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Substituent Effects on Redox Potentials of Novel Amphoteric Terphenoquinone Analogues. Unsymmetrically Substituted 2,5-Bis(4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophenes

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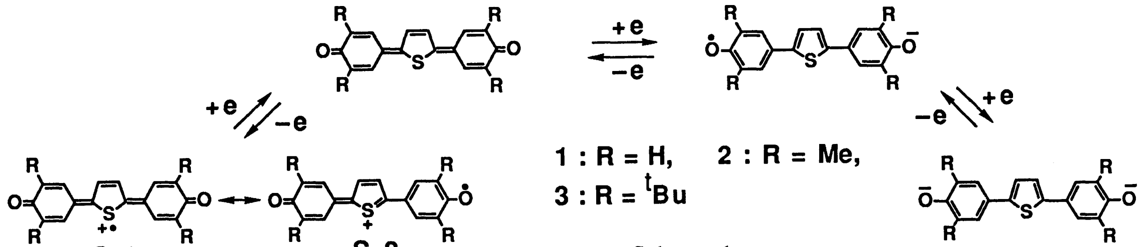
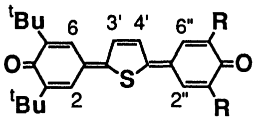
The unsymmetrically substituted derivatives of the title heterocycle-extended quinone have been synthesized and the substituents effects on their electrochemical properties have been investigated. The first reduction potentials and the first oxidation potentials correlate well with the Hammett $\Sigma\sigma_p$ and $\Sigma\sigma_p^+$ constants of the substituents, respectively.

Benzoquinones have occupied the most important positions in the chemistry of organic redox systems and have been used for the widespread studies on pure and applied chemistry due to their reversible single-electron accepting ability.1) Organic redox reagents exhibiting an intense absorption in the visible or near-infrared region in their electronic spectra have attracted current interest since they have high utility potential for electrochromic2) and optoelectronic3) display devices, optical storage media,4) or electron transfer mediators in the conversion of solar energy into chemical energy.5) We have recently synthesized conjugation-extended quinones **1**, **2**, and **3**,6) involving a central thienoquinonoid ring, as the first terphenoquinone analogues, and have disclosed that they show an intense absorption in the visible wave length region of 500—650 nm and undergo amphoteric single-electron three-stage redox reactions as shown in Scheme 1.



Scheme 1.

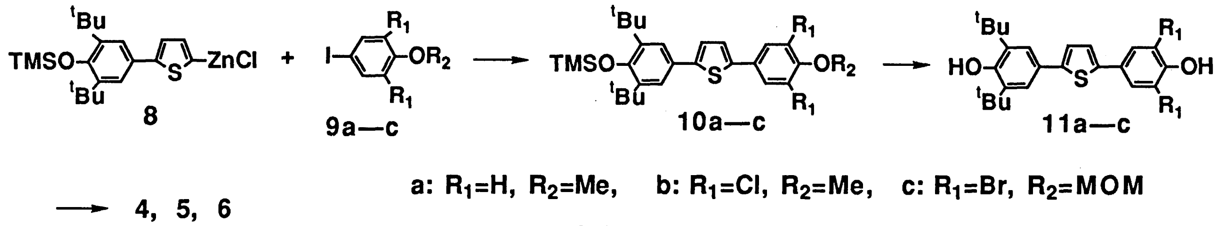
However, there has little been known on the strategies to control their redox potentials, amphotericities, and absorption spectra. Further investigation, therefore, is needed to get a general insight into the substituent effects on the electrochemical and spectroscopic behaviors of the heterocycle-extended quinones. Highly conjugation-extended quinones tend to undergo a one-step two-electron redox reaction owing to the decrease in the intramolecular Coulomb repulsive energy in the dianion state resulting from the long distance separation of the two terminal oxygen atoms, for which no accurate redox potentials can be determined. Such an inconvenience may be overcome on unsymmetrically substituted derivatives. To this end we have now synthesized the novel unsymmetrically substituted derivatives **4**—**7** and clarified the effect of substituents on their electrochemical and spectroscopic properties depositing an important guide for using these new quinones in various fields of studies on molecular electronics.



