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Novel Amphoteric 2,5-Furoquinonoid-Containing *p*-Terphenoquinone Analogues Giving Both a Stable Radical Anion and a Stable Radical Cation

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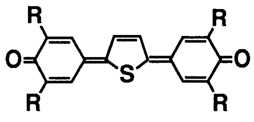
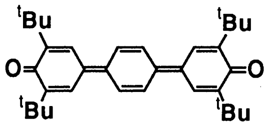
Novel *p*-terphenoquinone analogues incorporating a central dihydrofurandiylidene skeleton have been synthesized. These quinones gave a stable radical cation and a stable radical anion on one-electron redox reactions showing an amphoteric property even though they do not contain any sulfur atom as an integral component. The radical cation and the radical anion of the tetra-*t*-butyl derivative have been characterized by EPR spectroscopy.

We have recently synthesized *p*-terphenoquinone analogues **1a–c**1) and some other derivatives2) incorporating a 2,5-thieno- or a 1,4-dithia-2,5-pentaleno-quinonoid ring at the central part of the molecules, which are both cathodically reduced and anodically oxidized in amphoteric one-electron multi-stage electron transfer reactions. Amphoteric quinones having an intense colorlation may have high utility potential for functional materials such as novel multi-color switching electrochromic display devices3) and novel light-induced electron transporting mediators4) having both electron and hole transporting abilities for photoconducting devices of organic solar cells and for electrophotographic printing systems. However, the molecular design strategies to synthesize amphoteric extended quinones have not yet been well-known so far. Tetra-*t*-butylterphenoquinone **2**,5) synthesized more recently in stimulating by our work, does not show amphotericity, and indeed there has so far been no report on amphoteric extended quinones not having 3pπ electrons or a heavy chalcogen atom6) on the bridging ring. Therefore, the examination of electrochemical behavior of a 2,5-furoquinonoid-extended quinone **3** appears to be very much helpful to get a further insight into the effect of the central π-linking group on the amphotericity. To this end we have now synthesized the furoquinonoid analogues **3a** and **3b**, clarified their redox reactions, and characterized their corresponding radical ions.



1a: R = ^{t}Bu, **1b**: R = Me
1c: R = H



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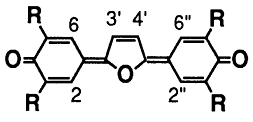
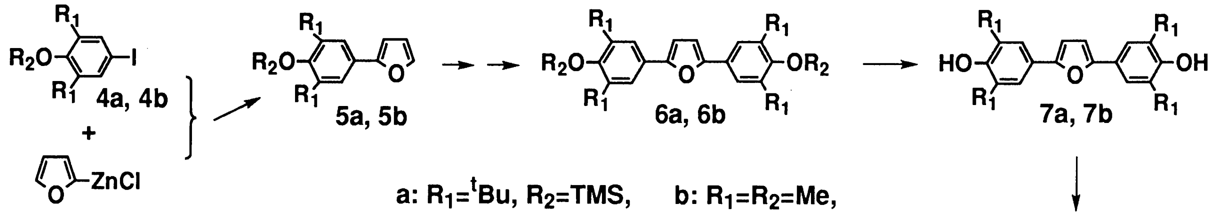


3a: R = ^{t}Bu, **3b**: R = Me

The quinones **3a** and **3b** were synthesized by the routes outlined in Scheme 1. When iodides **4a** and **4b** were allowed to react successively with 2-furylzinc chloride and then with zinc chloride derivatives of the intermediately prepared **5a** and **5b**, in the presence of 5 mol% of $Pd(PPh_3)_4$, 2,5-diarylfurans **6a** and **6b** were obtained, respectively, in reasonable yields. The desired quinones **3a** and **3b** were obtained by the desilylation of **6a** with 1 M HCl in aqueous MeCN and demethylation of **6b** with BBr_3 in CH_2Cl_2, respectively, followed by oxidation with potassium ferricyanide dissolved in 0.1 M KOH solution.



Scheme 1.

