Photochemical and Redox Switching in a Ring-closed Isomer of Thioindigo-extended Quinone

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A new dispiro π-system having a bis(2,6-di-*tert*-butylcyclohexadienone) unit was synthesized and characterized. Photoirradiation gave an ESR-active bis(phenoxy) radical and electrochemical reduction formed a bis(phenoxide) ion both by ring-opening.

Compounds which change their structure and properties in response to external stimuli have received much attention as molecular switches.[1] In particular, cleavage and formation of C–C bonds is one of the most frequently observed phenomena, such as in diarylethenes.[2] Recently, Suzuki et al. have reported,[3] in such systems, drastic conformational changes in the molecule caused by cleavage of the C–C bond between dispiro carbons and formation of stable cationic species play important roles in their switching properties. Oligothiophenes having a dispiro structure have also been reported.[4] We have been studying new functions of non-planar quinones extended with 2,6-di-*tert*-butylcyclohexadienon-4-ylidene, and have discovered their switching properties by redox treatment and/or photoirradiation of *p*- and *o*-quinonoid derivatives.[5] As an extension of these findings, we planned to study the synthesis and properties of the thioindigo-extended quinone **1** as a new type of non-planar extended quinone (Figure 1). Compound **1** was expected to show unique photochemical properties considering the reversible cis–trans photoisomerization of thioindigo dyes.[6] In the course of the synthesis of **1**, its ring-closed isoelectronic isomer **2** was obtained. A few molecules having such a bis(spirodienone) structure are known,[7] but their responses toward external stimuli have not been investigated. We report here the synthesis and fundamental properties of **2**, as well as its responses to external stimuli.

Bis-phenol **4**, a suitable precursor for **1**, was prepared from 3,3′-dibromo-2,2′-di(benzo[*b*]thiophene) (**3**) by Suzuki–Miyaura coupling with 3,5-di-*tert*-butyl-4-hydroxyphenylboronic acid. Oxidation of **4** with DDQ afforded **2** as a pale yellow powder (Scheme 1). Compound **2** was characterized by NMR and the other spectroscopic data.[8] One singlet signal of quinone methide protons at 6.73 ppm in the ^{1}H NMR spectrum was resonated at relatively high magnetic field. Moreover, one carbon-13 signal at 52.15 ppm indicated the existence of quaternary sp^3 carbons. The structure of **2** was finally established by X-ray crystallography (Figure 2).[9] The formation of **2** could be explained in terms of the intramolecular coupling of the initially formed diradical **6** at its *ipso*-carbons rich in spin density, when they were brought into close proximity.[7b]

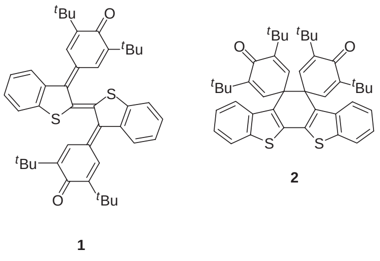
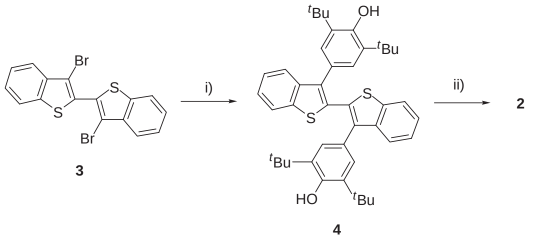


Figure 1. Thioindigo-extended quinone **1** and its ring-closed isomer **2**.



Scheme 1. Synthesis of **2**. i) 3,5-Di-*tert*-butyl-4-hydroxyphenylboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, DME–H$_2$O, 88%; ii) DDQ, THF, 99%.

The planes of the cyclohexadiene units lay perpendicular to the benzo[*b*]thiophene plane, and faced each other, offset to avoid overlap of the bulky *tert*-butyl groups (C2–C17–C23–C10 = 41.7(4)°). The two benzo[*b*]thiophene rings are slightly twisted, with an S1–C1–C9–S2 dihedral angle of 12.0°. The bond distance between the two spiro-carbons (C17 and C23) is 1.625 Å. This length is longer than those in previously known dispirobis(2,6-di-*tert*-butylcyclohexadienone) derivatives[6] (1.596–1.62 Å), but shorter than those in dispirobis(10-methylacridan) derivatives[3a,3c] (1.635–1.771 Å).

The redox properties of **2** were examined by cyclic voltammetry (Figure 3), which showed one irreversible reduction wave ($E_{\rm pc} = -1.77$ V) and one re-oxidation wave ($E_{\rm pa} = -0.66$ V). The large difference between these potentials ($\Delta E = 111$ mV) indicate that a drastic structural change occurred during electron transfer, in this case, formation of dianion **5** through the bond-cleavage of the central six-membered ring (Scheme 2). Alkali-metal reduction of **2** was carried out with sodium metal in a degassed THF solution to confirm the formation of **5**. The reaction was monitored by UV–vis spectroscopy (Figure 4). At the beginning of the reduction, the spectrum contained absorption maxima at 536, 425, and 287 nm. As reduction proceeded, absorptions at 445, 372, and 265 nm increased, with two isosbestic points. This change indicates the generation of dianion **5** from

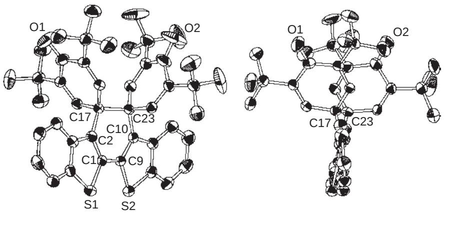


Figure 2. ORTEP drawings of **2**. a) Front view; b) Side view. Hydrogen atoms are omitted for clarity.

