations were determined as a function of time. The decay of all three anions showed an initial abnormal region of strong curvature before settling into a steady second order region. For **1a**$^{\bullet -}$, which had the highest initial concentration, the abnormal decay lasted for about 500 s, but for the other two anions this region was < 50 s. In slow reactions of this general type an equilibrium is sometimes set up between the radicals and an unstable dimer intermediate and this can lead to first-order or intermediate-order behaviour.[20,21] This seems unlikely in the present instance because normal second order kinetics supervened after the initial period. It is most probable therefore that this phenomenon was due to disturbances in the concentrations caused by migration of the radical anions into the sensitive area of the cavity. Discounting these abnormal regions, the decays fitted second-order behaviour better than first order (see Fig. 5) and the derived rate constants (2*k*) and half-lives ($t_{\frac{1}{2}}$) are in Table 4.

Although second-order termination reactions of many neutral radicals are very fast, radicals which do not produce

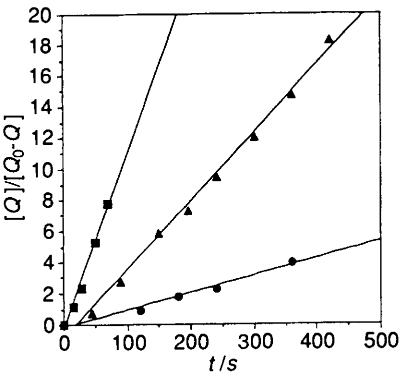


Fig. 5 Second-order plots of radical anion concentration data *vs.* time: ●, $\mathbf{1a}^{\bullet -}$; ▲, $\mathbf{1b}^{\bullet -}$; ■, $\mathbf{1c}^{\bullet -}$

thermodynamically stable products generally decay rather slowly. The observed second-order decay of $\mathbf{1}^{\bullet -}$ could be due to disproportionation [eqn. (4)]. Obviously, this process would be

$$Q^{\bullet -} + Q^{\bullet -} \longrightarrow Q + Q^{2-} \qquad (4)$$

slower than for neutral radicals because of electrostatic repulsion between the radical anions in the encounter complex. In addition, the dianion will be thermodynamically destabilised, and hence the slow decay is in accord with expectation. Alternatively, the second-order decay could be due to combination of the radical anions which would also be disfavoured electrostatically. The initial product would be a dianion formed either by oxygen-to-carbon coupling or oxygen-to-oxygen coupling. This dianion is expected to be thermodynamically unstable. The termination rate appears to be sensitive to electronic effects because the rate constants increase as the electron-releasing character of the substituents in the benzene ring increases (Table 4).

Experimental

^{1}H NMR spectra were recorded using a Varian EM-360 NMR spectrometer (60 MHz), a Bruker WP80 NMR spectrometer (80 MHz), a Varian Gemini-200 spectrometer (200 MHz) and a Bruker AM300 NMR spectrometer (300 MHz). ^{13}C NMR spectra were recorded using a Varian Gemini-200 spectrometer (50 MHz) and a Bruker AM300 NMR spectrometer (75.5 MHz) using DEPT-135 pulse techniques to assign peaks when necessary. FT–IR spectra were obtained with a Perkin-Elmer 1710 infra-red Fourier transform spectrometer, and were run as liquid film, Nujol mull, or KBr disc samples. Mass spectra were recorded using an AEI MS 902 spectrometer. GC–MS data was obtained with a Finnigan Incos 50 quadrupole mass spectrometer coupled to a Hewlett-Packard HP5890 capillary gas chromatograph. Cyclic voltammetric data were recorded using a Pine Instruments RDE 4 (EG & G, Wokingham, UK) with a Graphtec XY recorder WX2300. EPR spectra were recorded with a Bruker ER 200D spectrometer operating at 9.7 GHz with 100 kHz modulation; the controlled potentials across the electrochemical EPR cell being generated with a potentiostat. The electrochemical EPR cell consisted of a flat quartz cell (5 × 1.5 cm) of i.d. 0.15 mm. The platinum gauze working electrode (*ca.* 0.5 × 3 cm) was positioned in the centre surrounded by a loop of tungsten wire as the counter electrode. The reference electrode was silver metal. In later designs, aimed at ease of cleaning, a 0.5 mm diameter Pt wire counter electrode was positioned above the quartz cell region. Solutions were introduced into the cell with syringes and degassed *in situ* by bubbling nitrogen for *ca.* 10 min. The concentrations of the radical anions were determined by double integration of the spectra and comparison with a known concentration of 2,2-diphenyl-1-picrylhydrazyl in acetonitrile using the usual procedure.[22] The kinetics of the radical anion decay was followed by recording part of each spectrum at timed intervals after cutting off the applied potential.

