2,5-Bis(3,5-di-t-butyl-4-oxo-cyclohexa-2,5-dien-1-ylidene)-2,5-dihydro-1,4-dithiapentalene: A New Class of Amphoteric Multi-stage Redox Systems consisting of Both the Wurster and the Weitz Types

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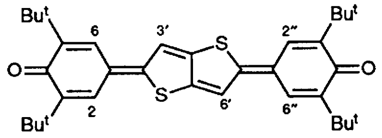
The dihydrodithiapentalene-extended diphenoquinone DTP-DQ (**1**) has been synthesized and characterized as a hitherto unknown amphoteric four-stage one-electron redox system involving both a two-stage one-electron redox reaction of the Weitz type and a two-stage one-electron redox reaction of the Wurster type.

Organic π-donors and π-acceptors undergoing stepwise transfer of single electrons have been classified into 'Weitz' or 'Wurster' types[1] depending on whether the end groups of the redox system are ring members or external groups of a cyclic π-system, respectively. There have appeared several reports on amphoteric hydrocarbons[2] and amphoteric heteroatom-containing compounds[3] which are both anodically oxidized and cathodically reduced in a multi-stage redox fashion. However, there has so far been no report on closed shell amphoteric four-stage redox systems involving different redox-active units, in which a single molecule is both anodically oxidized in a Weitz type manner and cathodically reduced in a Wurster type. This kind of redox system is of current interest in its possibilities for the creation of novel conducting complexes with three interacting components. 2,5-Bis(4-oxocyclohexa-2,5-dien-1-ylidene)-2,5-dihydro-1,4-dithiapentalene shows promise for such a hitherto unknown redox system since the corresponding radical ions and divalent ions could be significantly stabilized by the chalcogen atoms and the oxygen atoms which are incorporated as ring members (Weitz type) and as outside groups (Wurster type) of a cyclic π-system, respectively. With this in mind, we have now

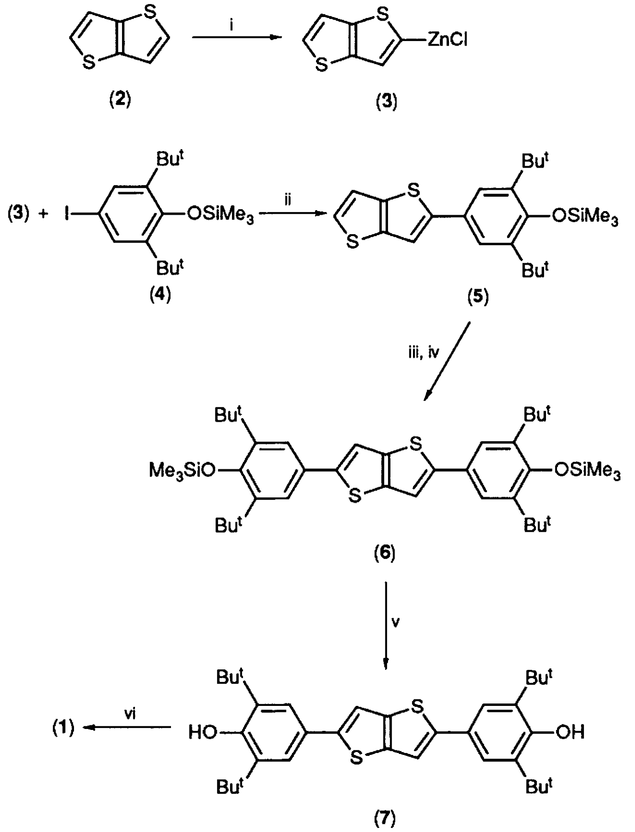
Table 1. Oxidation and reduction potentials,[a] and the difference between E_1 and E_2 of quinones (**1**), (**8**), and (**9**) (V *vs.* standard calomel electrode, SCE).