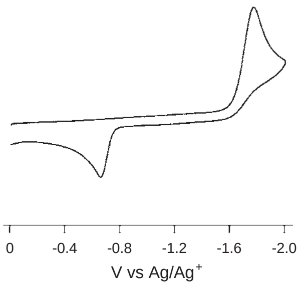
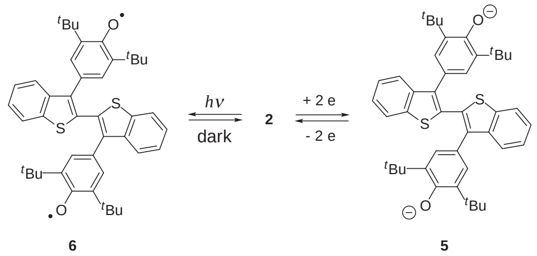


Figure 3. Cyclic voltammogram of **2** (V vs Ag/Ag$^+$; in 0.1 M n-Bu_4NClO_4/DMF, 25 °C, scan rate 100 mV/s, Fc/Fc$^+$ = +0.06 V).



Scheme 2. Transformation of **2** to dianion **5** and diradical **6**.

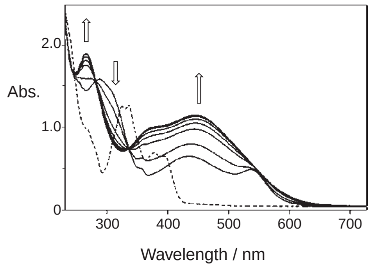


Figure 4. Change in UV–vis spectrum of **2** on reduction with sodium in degassed THF. Dashed line: before reduction.

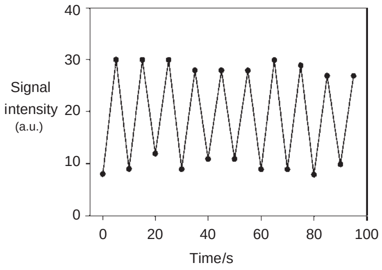


Figure 5. Change in ESR signal intensity of **2** under intermittent photoirradiation.

2 through the corresponding radical anion.[10] Re-generation of **2** was confirmed by exposing the solution to air. The ^1H and ^{13}C NMR spectra of **5** are appropriate for the ring-opened structure.[11]

Although compound **2** showed clear ^1H and ^{13}C NMR spectra, it exhibited weak ESR signals in degassed toluene solution at room temperature. The observed triplet pattern ($a_H = 0.17$ mT) is typical for 4-substituted 2,6-di-*tert*-butylphenoxy radicals, suggesting that **2** is in equilibrium with diradical **6**, to a small extent (Scheme 2).[12] Upon photoirradiation with a 500-W Xenon lamp, the signal intensity increased and reached a photostationary state within 4 min, then rapidly decreased when the light was turned off. This photo-responsivity of ESR signals was relatively quick; the signal intensity changed markedly during intermittent photoirradiation at 5-second intervals (Figure 5).

In conclusion, a new dispiro-compound having a bis(spirodienone) unit has been prepared, showing promise as a new candidate for redox- and photo-active molecular switches. Further modifications of the molecule toward the improvement of switching properties are in progress.

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References and Notes

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8 Spectroscopic data of **2**: yellow crystals; mp 246–247 °C; MS (EI) m/z 672 (M$^+$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 7.3$ Hz, 2H), 7.70 (d, $J = 7.9$ Hz, 2H), 7.36–7.23 (m, 4H), 6.73 (s, 4H), 1.20 (s, 36H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 185.63, 149.21, 139.50, 138.56, 137.55, 132.33, 127.05, 124.78, 124.69, 123.06, 122.82, 52.15, 35.42, 29.51; IR (KBr) ν 1658 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}/nm (log ε) 395 (4.08), 378 (4.11), 336 (4.39), 324 (4.37), 282 (4.09), 270 (4.21), 229 (4.70); Found: C, 78.32; H, 7.11%. Calcd for $C_{44}H_{46}O_2S_2$: C, 78.53; H, 7.19%.

9 Crystallographic data of **2**: $C_{44}H_{48}O_2S_2$, fw 672.98, monoclinic, $P2_1/c$, $a = 9.8962(8)$, $b = 22.373(2)$, $c = 17.550(2)$ Å, $\beta = 103.137(1)°$, $V = 3784.0(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.181$ g cm^{-3}, 38511 reflections measured, 8651 unique ($R_{int} = 0.039$), $R1 = 0.053$ (3782 data, $I > 2.0\sigma(I)$), $R_w = 0.120$ (all data), CCDC-632105.

10 Because the reduction potential corresponding to the radical anion of **2** is very close to the potential of the dianion **5**, only one reduction wave was observed on cyclic voltammetry.

11 NMR data of **5**: ^1H NMR (270 MHz, THF-d_8) δ 7.86 (dd, $J = 6.9$, 1.2 Hz, 2H), 7.48 (dd, $J = 6.9$, 1.2 Hz, 2H), 7.13–7.10 (m, 4H), 7.11 (s, 4H), 1.34 (s, 36H); ^{13}C NMR (67.8 MHz, THF-d_8) δ 171.04, 142.03, 141.54, 141.04, 136.06, 130.80, 127.40, 124.89, 123.38, 122.80, 121.66, 112.18, 35.83, 31.03.

12 The diradical concentration of **2** was estimated to be 0.2% by comparing the radical intensity of **2** with that of a 1,1-diphenyl-2-picrylhydrazyl solution.

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