4: R = H, **5**: R = Cl

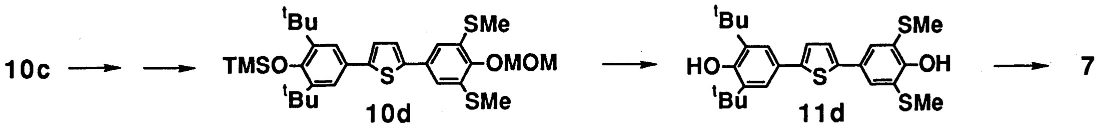
6: R = Br **7**: R = SMe

The synthetic routes to compounds **4**—**6** are outlined in Scheme 2. Organozinc chloride **8**⁶⁾ was allowed to react with the iodides **9a**, **9b**, and **9c**, in the presence of 5 mol% of $Pd(PPh_3)_4$ generated in situ by treating $Cl_2Pd(PPh_3)_2$ with $i\text{-}Bu_2AlH_4$, to give **10a**, **10b**, and **10c**, respectively (60—80% yields). The ethers **10a** and **10b** were cleaved with BBr_3 to give hydroquinones **11a** and **11b**, respectively (quantitative yields) and the ether **10c** was treated with 1 M HCl in THF to yield **11c**. Subsequent oxidation of **11a**—**11c** with potassium ferricyanide dissolved in 0.1 M KOH solution gave the desired quinones **4**, **5**, and **6**,⁷⁾ respectively (over 80% yields).



Scheme 2.

The route to the quinone **7** is shown in Scheme 3. Dimethylthio derivative **10d** was prepared by performing two consecutive stepwise methylthio-substitution reactions of **10c** with 2 equiv. of *t*-butyllithium and 1 equiv of dimethyl disulfide in a convenient one-pot manipulation (53% yield).



Scheme 3.

Quinone **7** was obtained from **10d** (80% yield) by a similar route for **6** from **10c**. Whereas the unsubstituted **1** decomposes gradually on a silica gel column, the di-*t*-butyl derivative **4**, as well as **5**—**7**, isolated as brilliant green crystals, is stable both in the solid state and in solution in common organic solvents.

Quinones **4**—**7** showed two well-defined reversible single-electron reduction waves in the cathodic direction and one single-electron oxidation wave in the anodic direction in the cyclic voltammograms. Thus the unsymmetric substitution has been proved to be favorable for stabilizing the radical anions of these quinones since symmetric **1** and **2** tend to give one coalescent two-electron reduction wave.⁶⁾ It would be noticeable that the oxidation in **5** and **6**, carrying two electron-withdrawing substituents, occurs in the potential range readily accessible for electrochemical studies. The second oxidation to the dication was really observed in **7** (Fig. 1), whereas it was not observed in **4**—**6**, proving that the methylthio groups are very much effective to stabilize the radical cation and the dication of this redox system. Compound **7** is the first example of terphenoquinone analogues undergoing amphoteric four-stage single-electron redox reactions.

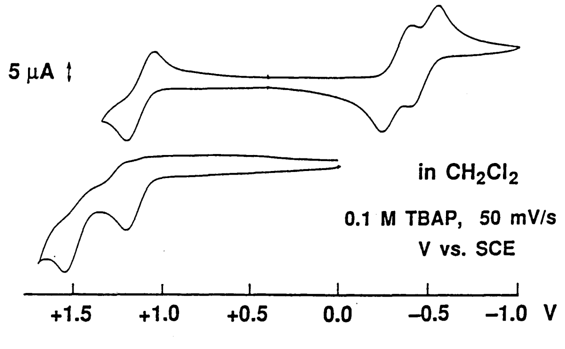


Fig. 1. Cyclic voltammograms of **7**.

The electrochemical data obtained by the cyclic voltammetry, along with the 1st excitation band in the electronic spectrum, are summarized in Table 1. The first reduction potentials (E_1^{red}) appeared in the more positive region as the electron withdrawing groups are incorporated and showed an excellent linear correlation ($r = 0.996$) with $\Sigma\sigma_p$ constants as shown in Fig. 2, indicating that the electron accepting ability of this quinone is in the linear resonance energy relationship to the electronic perturbation of the substituents.