Compd.	Solvent	E_{p2}^{ox}	E_{p1}^{ox}	E_1^{ox}	ΔE_p^{ox}	E_1^{red}	E_2^{red}	ΔE^{red}
(**1**)	PhCN	+1.59	+1.09	+1.04	0.50	−0.42	−0.55	0.13
(**1**)	CH_2Cl_2	+1.66	+1.14	+1.06	0.52	−0.45[b]	−0.55[b]	0.10
(**8**)	CH_2Cl_2					−0.52	−0.89	0.37
(**9**)	CH_2Cl_2			+1.20		−0.46	−0.60	0.14

[a] Obtained by cyclic voltammetry operated under the conditions given in the caption to Figure 1. [b] Divided from a coalescent peak according to the Myers–Shain method.[5] E^{ox} and E^{red} values were calculated by averaging peak potentials of the reversible anodic and cathodic segments of the cycle; $E = (E_p^a + E_p^c)/2$.



(1)



Scheme 1. *Reagents and conditions:* i, Bu^tLi, ether, 0 °C, then $ZnCl_2$, tetrahydrofuran (THF), 0 °C; ii, $Cl_2Pd(PPh_3)_2$, THF, BuⁱAlH_4, hexane, room temp., 60.3% from (**2**); iii, Bu^tLi, ether, −78 °C, then $ZnCl_2$, THF; iv, $Cl_2Pd(PPh_3)_2$, THF, BuⁱAlH_4, hexane, room temp., 59% from (**5**); v, 12 M HCl, THF, room temp., 83%; vi, $K_3[Fe(CN)_6]$, benzene, 0.1 M aq. KOH, room temp., 78%.

synthesized a tetra-t-butyl derivative of the dihydrodithiapentalenediylidene-extended diphenoquinone, DTP-DQ (**1**), and have demonstrated that DTP-DQ can be categorised as the first example in this new mode of redox system. The novel quinone (**1**) was synthesised as shown in Scheme 1.†

DTP-DQ (**1**) is quite stable both in the solid state and in solution in common organic solvents. Rotation of the terminal rings of (**1**) about the intercyclic bonds does not take place at ordinary temperatures, as shown by ^1H and ^{13}C NMR spectroscopy, H-2,2″ being in a different magnetic environment from H-6,6″ and C-3,3″ and C-2,2″ in a different environment from C-5,5″ and C-6,6″, respectively. The C_{2h} symmetrical structure of (**1**) is evident from the ^1H and ^{13}C NMR data.

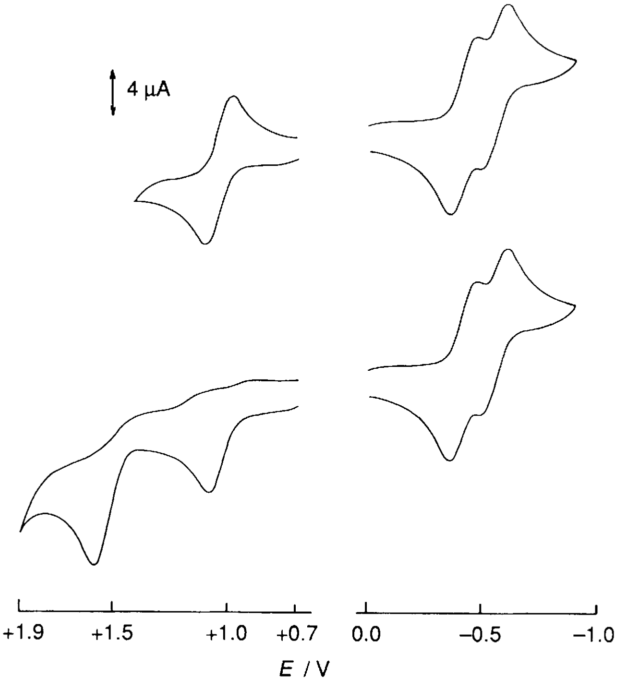
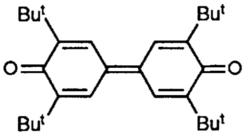


Figure 1. Cyclic voltammograms of (**1**), 0.1 mM in PhCN–0.1 M Bu_4NClO_4 at room temperature (scan rate: 50 mV s^{-1}; reference electrode: SCE). A: Swept at the potential range from −1.0 to +1.4 V; B: from −1.0 to +2.0 V.