The quinones **3a** and **3b** are stable in the solid state and in solution in commonly used organic solvents and exhibit a very intense absorption maximum at 556–550 nm in their electronic spectra.7)

The reduction of **3a** and **3b** occurred in reversible two-step one-electron processes at the cathodic direction in cyclic voltammetry. Interestingly, the quinones **3a** and **3b** were oxidized in one-electron transfer reaction in the cathodic direction and the wave is clearly reversible. The E_1^{ox} value of **3a** is almost identical with that of **1a** (Table 1). Thus, it is indicated that the furoquinonoid-extended terphenoquinones without containing 3pπ electrons can afford a stable radical cation and exhibit an oxidation potential nearly identical with the thienoquinonoid-extended ones. The E_1^{red} value of **3a** is more negative by about 0.06—0.07 V than that of **1a**, which can be ascribable to the fact that the radical anion of **3a** acquires a less stabilization energy than that of **1a**, on aromatization of the corresponding central heterocycle, since furan is less aromatic than thiophene. The E_1^{sum} value of **3a** is a little larger by about 0.06—0.09 V than that of **1a**, which is essentially attributed to the lower E_1^{red} value of the former. We are now able to advance the molecular design strategies for amphoteric extended quinones more widely using furoquinonoid moieties for the conjugation-extending building blocks.

Table 1. Oxidation and reduction potentials (V *vs.* SCE)a) of **3a**, **3b**, **1a**, and **1b**

Compound	Solvent	E_1^{red}	E_2^{red}	ΔE^{red}	E_1^{ox}	E_{p1}^{ox}	E_1^{sum}
3a R=*t*-Bu	C_6H_5CN	–0.54	–0.74	0.20	+1.25	+1.30	1.79
3a R=*t*-Bu	MeCN	–0.52	–0.68	0.16	+1.20	+1.25	1.72
3b R=Me	C_6H_5CN	–0.42b)	–0.49b)	0.07	+1.22c)	+1.26	1.63
3b R=Me	DMF	–0.39	–0.53	0.14	+1.24c)	+1.28	1.63
1a R=*t*-Bu	C_6H_5CN	–0.47	–0.67	0.20	+1.23	+1.28	1.70
1a R=*t*-Bu	MeCN	–0.46	–0.60	0.14	+1.20	+1.24	1.66
1b R=Me	C_6H_5CN	–0.37b)	–0.44b)	0.07	+1.20c)	+1.24	1.57
1b R=Me	DMF	–0.34	–0.48	0.14	+1.22c)	+1.26	1.56

a) Measured by cyclic voltammetry / 0.1 M TBAP : 50 mV / sec. b) Divided from a reversible coalescent peak according to the Myers-Shain method. c) $E_1^{ox} = E_{p1}^{ox}$ – 40 mV (irreversible): the E_p^{ox} value represents the anodic peak potential of the oxidation wave.

On the electrolysis in dichloromethane and on the chemical reduction with Na-metal in THF, **3a** formed a very stable radical anion, $\mathbf{3a}^{\bullet-}$, whose EPR spectrum (Fig. 1) provided a hyperfine splitting constant, 0.267 mT (2H) which was easily assigned to the H-3', 4' based on the large 2pπAO's at C-3', 4' and on the small ones at C-2, 2", 6, 6" in the LUMO (Fig. 2) yielded by the PPP-MO method. The radical cation $\mathbf{3a}^{\bullet+}$, generated by the electrochemical oxidation of **3a** in dichloromethane, is also very stable and hfs constants, 0.17 mT (2H) and 0.135 (0.125) mT (4H), revealed from the EPR spectrum, were also assigned to the H-3', 4' and H-2, 2", 6, 6",

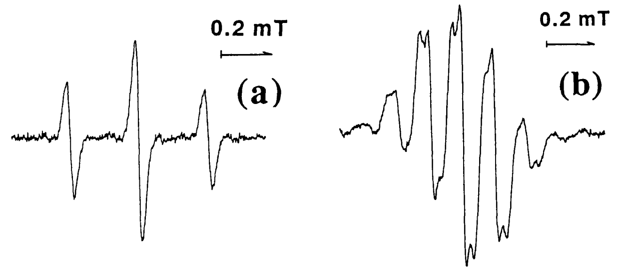


Fig. 1. EPR spectra of **3a**$^{\bullet-}$ (a) and **3a**$^{\bullet+}$ (b).