Thiophene-3,4-*dicarboxylic Acid* (**6**) via *Diethyl Thiophene*-3,4-*dicarboxylate*.[3]—Dry toluene (210 cm^3), diethyl 1-formyl-2-diethoxymethylsuccinate (50.0 g, 164.5 mmol) and phosphorus pentasulfide (35.48 g, 79.8 mmol) were placed in a flask fitted with a stirrer and reflux condenser. The mixture was stirred rapidly under reflux for 2 h. After cooling the toluene was decanted off from the dark resin. The resin was washed with fresh toluene and this too was decanted off. The combined toluene solutions were washed with water (*ca.* 160 cm^3) and twice with ice-cold 2 mol dm^{-3} sodium hydroxide solution (2 × *ca.* 160 cm^3). The toluene solution was then dried over magnesium sulfate and evaporated to dryness. The residual liquid was distilled and the fraction boiling from 100 °C to 160 °C at 5 Torr was collected. This was hydrolysed by heating with a solution of sodium hydroxide (6.46 g, 161.5 mmol) in 16 cm^3 of water and 16 cm^3 of ethanol for 30 min. The red solution was then evaporated to dryness at reduced pressure. Warm water (50 cm^3) was added to the solid residue and the resulting solution acidified with concentrated hydrochloric acid, and chilled. The precipitate which separated was filtered and washed with cold ether. This yielded 6.79 g (39.44 mmol, 24%) of thiophene-3,4-dicarboxylic acid, which was used without further purification. δ_H(200 MHz; [^{2}H$_6$]DMSO) 8.20 (s, 2 H) and 8.05 (br s, 2 H); δ_C(50 MHz; [^{2}H$_6$]DMSO) 135.54 (CH), 136.18 (C) and 164.94 (COOH).

3,4-*Dicyanothiophene* (**5**).[2]—3,4-Dibromothiophene[23] (22.36 g, 92.4 mmol) and cuprous cyanide (24.10 g, 269.0 mmol) in dry DMF (25 cm^3) was stirred under reflux for 4 h. The dark solution thereby formed was poured into a solution of hydrated ferric chloride (93.0 g in 162 cm^3 of 1.7 mol dm^{-3} hydrochloric acid), and maintained at 60 °C to 70 °C for 0.5 h. When cool this mixture was extracted five times with methylene chloride, each extract being washed successively with two portions of 6.0 mol dm^{-3} hydrochloric acid, water, saturated sodium hydrogen carbonate solution and again with water. The methylene chloride layers were combined, dried over magnesium sulfate and then evaporated to dryness. The crude solid produced was then sublimed at 0.1 Torr to give 10.0 g (74.6 mmol, 81%) of 3,4-dicyanothiophene. ν_{max}(Nujol)/cm^{-1} 2210 (CN).

Thiophene-3,4-*dicarboxylic Acid*.[2]—3,4-Dicyanothiophene (8.44 g, 62.9 mmol) and potassium hydroxide (23.30 g, 415.3 mmol) in ethylene glycol (90 cm^3) were stirred under reflux for 4 h. On cooling this was poured into water and the resulting solution was washed with diethyl ether. The aqueous phase was cooled in an ice bath and acidified with 2 mol dm^{-3} hydrochloric acid. The white precipitate produced was filtered and taken up in ether. The aqueous filtrate was extracted thoroughly with ether and all the ethereal solutions were combined and dried over magnesium sulfate. Removal of the solvent yielded 9.7 g (56.3 mmol, 90%) of thiophene-3,4-dicarboxylic acid. δ_H(60 MHz; [^{2}H$_6$]DMSO) 10.18 (br s, 2 H) and 8.25 (s, 2 H). ν_{max}(Nujol)/cm^{-1} 1690 (C=O).