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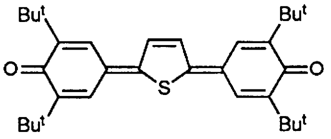

(9)

Direct evidence of the four-stage amphoteric redox reaction for (**1**) was given by its cyclic voltammograms (CV) shown in Figure 1. The occurrence of two-stage one-electron reduction and two-stage one-electron oxidation in (**1**) is clearly demonstrated; the second oxidation wave at 1.59 V is irreversible. The electrochemically generated radical ions ($1^{-\bullet}$) and ($1^{+\bullet}$) are highly stable species and were characterized by ESR spectroscopy. The peak potentials and half-wave oxidation and reduction potentials are summarized in Table 1 along with those of reference quinones (**8**) and (**9**).[3d]

The ΔE^{red} (= $E_2^{red} - E_1^{red}$) value of DTP-DQ (**1**) is smaller than those of (**8**) and (**9**), indicating a smaller Coulomb repulsion[4] in (1^{2-})‡ than in dianions (8^{2-}) and (9^{2-}). The two oxygen atoms bearing the bulk of the negative charge in (1^{2-}) are well separated, and behave as the end groups of the Wurster-type reduction process. The ΔE_p^{ox} (= $E_{p2}^{ox} - E_{p1}^{ox}$)

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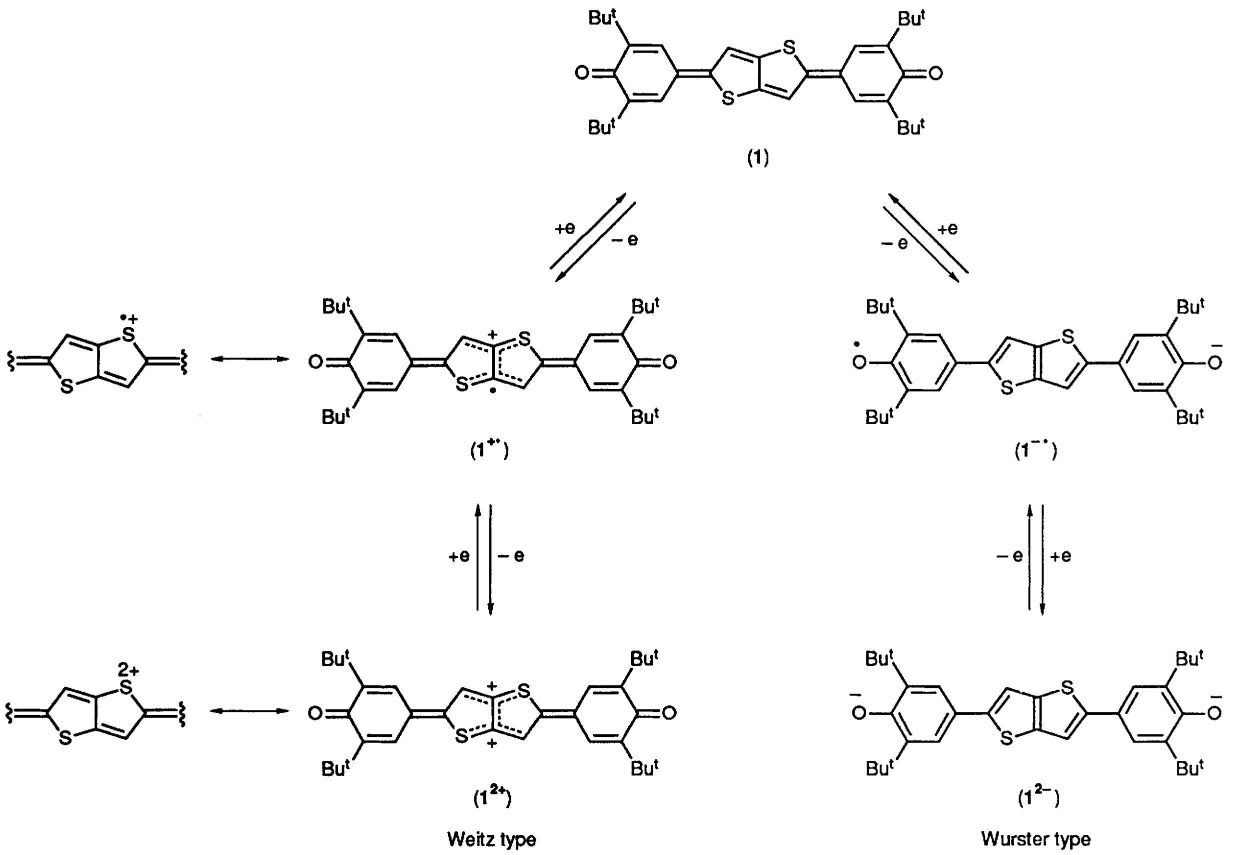
† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds. Selected physical data for (**1**): blue-black needles, m.p. 275—276 °C; EI-MS: *m/z* 546 (M^+, 100%); ^1H NMR (200 MHz, $CDCl_3$), δ 1;36 (36H, s, Bu^t), 7.21 (2H, d, *J* 2.4 Hz, H-6,6″), 7.415 (2H, d, *J* 2.4 Hz, H-2,2″), and 7.416 (2H, s, H-3′,6′); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 126.98 (C-1,1″), 118.25 (C-2,2″), 149.74 (C-3,3″), 185.61 (C-4,4″), 147.88 (C-5,5″), 127.49 (C-6,6″), 152.01 (C-2′,5′), 125.39 (C-3′,6′), and 156.11 (C-3a′, 6a′); UV/VIS (MeCN) λ_{max} (log ε) 594 (5.24), 549 (4.74), 510 sh (4.14), 397 (3.70), 375 (3.69), and 260 nm (3.94); IR (KBr) ν_{max} 2970—2870, 1590 (C=O), 1492, 1365, 1090, 1033, and 892 cm^{-1}.