Table 2. Observed hfs constants (a in mT) and g values of the radical ions of **3a** and **1a**

Radical	a /H-3', 4'	a /H-2, 2", 6, 6"	g value
3a$^{\bullet-}$	0.267	<0.04	2.0034
3a$^{\bullet+}$	0.170	0.135, 0.125	2.0047
1a$^{\bullet-}$	0.205	<0.045	2.0037
1a$^{\bullet+}$	0.130	0.130	2.0055

respectively, on reference to the 2pπAO's in the HOMO. Thus the significant distribution of the unpaired electron on the central furoquinonoid ring in both **3a**$^{\bullet-}$ and **3a**$^{\bullet+}$ was proved (Table 2). The spin population in the radical anions, **3a**$^{\bullet-}$ and **1a**$^{\bullet-}$ does not reside on the heteroatom, because there is no distinct difference in the g values between **3a**$^{\bullet-}$ and **1a**$^{\bullet-}$, which is in accord with the prominent feature of the LUMO having no MO coefficient on the central heteroatom. In contrast, the bulk of the spin population in the radical cations resides on the central heteroatom, since there is a significant difference in the g values between **3a**$^{\bullet+}$ and **1a**$^{\bullet+}$, which is fully appreciated from the large MO on the heteroatom in the HOMO. This would be the main reason why **2** is difficult to give the radical cation **2**$^{\bullet+}$.

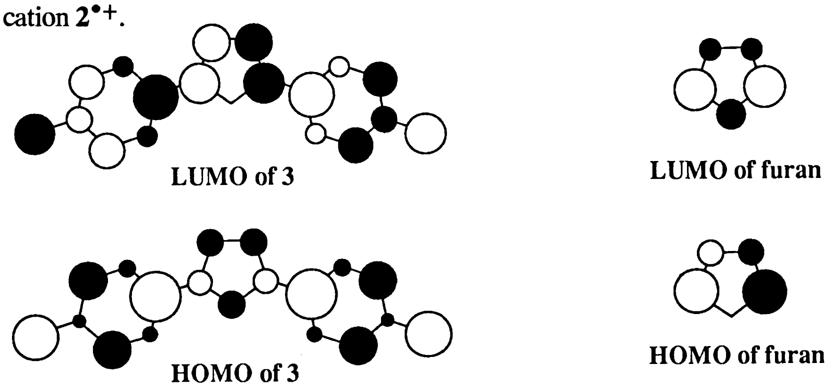


Fig. 2. 2pπAO coefficients calcd. by the PPP MO method.

The radical anions of furanoid compounds in general tend to undergo ring scission at a C—O bond due to the strong antibonding character between the C and O atoms in the LUMO.[8] However, as shown in Fig. 2, the LUMO of furan is incorporated in the HOMO of **3** and the HOMO of furan having no MO at the oxygen atom is incorporated in the LUMO of **3**, so that the C—O bond should not be cleaved in **3**$^{\bullet-}$ and should be strengthened in **3**$^{\bullet+}$, even though the central furoquinonoid ring accommodates the high spin population in these radical ions. Rotation around the intercyclic bonds does not occur in the radical cation because H-2, 2" are inequivalent to H-6, 6" in the EPR spectrum of **3a**$^{\bullet+}$ (Table 2).

We could measure the complete absorption spectrum of **3a**$^{\bullet-}$ (Fig. 3) formed by the Na-metal reduction of **3a**. The conjugation appears to be greater through the sulfur atom than through the oxygen atom, since the characteristic absorption bands of **3a**$^{\bullet-}$ (598, 1059, and 1222 cm^{-1}) are in hypsochromic shift from that of **1a**$^{\bullet-}$ (660, 1095, and 1285 cm^{-1}) in THF. This phenomenon can be explained in terms of the significant contribution of the sulfur bonding orbitals, the p-π conjugation through the sulfur atom, which have been proposed for the discussion of the aromaticity of thiophenes and other compounds containing sulfur atoms as integral components of the cojugation system.[9]

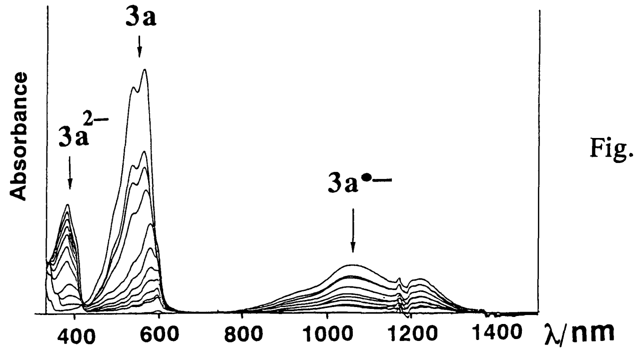


Fig. 3. Electronic spectral changes brought about on the Na-metal reduction of **3a** in THF.