Reaction of **4** *with Butyllithium and Carbon Dioxide*.—To a stirred solution of butyllithium (18.4 cm^3, 2.5 mol dm^{-3} in hexane), at −70 °C under a dry nitrogen atmosphere, was added 3,4-dibromothiophene (5.0 g, 20.67 mmol) in dry diethyl ether (50 cm^3), over a period of 10 min. The resulting mixture was stirred at −70 °C for 20 min. Carbon dioxide was then bubbled through the solution for approximately 2.5 h, at which point water was added and the solution washed with ether. The ether layers were washed with water and the combined aqueous layers acidifed with 1.0 mol dm^{-3} hydrochloric acid and left at 5 °C overnight. No precipitate separated and thus the solution was extracted with ether and dried over magnesium sulfate. Removal of the solvent produced 3.95 g (18.6 mmol, 90%) of 3-bromothiophene-4-carboxylic acid. δ_H(60 MHz; [$^2H_6$]DMSO) 12.4 (s, 1 H) and 8.4 (m, 2 H); ν_{max}(Nujol)/cm^{-1} 1710 (C=O); *m/z* 208 (M$^+$, 36%), 206 (M$^+$, 36), 191 (29), 189 (31), 128 (22), 111 (28), 82 (23), 81 (31), 73 (15), 60 (28) and 59 (19).

Naphtho[2,3-c]*thiophene*-4,9-*dione* (*Tetrahydrothienonaphthoquinone*) (**1a**).[2]—Thiophene-3,4-dicarboxylic acid (2.0 g, 11.62 mmol) in thionyl chloride (5 cm^3) was stirred under reflux for 1 h. The excess thionyl chloride was distilled off at reduced pressure, with the final traces being azeotropically removed with benzene. The dark brown material thereby obtained was then left under vacuum in a desiccator for 1 h. The dicarbonyl chloride was taken up in dry 1,2-dichloroethane (12 cm^3) and added dropwise to a stirred suspension of aluminium trichloride (3.49 g, 26.17 mmol) in dry 1,2-dichloroethane (12 cm^3) maintained at 4 °C. This mixture was stirred at 4 °C for 10 min, at which point a solution of dry benzene (1.1 cm^3, 12.31 mmol) in dry 1,2-dichloroethane (6 cm^3) was slowly added. The resulting solution was stirred at room temperature for approximately 18 h. The solution was then poured into a mixture of ice and hydrochloric acid (15 cm^3, 2 mol dm^{-3}). Chloroform was added and the solution shaken vigorously. It was then extracted with chloroform and the organic extracts were washed with saturated sodium hydrogen carbonate solution, followed by water and dried over magnesium sulfate. The solution was concentrated down to about 70 cm^3, loaded onto a column of neutral alumina (Brockmann type 1) and eluted with 400 to 450 cm^3 of chloroform. The chloroform was removed and the product was recrystallised from dichloromethane to yield 0.24 g (9.6%) of (**1a**), m.p. 283 °C (sublimes). δ_H(300 MHz; CDCl$_3$) 7.8 (m, 2 H), 8.3 (m, 2 H) and 8.37 (s, 2 H); δ_C(75.5 MHz; CDCl$_3$) 127.73 (CH), 132.76 (CHS), 134.12 (CH), 134.78 (C), 137.25 (C) and 179.25 (C=O); ν_{max}(Nujol)/cm^{-1} 1670 (C=O); *m/z* 214 (M$^+$, 82%), 186 (92), 158 (100), 114 (46), 113 (32), 93 (18), 82 (21), 81 (20), 79 (22), 76 (21), 74 (14) and 69 (21) (Found: M$^+$, 214.0087. Calc. for $C_{12}H_6O_2S$, *M*, 214.0089).

Tetramethylthienonaphthoquinone (**1b**).—The procedure was essentially the same as for (**1a**) except that 1,2,3,4-tetramethylbenzene was used as the aromatic. The crude product was recrystallised from ethyl acetate, yield 11%, m.p. 238 °C, δ_H(300 MHz; CDCl$_3$) 2.37 (s, 6 H), 2.71 (s, 6 H) and 8.14 (s, 2 H); δ_C(75.5 MHz; CDCl$_3$) 17.72 (CH$_3$), 19.01 (CH$_3$), 130.50 (CH), 132.99 (C), 138.38 (C), 138.81 (C), 143.05 (C) and 183.00 (C=O); *m/z* 270 (M$^+$, 100%), 269 (41), 255 (38), 227 (21), 226 (11), 199 (20), 198 (13), 196 (12), 184 (18), 165 (15), 152 (10), 145 (10), 127 (11), 115 (12) and 111 (11) (Found: M$^+$, 270.0715. $C_{16}H_{14}O_2S$ requires *M*, 270.0715) (Found: C, 70.7; H, 5.1. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.2%).

