

Synthesis, Structure, and Properties of a Dibenzo-*ortho*-terphenylquinone. The First *o*-Terphenylquinone Derivative

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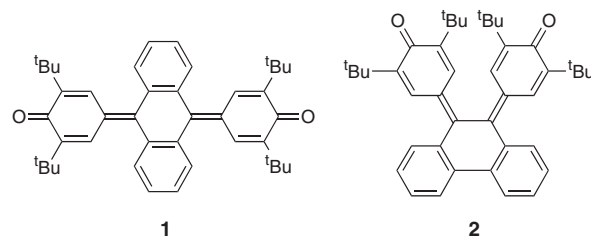
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A dibenzo-*ortho*-terphenylquinone derivative, the first *o*-terphenylquinone derivative, is largely deviated from coplanarity, is in a slight equilibrium with its diradical form, displays an easy rotation of the exocyclic double bonds, and shows photoresponsive switching property traceable by ESR spectroscopy.

Extended quinones have attracted considerable attention from the structural and physicochemical, in particular electrochemical points of view.¹ Extended *p*-phenylquinones tend to be in equilibrium between the quinoid forms and diradical forms depending on the degree of extension and substituent effect.² Recently, we have reported the synthesis and a switching functionality (ESR detection) of dibenzannulated *p*-terphenylquinone (**1**) which shows a cleanly reversible photochemical and thermal interconversion between the quinone and diradical forms involving restricted conformational change.³ The nonplanarity of **1** plays an important role in this interconversion. Thus, in theory, there can be other switching systems based on nonplanar extended quinones and quinomethides. In this context, we have been interested in the development of novel extended quinones rich in dynamic processes. Here we report the synthesis, structure, and properties of dibenzo-*o*-terphenylquinone (**2**), the first derivative of this kind as well as the structural isomer of **1**.

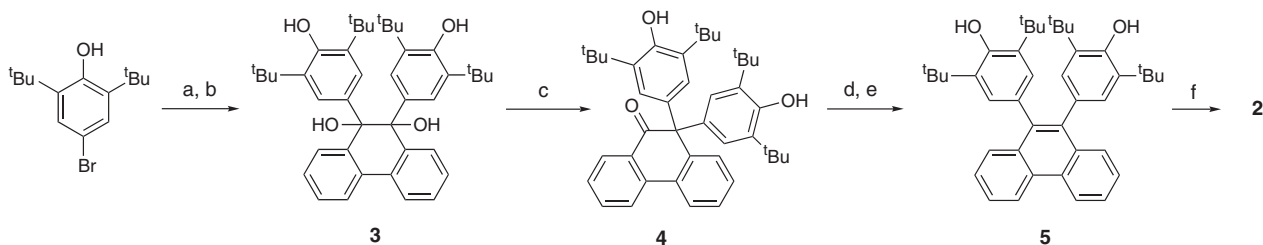
Synthesis of **2** was outlined in Scheme 1. Reaction of 4-lithio-2,6-di-*t*-butylphenoxide, generated by treatment of 4-bromo-2,6-di-*t*-butylphenol with three equivalents of *t*-BuLi,⁴ with 9,10-phenanthrenequinone in ether afforded bisadduct (**3**)⁵ as a single stereoisomer in 35% yield. Use of THF as solvent did not yield **3** at all probably because of electron transfer reaction as judged from deep blue coloration of the reaction mixture. Attempted dehydration of **3** to **2** with either POCl₃/pyridine or CuSO₄/THF was not successful, producing a complex mixture or ketone (**4**) by the pinacol rearrangement. We, therefore, transformed **3** to bisphenol (**5**) through the acid-catalyzed pinacol rearrangement to **4** and its reductive rearrangement (LiAlH₄/THF and then I₂/CH₃COOH).⁶ Oxidation of **5** with alkaline K₃Fe(CN)₆ afforded **2** as orange crystals in 99% yield.⁷



