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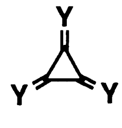
Synthesis and Properties of a Bis(benzoquino)-*o*-tropoquinocyclopropane Derivative. A Novel [3]Radialene Involving a Seven-membered Ring System

Kazuko TAKAHASHI* and Masashi OGIYAMA
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

The title [3]radialene derivative, 1,2-bis(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(dibenzo[d,f]-1,3-dioxo-4,6-cycloheptadien-2-ylidene)cyclopropane has been synthesized, and its spectroscopic properties and redox reactions have been investigated. The powerful electron accepting ability of this compound is ascribed to the high electron affinity of the *o*-tropoquinone methide residue.

Several approaches to the design and synthesis of [3]radialene derivatives **1** where Y's represent electron-withdrawing1) or -donating2) functional groups have recently been performed, since such compounds have accepted current interest as new multistage redox type donors and acceptors, and as organic ferromagnets3) if they could exist in a triplet ground state. In these efforts, however, [3]radialene derivatives involving conjugated seven-membered ring(s) have never been reported to date, although those substituted with two or three 4-oxo-2,5-cyclohexadien-1-ylidene moieties1a,4) or one cyclopentene-1,3-dion-2-ylidene moiety4) have been synthesized. We have already synthesized a series of *p*-5) and *o*-tropoquinone methides6) including heptatriafulvalene dinone derivatives7) and have clarified that the electron-accepting ability of the tropoquinone methide group is stronger than the corresponding benzoquinone methide one. It has also been known that *o*-8) and *p*-tropoquinones9) are more easily reduced than the corresponding benzoquinones. Therefore, one can create new multi-stage and enhanced electron acceptor molecules by designing [3]radialene **2** whose radical anion might be significantly stabilized by the *o*-tropoquinone methide residue. Although attempts to synthesize **2** have failed, we have now synthesized compound **3**, the first radialene derivative involving a seven-membered ring system and characterized its electrochemical properties, which are reported herein.



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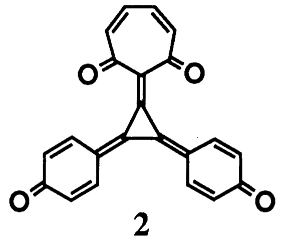

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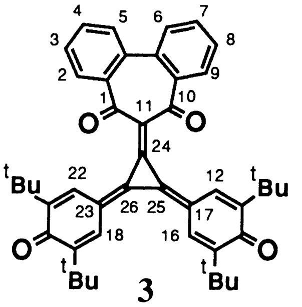

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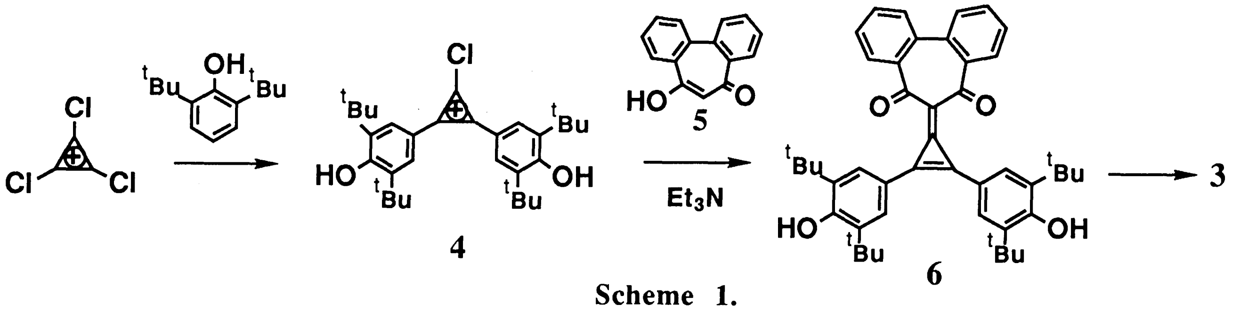
The direct C-C bond formation between troponoids and cyclopropenium ions proceeds quite sluggishly in acidic or neutral media, but occurs more easily in the presence of tertiary amine base such as triethylamine,7) which was succefully applied to the synthesis of **3**, as shown in Scheme 1.