Dimethoxythienonaphthoquinone (**1c**).—The procedure was essentially the same as for **1a** except that 2-methoxyanisole was used as the aromatic. The crude material was recrystallised from ethyl acetate then dichloromethane, yield 16%, m.p. 260 °C, δ_H(60 MHz; CDCl$_3$) 4.03 (s, 6 H), 7.60 (s, 2 H) and 8.20 (s, 2 H); *m/z* 274 (M$^+$, 98%), 259 (21), 203 (68), 160 (50), 132 (37), 131 (22), 111 (38), 110 (39), 82 (49), 81 (43), 77 (20), 69 (27), 63 (45), 62 (44), 53 (60) and 50 (72) (Found: M$^+$, 274.0294. Calc. for $C_{14}H_{10}O_4S$: *M*, 274.0300).

Electrochemical Polymerisation of the Thienonaphthoquinones.—Saturated solutions (*ca.* 0.6 mmol dm^{-3}) of the thienonaphthoquinones in acetonitrile with TBAT or TBAPF$_6$ as supporting electrolyte were prepared. Three polymerisation techniques were then attempted with each monomer solution: (*i*) the solutions were subjected to a potential repeatedly scanning from −2.0 V to +2.0 V, (*ii*) the solutions were subjected to a potential repeatedly scanning from 0.0 V to +2.0 V, (*iii*) the solutions were subjected to a constant potential of about +2.0 V. However, no polymer formed with any of these methods. The solvent system CH_2Cl_2–CF_3COOH–$(CF_3CO)_2O$ (20:1:1) medium (which is known to stabilise cations) also failed to lead to polymerisation.

Chemical Polymerisation of the Thienonaphthoquinones.—(*a*) *Sulfuric acid.*[24] 1 cm^3 of concentrated sulfuric acid was added to the tetrahydrothienonaphthoquinone (10 mg, 0.047 mmol), upon which the colour instantly changed from yellow to crimson and the mixture was stirred overnight. The reaction mixture was then poured into 20 cm^3 of methanol and stirred overnight. No polymer precipitated from the solution which was thoroughly extracted with chloroform and the starting material was reclaimed.

(*b*) *Ferric chloride.* Tetrahydrothienonaphthoquinone (0.10 g, 0.47 mmol) and ferric chloride (0.038 g, 0.23 mmol) were taken up in nitromethane (0.5 cm^3) and dichloromethane (25 cm^3) and stirred for 48 h. The solid precipitate was then separated. Examination revealed this precipitate to be the starting thienonaphthoquinone, which had presumably precipitated owing to solvent evaporation. However, if the procedure was repeated with more solvent to allow for this no precipitate was produced and no polymer was isolated.

Attempted Coupling of 2-*Bromothiophene and Tetramethylthienonaphthoquinone–Zinc Chloride.*[25]—To a stirred solution of **1b** (0.10 g, 0.37 mmol) in dry THF (40 cm^3), at 0 °C under nitrogen, was added 1.6 mol dm^{-3} butyllithium (0.5 cm^3, 0.80 mmol) in hexane. This mixture was stirred at 0 °C for 3.5 h and then added, *via* a double-ended catheter, to a stirred solution of zinc chloride (0.11 g, 0.81 mmol) in dry THF (30 cm^3), under nitrogen at room temperature. This solution was then stirred for a further hour. Prior to use the zinc chloride had been heated at 150 °C with stirring under nitrogen for 30 min. The thienyl–zinc chloride solution was then added *via* a double-ended catheter to tetrakis(triphenylphosphine)palladium(0) (5.6 mg, 0.0048 mmol) and 2-bromothiophene (0.12 g, 0.74 mmol) under nitrogen and the resulting solution was stirred for 30 min. The temperature was raised to about 50 °C and stirring continued for 24 h. Dilute HCl (5 cm^3; 0.1 mol dm^{-3}) was added to the cooled reaction mixture followed by extraction with ether. The combined organic extracts were washed with saturated NaHCO$_3$, water and dried over MgSO$_4$. Removal of the solvent produced crude material, which was found to consist of 2-bromothiophene and the tetramethylthionaphthoquinone.