Table 1. Oxidation and reduction potentials (V *vs.* SCE),[a] and the longest wavelength absorption band of **3**—**7**

Compound	E_1^{red}	E_2^{red}	ΔE^{red}	E_1^{ox}	E_{p1}^{ox}	E_{p2}^{ox}	E_1sum	λ max / nm (log ε)[b]
3 R=*t*-Bu	−0.47	−0.67	0.20	+1.23	+1.28	—	1.70	558 (4.90)
7 R=SMe	−0.31	−0.49	0.18	+1.09	+1.16	+1.48[c]	1.40	609 (4.97), 692sh(4.20)
4 R=H	−0.29	−0.48	0.19	+1.26[c]	+1.32	—	1.55	547 (4.96), 596sh(4.39)
5 R= Cl	−0.10	−0.46	0.36	+1.51[c]	+1.57	—	1.61	564 (4.93), 657sh (4.40)
6 R=Br	−0.07	−0.43	0.36	+1.46[c]	+1.52	—	1.53	567 (4.63), 660sh (4.15)

[a] Measured by cyclic voltammetry in C_6H_5CN / 0.1 M TBAP : 50 mV / s. [b] In MeCN. [c] $E_1^{ox} = E_{p1}^{ox} - 60$ mV (irreversible): the E_p^{ox} value represents the anodic peak potential of the oxidation wave.

Although the E_2^{red} values appear to be in approximately linear relationship with the $\Sigma\sigma_p$ constants, the significant deviation does exist ($r = 0.847$) and the sensitivity to the substituent effects (the slope of the Hammett plot) is relatively low, which may be ascribed to the occurrence of the 2nd-step reduction at the oxygen atom of C-4 rather than that of C-4". A linear correlation ($r = 0.896$) obtained by the plot of the ΔE^{red} ($E_2^{red} - E_1^{red}$) values *vs.* the $\Sigma\sigma_p$ constants demonstrates quite reasonably that the radical anion can be thermodynamically stabilized by the important resonance interaction of the substituents. The first oxidation potentials (E_1^{ox}) become lower as the electron-donating groups are substituted, which, however, show a linear dependence not on $\Sigma\sigma p$, but on $\Sigma\sigma_p^+$ constants (Fig. 3). This fact suggests that strong resonance interaction is possible between the positively charged central thiophene ring and the electron-supplying substituents at the α-positions of the carbonyl groups in the radical cation. The relatively poor correlation and the lower sensitivity exhibited by the E_1^{ox} values for the $\Sigma\sigma_p^+$ values, compared with the relationship between the values of E_1^{red} and $\Sigma\sigma_p$, may be ascribed to the contribution in some extent of unsymmetrical resonance structure S-2 to the radical cation and to

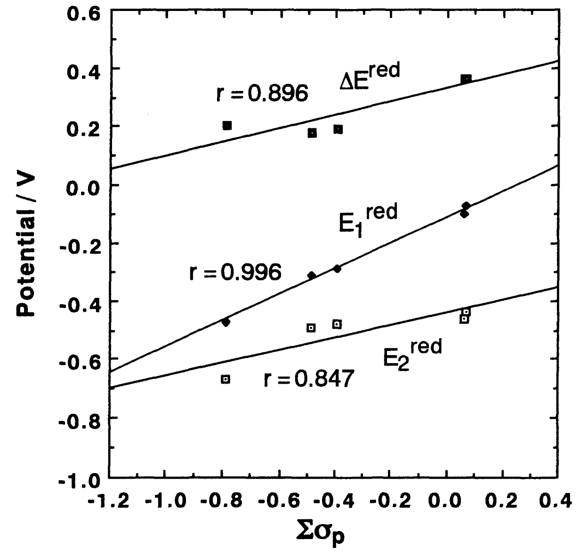


Fig. 2. Plot of the E_1^{red}, E_2^{red}, and ΔE^{red} *vs.* $\Sigma\sigma_p$.