Bis(hydroxyphenyl)chlorocyclopropenium ion **4**,10) obtained through the nucleophilic reaction of 2,6-di-*t*-butylphenol with trichlorocyclopropenium ion at -50 °C in chloroform, was allowed to react with an equimolar amount of dibenzo-*β*-tropolone **5** at room temperature in the presence of 2 molar equivalents of triethylamine and then the resulting mixture was refluxed for 3 h. After usual work up, the reaction mixture was purified by chromatography on silica gel and then by recrystallization from dichloromethane-acetonitrile to give 7,8-bis(hydroxyphenyl)heptatriafulvalene-1,6-dione **6**.11) Two-phase oxidation of **6** in dichloromethane with potassium ferricyanide dissolved in 0.1 M KOH solution afforded a deeply blue-colored organic layer, from which [3]radialene **3**12) was obtained as blue-black needles after purification by recrystallization from the same solvent that for **6**. [3]Radialene **3** is stable on exposure to light and air at room temperature in the solid state.



Scheme 1.

The ^{1}H NMR spectrum of **3** exhibits two different *t*-butyl signals and two different aromatic ring proton signals at 8.30 (H-12, 22) and at 7.56 ppm (H-16,18) in addition to the fused aromatic ring proton signals. In the ^{13}C NMR spectrum of **3**, C-12 and C-22 are also shown to be in a different magnetic environment from C-16 and C-18, respectively. Such a non-equivalency in ^{1}H and ^{13}C NMR spectra was not observed in **6**. Therefore, it has been proved that the rotation of the benzoquinonoid groups about the exocyclic bond of the [3]radialene moiety does not occur in **3** at ordinary temperatures in solution.

According to the anisotropic deshielding caused by the carbonyl groups at C-1 (C-10), the ^{1}H NMR resonance of H-22 (H-12) is shifted further downfield by 0.75 ppm from that of H-18 (H-16). The longest wave-length absorption maximum in the electronic spectrum of **3** showed a hyperchromic effect relative to that of **6**. From these facts it is suggested that **3** is not seriously twisted and would exist in a nearly coplanar conformation not only in the solid state but also in solution.

Apparently, **3** is characterized as a highly electron-deficient compound, because the ^{13}C NMR resonances13) of the three-membered ring carbons appeared at a very low field region (δ 151–152 ppm) and the seven-membered ring carbonyl frequency (1716 cm^{-1}) in the IR spectrum of **3** 14) is much higher by 126 and 111 cm^{-1} than those of **6** (1590 cm^{-1}) and **8** (1605 cm^{-1}),7e) respectively, due to the difficult electron-release from the C-11–C-24 π-bond to the carbonyl carbons of the seven-membered ring. Such an electronic structural feature is in harmony with the electrochemical properties of **3** mentioned below.

The cyclic voltammogram of **3** (Fig. 1) shows two well-defined reversible one-electron reduction waves indicating the formation of stable radical anion $\mathbf{3}^{-\bullet}$ and dianion $\mathbf{3}^{2-}$, and not causing conformational changes through the redox process. The half-wave reduction potentials (E_1^{red} and E_2^{red}) and ΔE^{red} values obtained from Fig. 1 are summarized in Table 1 along with those of some related compounds. Whereas the E_1^{red} of **3** is more negative than that of DDQ, it is more positive by 0.17 and 0.12 V than those of chloranil and trisbenzoquino[3]radialene **7**,15) respectively. The E_2^{red} of **3** is also more positive by 0.13 V than that of **7**. These facts demonstrate that both $\mathbf{3}^{-\bullet}$ and $\mathbf{3}^{2-}$ are stabilized effectively by the electron-withdrawing effect of the