Acknowledgements

We thank the Science and Engineering Research Council for financial support of this work (GR/F 54075).

References

1 (*a*) F. MacCorquodale, J. A. Crayston, J. C. Walton and D. J. Worsfold, *Tetrahedron Lett.*, 1990, **31**, 771; (*b*) J. A. Crayston, C. Kakouris and J. C. Walton, *Magn. Reson. Chem.*, 1992, **30**, 77; (*c*) C. Kakouris, J. A. Crayston and J. C. Walton, *Synth. Metals*, 1992, **48**, 65; (*d*) J. A. Crayston, A. Iraqi, P. Mallon, J. C. Walton and D. P. Tunstall, *Synth. Metals*, 1993, **55**, 867; (*e*) J. A. Crayston, A. Iraqi, P. Mallon, J. C. Walton and D. P. Tunstall, *Mol. Cryst. Liq. Cryst.*, in press.

2 D. H. W. MacDowell and J. C. Wisowaty, *J. Org. Chem.*, 1972, **37**, 1712.

3 E. C. Kornfield and R. G. Jones, *J. Org. Chem.*, 1954, **19**, 1671.
4 J. Q. Chambers, in *Chemistry of the Quinonoid Compounds*, ed. S. Patai, Vol. I, Part II, Wiley, New York, 1974, ch. 14.
5 J. Q. Chambers, in *Chemistry of the Quinonoid Compounds*, eds. S. Patai and Z. Rappoport, Vol. II, Part I, Wiley, New York, 1988, ch. 12.
6 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902; J. J. P. Stewart, *QCPE*, No. 455, University of Indiana, Indiana, 1987.
7 K. Sasaki, T. Kashimura, M. Ohura, Y. Ohsaki and N. Ohta, *J. Electrochem. Soc.*, 1990, **137**, 2437.
8 K. Umemoto, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1058.
9 V. Koshy, V. Swayamabunathan and N. Periasamy, *J. Electrochem. Soc.*, 1980, **127**, 2761.
10 K. Pekmez, M. Can and A. Yildiz, *Electrochim. Acta*, 1993, **38**, 607.
11 T. C. Simpson and R. R. Durand, Jr, *Electrochim. Acta*, 1990, 1399.
12 T. Nagaoka, S. Okazaki and T. Fujinaga, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1967.
13 C. Rüssel and W. Jaenicke, *J. Electroanal. Chem.*, 1983, **149**, 101; J. Posdorfer, M. Olbrich-Stock and R. N. Schindler, *Z. Phys. Chem.*, 1991, **171**, 33.
14 K. S. Chen and N. Hirota, *J. Am. Chem. Soc.*, 1972, **94**, 5550.
15 A. Magnus, *Z. Phys. Chem.*, 1956, **9**, 141.
16 J. A. Pedersen, *CRC Handbook of EPR Spectra from Quinones and Quinols*, CRC Press, Cleveland, 1985.
17 R. Hulme and M. C. R. Symons, *Proc. Chem. Soc.*, 1963, 241; *J. Chem. Soc.*, 1965, 1120.
18 A. Zweig, W. G. Hodgson and W. H. Jura, *J. Am. Chem. Soc.*, 1964, **86**, 4124.
19 G. Vincow, in *Radical Ions*, ed. E. T. Kaiser and L. Kevan, Wiley, New York, 1968, ch. 4, p. 151.
20 S. A. Weiner and L. R. Mahoney, *J. Am. Chem. Soc.*, 1972, **94**, 5029.
21 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 193.
22 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317; M. Castaing, M. Ratier, P. Blum and A. G. Davies, *J. Chem. Soc., Perkin Trans. 2*, 1979, 287.
23 S. Gronowitz, *Acta Chem. Scand.*, 1959, **13**, 1045.
24 F. Wudl, M. Kobayashi and A. J. Heeger, *J. Org. Chem.*, 1984, **49**, 3382.
25 A. Petter, M. Rowlands and G. Clements, *Synthesis*, 1987, 51.

Paper 3/02468G
Received 29th *April* 1993
Accepted 3rd *June* 1993