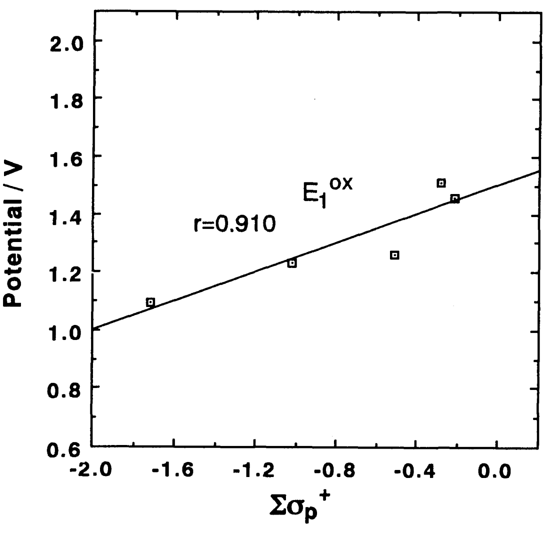


Fig. 3. Plot of the E_1^{ox} *vs.* $\Sigma\sigma_p^+$.

the long distance between the radical cation center and the substituents. The smallest E_1^{sum} value, the highest amphotericity,[6,8] is found in the dimethylthio derivative **7**, not in the dihalo derivatives **5** and **6**, indicating noticeably that the relatively large decrease in the oxidation potential rather than the increase in the reduction potential brings a more decrease in the E_1^{sum} value. Quinones **4**—**7** showed a characteristic and intense $\pi - \pi^*$ absorption maximum at around 550 — 600 nm accompanied by an absorption tail reaching to near-infrared region of 700—750 nm in the electronic spectrum. Whereas no direct linear relationship exists between the E_1^{sum} and the absorption maximum, the bathochromic shift observed in **7** seems to be a good indication of the high amphotericity of this compound, since the 1st excitation band can be assigned to the HOMO-LUMO transition by the CNDO/S and INDO calculations.

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7) Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds, **10a**—**d**, **11a**—**d**, and **4**—**7**. Selected physical data for **4**: brilliant green needles, mp>300 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35 (18H, s, *t*-Bu), 6.52 (1H, d, *J*=10.2 Hz, H-5"), 6.57 (1H, d, *J*=10.2 Hz, H-3"), 7.25 (1H, s, H-2), 7.42 (1H, s, H-6), 7.57 (1H, d, *J*=10.2 Hz, H-2"), 7.66 (1H, d, *J*=10.2 Hz, H-6"), 7.68 (1H, d, *J*=5.6 Hz, H-4'), 7.79 (1H, d, *J*=5.6 Hz, H-3'); **5**: deep green needles, mp>300 °C, ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.36 (9H, s, *t*-Bu at C-5), 1.37 (9H, s, *t*-Bu at C-3), 7.24 (1H, d, *J*=2.5 Hz, H-2), 7.43 (1H, d, *J*=2.5 Hz, H-6), 7.76 (1H, d, *J*=2.5 Hz, H-2"), 7.83 (1H, d, *J*=2.5 Hz, H-6"), 7.88 (1H, d, *J*=5.8 Hz, H-3'), 7.66 (1H, d, *J*=5.8 Hz, H-4'); **6**: brilliant green needles, mp 253 °C (decomp), ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.36 (9H, s, *t*-Bu at C-5), 1.37 (9H, s, *t*-Bu at C-3), 7.24 (1H, d, *J*=2.5 Hz, H-2), 7.41 (1H, d, *J*=2.5 Hz, H-6), 8.01 (1H, d, *J*=2.5 Hz, H-2"), 8.07 (1H, d, *J*=2.5 Hz, H-6"), 7.90 (1H, d, *J*=5.8 Hz, H-3'), 7.64 (1H, d, *J*=5.8 Hz, H-4'); **7**: brilliant dark brown needles, mp 239—240.5 °C, ^{1}H NMR (600 MHz) δ 1.38 (9H, s, *t*-Bu at C-3), 1.36 (9H, s, *t*-Bu at C-5), 2.48 (3H, s, SMe at C-3"), 2.44 (3H, s, SMe at C-5"), 7.27 (1H, d, *J*=2.6 Hz, H-2), 7.43 (1H, d, *J*=2.6 Hz, H-6), 6.94 (1H, d, *J*=2.2 Hz, H-2"), 7.14 (1H, d, *J*=2.2 Hz, H-6"), 7.73 (1H, d, *J*=5.7 Hz, H-3'), 7.68 (1H, d, *J*=5.7 Hz, H-4').
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