Dibenzoannulated 3,5,3'',5''-Tetra(*t*-butyl)-*p*-terphenoquinone. A Reversible, Photochemical-Thermal Switching System Involving Restricted Conformational Change

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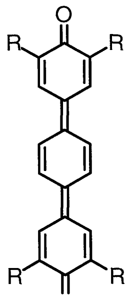
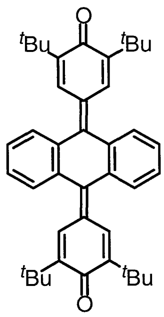
The title compound, a new terphenoquinone derivative, shows a dynamic redox behavior upon cyclic voltammetry and a reversible, photochemical-thermal isomerization between the quinone and diradical forms, both phenomena involving restricted conformational change.

Quinones and extended quinones are an important group of compounds in organic electrochemistry and organic material science because of their multistage redox properties.[1] The equilibrium between a diamagnetic quinoid form and a paramagnetic benzenoid diradical form in extended *p*-quinones depends on the degree of extension and substitutent effects. As to *p*-terphenoquinones, while tetraphenyl *p*-terquinone **1** exists reportedly as a paramagnetic substance exhibiting strong ESR signals probably due to a diradical structure,[2] tetra-*t*-butyl *p*-terquionone **2** shows diamagnetism having a nearly planar structure.[3,4] For both quinones, the energy barriers for the rotation of the exocyclic double bonds should be considerably low. Introduction of benzo group(s) onto the central ring of **2** would increase steric congestion to make the energy barrier between the quinoid form and diradical form higher. It has been briefly described that oxidation of the precursor hydroquinone generates diradical **3'**, without mentioning its quinone form **3**.[5] We report here the synthesis and properties of **3**, a stable, hitherto unknown terphenoquinone derivative, which shows a dynamic redox behavior and a reversible photochemical and thermal isomerization between the quinone and diradical forms involving restricted conformational change.



1 (R = Ph)
2 (R = ^{t}Bu)



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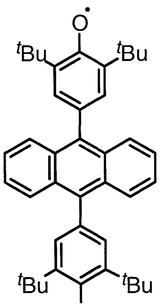
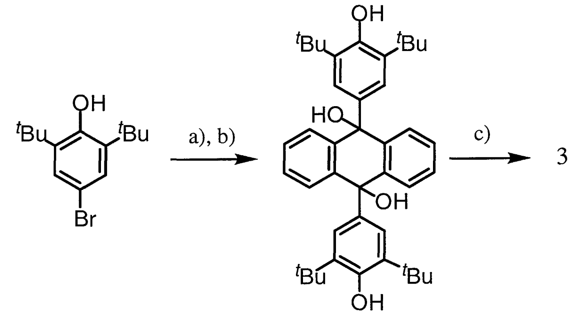


3'

Reaction of 4-lithio-2,6-di-*t*-butylphenoxide,[6] generated by treatment of 4-bromo-2,6-di-*t*-butylphenol with three equivalents of *t*-BuLi, with 9,10-anthraquinone afforded bisadduct **4** as colorless crystals in 52% yield. Treatment of **4** with phosphorus oxychloride in refluxing pyridine gave terquinone **3**[7] in quantitative yield. Terquinone **3** is an orange crystalline substance with good air and thermal stability, exhibits sharp NMR signals, and does not show any ESR signals in solutions, indicating the definite existence of **3** in the quinoid form. The longest absorption maximum of **3** (424 nm) in the UV-Vis spectrum is largely blue-shifted compared to that of **2** (631 nm)[3], suggesting a highly hindered conjugation.



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Reagents and conditions: a) 3 eq. *t*-BuLi/THF, 0 °C, 1 h, b) 0.3 eq. 9,10-anthraquinone, c) $POCl_3$/pyridine, 80 °C, 12 h.

Scheme 1.

A single crystal of **3** suitable for X-ray crystallographic analysis was obtained from a toluene-hexane solution, and the molecular structure is shown in Figure 1.[8] The molecules take a butterfly-structure similar to that of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCNAQ)[9]. The dihedral angle between the plane formed by C(8)-C(13)-C(15)-C(20) and the plane by C(4)-C(7)-C(8)-C(20) or C(13)-C(14)-C(15)-C(21) are 36.7° or 36.5°; thus, the boat form of the central six-membered ring of **3** is deeper than that of TCNAQ (18.9° and 16.6°)[9] and even than tetracyanobianthraquinodimethane (35.4° and 29.8°)[10], an extended homologue of TCNAQ. The bond lengths of C(4)-C(7) and C(14)-C(21) (both 1.37 Å) are considerably shorter than those of **2** (1.42 Å)[3]. These results agree with the poorer conjugation between the two quinoid units suggested from the UV-Vis spectrum.