‡ A Planar conformation of (1^{2-}) is supported from the relatively high quantum yield of the fluorescence emission spectrum. The details will be reported in a separate paper.



Scheme 2

value§ is far larger than the ΔE^{red} value in (**1**), and is even larger than the ΔE^{ox} of tetrathiafulvalene (TTF) (0.33 V). This clearly indicates the significantly increased Coulomb repulsion in ($\mathbf{1}^{2+}$) whose groups bearing the bulk of the positive charge are close to each other. Thus, the central sulphur atoms should function as the end groups of the Weitz-type oxidation sequence. The presence of the two central sulphur atoms in (**1**) might be an important prerequisite for the formation of ($\mathbf{1}^{2+}$), since the monosulphide (**9**) failed to give ($\mathbf{9}^{2+}$) and gave only ($\mathbf{9}^{+\bullet}$). From the ESR study, the bulk of the spin population in ($\mathbf{1}^{+\bullet}$) resides on the sulphur atoms, since the g value of ($\mathbf{1}^{+\bullet}$) (2.0055) is substantially larger than that of ($\mathbf{1}^{-\bullet}$) (2.0035). The significant difference in the g values between ($\mathbf{1}^{+\bullet}$) and ($\mathbf{1}^{-\bullet}$) can be fully appreciated from the prominent features of the HOMO and the LUMO calculated by the CNDO/2 method: the 2pπ or 3pπ AO coefficients are large at the oxygen atoms and almost vanish at the sulphur atoms in the LUMO; in contrast, they are very large at the sulphur atoms and C-3′,6′ in the HOMO.

Therefore, the amphoteric four-stage redox reaction of (**1**) proceeds according to the sequence shown in Scheme 2, involving both two-stage one-electron reduction of the Wurster type and two-stage one-electron oxidation of the Weitz type. The central dithiapentalene ring may have pseudo 8π, 10π, and 6π electron character in (**1**), ($\mathbf{1}^{2-}$), and ($\mathbf{1}^{2+}$), respectively.

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§ The second half-wave oxidation potential, E_2^{ox}, cannot be determined exactly from Figure 1, since the corresponding reduction segment of the cycle is missing. The Coulomb repulsion in ($\mathbf{1}^{2+}$) was therefore evaluated from the $\Delta E_{\mathrm{p}}^{\mathrm{ox}}$ value instead of ΔE^{ox}.

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