The visible absorption of **2** [$\lambda_{\max}$ 423 nm/CH₂Cl₂ (ϵ 21900)] is very similar to that of **1** [424 nm/CH₂Cl₂ (42700)] in the wavelength but nearly half in the absorption coefficient to suggest deviation of the quinomethide chromophores from coplanarity more than **1**. The ¹H NMR spectra revealed the dynamic stereochemical process of **2** around room temperature: while the spectrum at 30 °C shows the *t*-butyl protons as a singlet and the olefinic protons of quinomethide part almost invisible owing to broadening, that at -60 °C shows two singlets of the *t*-butyl groups at δ 1.21 and 1.24 and two doublets of the quinomethide protons at δ 7.22 and 7.55. These observations indicate fairly easy rotation of the exocyclic double bonds (pinch bonds) of **2** around room temperature.⁸ From the variable-temperature NMR measurements, the rotational barrier ($\Delta G^\ddagger$) is estimated to be as low as 13.6 ± 0.3 kcal mol⁻¹ ($T_c = -15 \pm 3$ °C).

Recrystallization of **2** from ethanol gave single crystals suitable for X-ray analysis.⁹ Figure 1 shows the ORTEP drawings. The central six-membered ring takes a twisted chair form probably to reduce the steric crowding around the quinomethide units. Dihedral angle of the two pinch bonds (C4-C13-C26-C10) is as large as 68.0°. The biphenyl part (C18-C19-C20-C21) is twisted by 22.2°. On the other hand, the pinch bonds are only slightly twisted with the average torsion angles of 4.1°. The average length of the pinch bonds of **2** (1.38 Å) is similar to that of dibenzo-*p*-terphenylquinone (**1**) (1.37 Å) but is shorter than that of a nonbenzannulated *p*-terphenylquinone derivative (1.42 Å).^{2a,b}

Electrochemical properties of **2** (cyclic voltammetry) are also significantly different from **1**. First, **2** ($E_{pc} = -0.87$ V) has a higher electron affinity than **1** ($E_{pc} = -1.08$ V; 25 °C).¹⁰



Scheme 1. a; 3 equiv. *t*-BuLi/ether, 0 °C, 1 h, b; 0.4 equiv. 9,10-phenanthrenequinone, 35%, c; CF₃CO₂H/CH₃CO₂H, r.t., 1 h, 75%, d; LiAlH₄/THF, reflux, 1.5 h, 81%, e; 0.3% I₂/CH₃CO₂H, reflux, 1.5 h, 74%, f; K₃Fe(CN)₆/0.1 M KOH aq./benzene, r.t., 3 d, 99%.

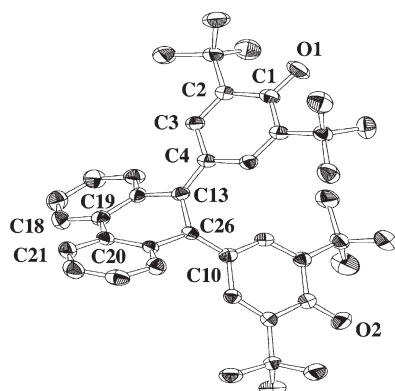


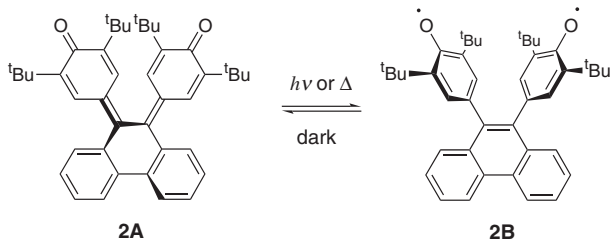
Figure 1. ORTEP drawings (50% thermal ellipsoids) of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): O1–C1 1.228(3), C1–C2 1.485(4), C2–C3 1.350(4), C3–C4 1.455(4), C4–C13 1.378(4), C13–C26 1.490(4), O1–C1–C2 121.1(3), C1–C2–C3 119.2(3), C2–C3–C4 123.0(3), C3–C4–C13 122.0(2), C4–C13–C26 125.1(2), C13–C26–C10 123.3(2).