References

1) K. Takahashi and T. Suzuki, *J. Am. Chem. Soc.*, **111**, 5483 (1989); K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, and Y. Fukazawa, *ibid.*, **113**, 4576 (1991).
2) K. Takahashi and T. Sakai, *Chem. Lett.*, **1993**, 157; K. Takahashi and M. Ogiyama, *J. Chem. Soc., Chem. Commun.*, **1990**, 1196.
3) T. Ueno, Y. Hirai, and C. Tani, *Jpn. J. Appl. Phys.*, **24**, L178 (1985).
4) Y. Yamaguchi, H. Tanaka, and M. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1990**, 222; F. L. Carter "Molecular Electronic Devices," Marcel Dekker, New York (1982); L. Alxandru and M. A. Hopper, *Mater Microlichogr.*, **22**, 435 (1984).
5) R. West, J. A. Jorgenson, K. L. Stearley, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, **1991**, 1234; P. Boldt, D. Bruhnke, F. Gerson, M. Schalz, P.G. Jones, and F. Bar, *Helv. Chim. Acta*, **76**, 1739 (1993).
6) R. Tamura, Y. Nagata, H. Shimizu, A. Matsumoto, N. Ono, A. Kamimura, and K. Hori, *Adv. Mater.*, **5**, 719 (1993).
7) All new compounds, **5a**, **5b**, **6a**, **6b**, **7a**, **7b**, **3a**, and **3b** gave satisfactory elemental analyses and spectroscopic data supporting their structures. Selected physical data for **3a**: deep violet needles, mp 256–257 °C; EI-MS m/z 476 (M^++2, 12%), 475 (M^++1, 32%), 474 (M^+, 100%); IR (KBr) 1593 (C=O), 1549, 1358, 1327, 928 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.36 (18H, s, *t*-Bu at C-5, 5"), 1.39 (18H, s, *t*-Bu at C-3, 3"), 7.23 (2H, d, *J*=2.3 Hz, H-6, 6"), 7.72 (2H, d, *J*=2.3 Hz, H-2, 2"), 7.48 (2H, s, H-3', 4'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.45 (C-$\underline{\text{Me}}$ at C-3, 3"), 29.60 (C-$\underline{\text{Me}}$ at C-5, 5"), 35.82 ($\underline{\text{C}}$-Me at C-3, 3"), 35.64 ($\underline{\text{C}}$-Me at C-5, 5"), 116.18 (C-1, 1"), 124.56 (C-2, 2"), 125.79 (C-6, 6"), 126.35 (C-3', 4'), 148.84 (C-5, 5"), 149.84 (C-3, 3"), 160.67 (C-2', 5'), 185.72 (C-4, 4"); UV/VIS (MeCN) λ max nm (log ε) 290 (4.02), 321 (4.17), 540sh (4.88), 557 (4.91). **3b**: deep violet plates, mp 173–175 °C (decomp); DEI-MS m/z 308 (100%), 307 (27%), 306 (M^+, 49%); IR (KBr) 1595 (C=O), 1545, 1188, 931 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.13 (6H, s, Me at C-5, 5"), 2.19 (6H, s, Me at C-3, 3"), 7.28 (2H, d, *J*=1.0 Hz, H-6, 6"), 7.71 (2H, d, *J*=1.0 Hz, H-2, 2"), 7.49 (2H, s, H-3', 4'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.95, 17.04 (Me at C-3, 3", 5, 5"), 116.51(C-1, 1"), 129.72 (C-2, 2"), 129.57(C-6, 6"),126.86, (C-3', 4'), 136.86 (C-5, 5"), 138.13 (C-3, 3"), 160.51 (C-2', 5'), 186.65 (C-4, 4") ; UV/VIS (MeCN) λ max nm (log ε) 286 (3.94), 321 (4.19), 490sh (4.58), 536 (4.91), 561sh (4.83).
8) P. H. Kasai and D. Macleod, *J. Am. Chem. Soc.*, **95**, 4801 (1973); R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
9) V. Schomacher and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939); M. M. Urberg and E. T. Kaiser, "Radical Ions," ed by E. T. Kaiser and L. Kevan, Wiley (1968), Chap. 8.

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