Upon cyclic voltammetry, **3** exhibited a couple of quasi-reversible redox waves at 25 °C: a reduction peak (E_{pc}) at -1.08 V (two-electron transfer), and a reoxidation peak (E_{pa}) at -0.42 V (ΔE = 0.66 V).[11] The ΔE became larger as the temperature was lowered; for example, ΔE = 0.87 V (E_{pc} = -1.15 V, E_{pa} = -0.28 V) at -30 °C. This suggests involvement of a conformational change between **3** and its dianion. A similar phenomenon has also been reported for the electrochemical oxidation of anthraquinodimethane derivative of tetrathiafulvalene.[12]

The most notable feature of **3** is its reversible, photochemical and thermal isomerization between the quinone form **3** and diradical form **3'**. ESR signals appeared immediately when a degassed benzene solution of **3** was irradiated with a 500 W

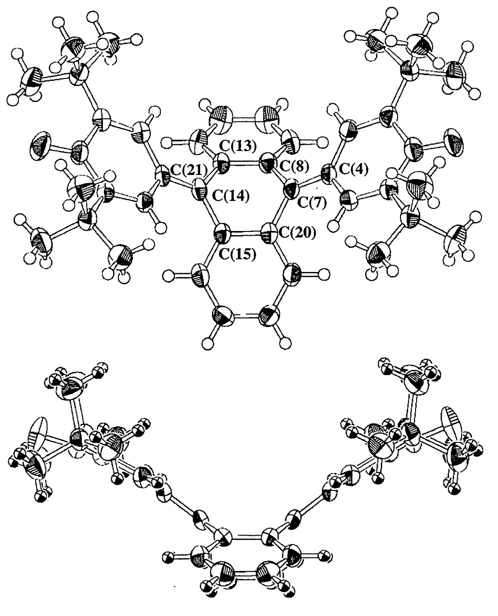
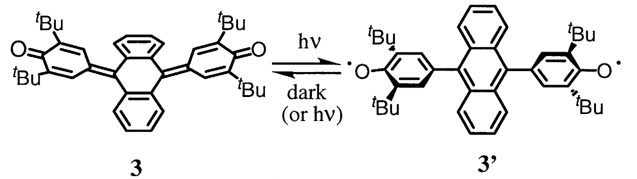


Figure 1. ORTEP drawing of **3** (50% probability).
Top: overlooked view, bottom: side view.



3 **3'**

Scheme 2.

Xenon lamp (or a 400 W high pressure Hg lamp through pyrex filter). The signal intensity rapidly increased with time and reached maximum within 5 min, probably at a photo-equilibrium. The observed ESR spectrum (a triplet with a_H = 1.85 G and g = 2.0044) is essentially the same with that reported for **3'**.[5] The concentration of **3'** relative to **3** at the equilibrium seems, however, as low as about 4% by estimation using 1,1-diphenyl-2-picrylhydrazyl as a standard.[13] The ESR signals of **3'** decreased in turn in the dark with a half-life of 4 ± 1 min at 25 °C ($\Delta G^{\neq} \approx$ 21 kcal/mol). This energy barrier should correspond to that for the conformational change from a twisted structure of **3'** having a planar anthracene to the butterfly structure of **3** (Scheme 2). This to-and-fro process was repeatable with some decomposition (Figure 2) and could also be monitored even by ^{1}H NMR spectra by broadening (almost disappearance) and sharpening of the signals. Thus, in spite of the low concentration of diradical **3'** and the somewhat slow thermal back process, the present reversible isomerization of **3** substantiates a molecular switch. The high sensitivity of ESR spectroscopy will give a merit in the requirement of only small amount of samples for detection of the switching.

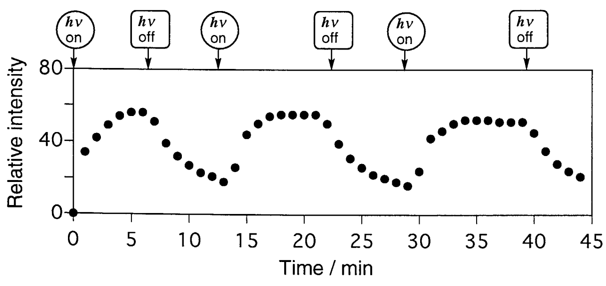


Figure 2. Reversible photochemical-thermal isomerization of **3** traced by ESR spectroscopy.

Further studies toward the development of an improved molecular switch system by structural modification of **3** are in progress.

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7 **3**: orange crystals, m.p. >280 °C (decomp.); MS(FAB) m/z 586.2 ($[M+2]^+$), 584.2 (M^+); ^{1}H-NMR (270 MHz / $CDCl_3$) δ = 7.76 (s, 4H), 7.65 (q, AA'BB', 4H), 7.45 (q, AA'BB', 4H), 1.32 (s, 36H); ^{13}C-NMR (67.8 MHz / $CDCl_3$) δ = 186.87, 148.99, 145.07, 136.35, 130.05, 129.45, 127.37, 126.63, 35.71, 29.65; UV-Vis (CH_2Cl_2) λ_{max}/nm (log ε) = 424 (4.64), 356 (4.59), 322 (4.38), 241 (4.09); IR (KBr) ν(CO) = 1610 cm^{-1}; Found: C, 86.15; H, 8.24%. Calcd. for $C_{42}H_{48}O_2$: C, 86.26; H, 8.24%.

8 Crystal data for **3**: recrystalized from toluene- hexane; triclinic, space group *P1 (#2)*, a = 11.872(4), b = 14.786(3), c = 9.928(3) Å, α = 94.99(2), β= 91.80(3), γ = 83.32(2)°, V = 1723.9(9) Å^3, Z = 2, D_{calc} = 1.127 gcm^{-3}, μ = 0.67 cm^{-1}, 2712 independent observed reflections [F>3σ(F), 6°<2θ<55°], refined to R(Rw) = 0.046 (0.047).

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13 No appreciable change was observed in UV-Vis spectrum before and after irradiation.