Second, **2** exhibits two re-oxidation peaks (E_{pa}) at -0.79 and -0.52 V, which we tentatively assign to each one-electron oxidation forming anion radical **2**^{•−} and diradical form of **2** (**2B**) rather than involvement of hysteresis behavior, whereas **1** clearly shows temperature dependent hysteresis behavior involving conformational change (large differences between E_{pc} and E_{pa}).³

Although *p*-terquinone **1** is ESR silent, *o*-terquinone **2** exhibits weak ESR signals in a degassed toluene solution at room temperature. The observed triplet pattern ($a^H = 0.18$ mT, $g = 2.0045$) is similar to that of the diradical form of **1** and other 4-substituted-2,6-di-*t*-butylphenoxy radicals, suggesting a slight equilibrium of **2** with diradical **2B** (Scheme 2).¹¹ The signals become larger upon heating or more effectively upon photoirradiation: irradiation of **2** with a high pressure Hg lamp causes gradual increase of the signal intensity which returns to the original intensity in the dark in about 1.5 h at room temperature (Figure 2). Thus, like **1**, *o*-terquinone **2** shows switching function to some extent, although the response is slower.¹²

Further studies toward the development of an improved photoresponsive switching system by structural modification of **2** are in progress.

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Scheme 2.

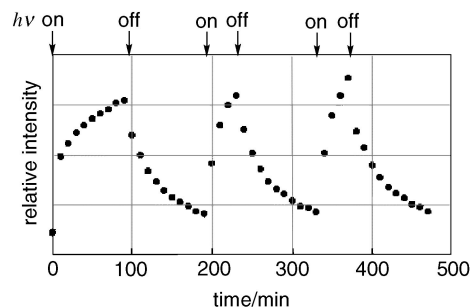


Figure 2. Change of ESR signal intensity of **2** under intermittent photoirradiation.

References and Notes

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- We tentatively assign the *trans* configuration for **3** from the viewpoint of steric hindrance on the second nucleophilic addition of the dianion.
- For similar way for the synthesis of 9,10-disubstituted phenanthrenes, see; Y.-H. Lai, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1667.
- 2**: reddish-orange prisms (EtOH), mp 213–214 °C; MS (EI) m/z 586 [(M+2)⁺, 27%], 585 [(M+1)⁺, 41], 584 (M⁺, 95), 528 [(M+1-^tBu)⁺, 100]; UV-vis (cyclohexane) λ_{max}/nm (log ϵ) = 419 (4.34), 346 (4.72), 333sh, 244 (4.41); IR (KBr) ν (CO) = 1612 cm^{−1}; Found: C, 86.05; H, 8.18%. Calcd. for C₄₂H₄₈O₂: C, 86.26, H, 8.27%.
- The thermal equilibrium with the diradical form may be responsible for the easy rotation of the pinch bonds.
- Crystal data for **2**: C₄₂H₄₈O₂, M_r = 584.84, monoclinic, space group $P2_1/n$ (no. 14), a = 12.41(2), b = 18.35(2), c = 15.36(2) Å, β = 95.4(1), V = 3483(8) Å³, Z = 4, D_{calcd} = 1.115 g cm^{−3}, 31553 reflections measured, 7835 unique (R_{int} = 0.094) used in refinement. $R1$ = 0.059 (7835 data, $I > 2\sigma(I)$), wR = 0.140 (all data), T = 203 K. CCDC 206981.
- V vs Ag/Ag⁺, in 0.1 M *n*-Bu₄NClO₄/CH₂Cl₂, sweep rate 100 mV/s, ferrocene = +0.32 V, 25 °C.
- The fact that ¹H NMR signals of **2** are observed normally indicates very low concentration of diradical **2B**.
- Photoirradiation of **2** gave rise to weak ESR signals other than the triplet pattern that also disappear in the dark to suggest occurrence of a reversible side reaction. There seems a possibility of electro-cyclization of the bisquinomethylenethane moiety with some similarity to the photochemical cyclization of *cis*-stilbene, and further studies on this point are underway.