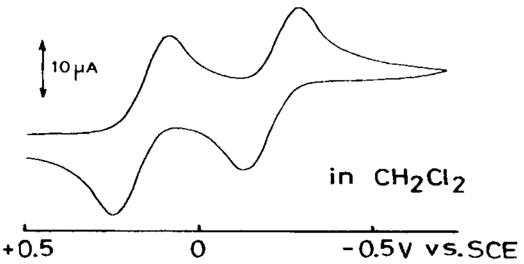


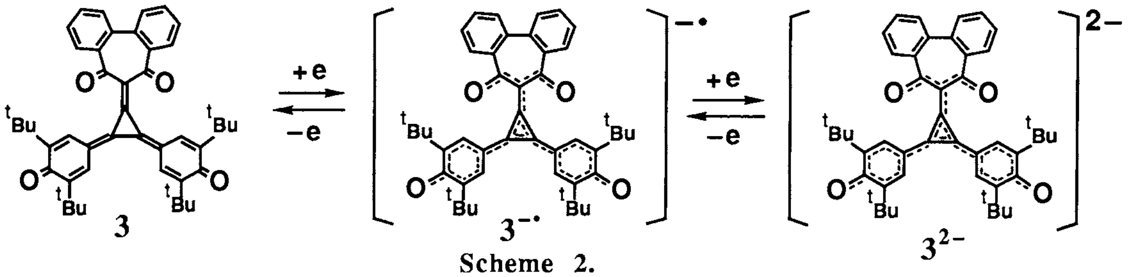
Fig. 1. Cyclic voltammogram of **3** (1 mM), 0.1 M Bu_4NClO_4, 50 mV/s.

Table 1. Half-wave redox potentials[a)] of **3** and related compounds V vs. SCE in CH_2Cl_2

Compound	E_1^{red}	E_2^{red}	ΔE^{red}
3	+0.17	−0.20	0.37
$7^{b)}$	+0.05	−0.33	0.38
Chloranil$^{b)}$	0.00	−0.78	0.78
DDQ$^{b)}$	+0.57	−0.32	0.89

a) Obtained under the conditions given in the caption to Fig. 1.
b) Ref. 15.

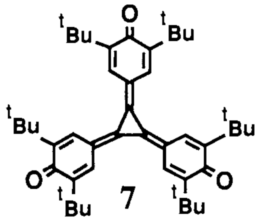
o-tropoquinonoid group, developing the strong electron-accepting properties of **3**. The unpaired electron in **3**$^{-\bullet}$ and the negative charge in **3**$^{2-}$ should be delocalized over the oxygen atoms not only of the six-membered rings but also of the seven-membered ring as shown in Scheme 2, because the ΔE^{red} value of **3**, a measure to estimate the thermodynamic stability of the anion radical and the Coulomb repulsion in the dianion state, is almost the same as that of **7**, whereas **3** (C_{2v}) exhibits a lower symmetry than **7** (D_3).



Scheme 2.

The EPR spectrum of the radical anion **3**$^{-\bullet}$ formed by the electrolysis of **3** in dichloromethane provided a hfs constant, 0.066 mT (4H) which was easily assigned to the four protons of *p*-benzoquinonoid groups (H-12, 16, 18, and 22) according to the π-LUMO coefficients of **3** calculated by PPP-MO method. Although we have no evidence to estimate the spin densities at C-1a, 5a, 5b, 9a, they would be not so high, since the hfs constants of the fused benzene ring protons are too small to be determined.

Compound **3** exhibits a very intense absorption maximum in the electronic spectrum at around 620 nm accompanied with a broad absorption tail reaching to 800 nm, so that it may be favorable for use in optical storage media sensitive to semiconducting laser light.[16)] Moreover, **3** appears to be useful for electrochromic display devices,[17)] since remarkable and reversible color changes are observed in the process of the electrochemical redox reaction participated with yellow colored **3**$^{2-}$: λmax = 433 nm (log ε 4.63), deep orange-red colored **3**$^{-\bullet}$ (in dichloromethane), and blue colored **3**. Formation of the solid complexes of **3** with appropriate donor molecules and isolation of the solid radical salts of **3** are now in progress.



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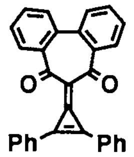

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11) **6**: Pale yellow needles, mp>300 °C, 20% yield, FD-MS: m/z 666 (M^+), 667 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (36H, s, *t*-Bu), 5.96 (2H, s, OH), 7.47 (2H, ddd, J=7.5, 7.5, 1.5 Hz, H-3,8), 7.53 (2H, ddd, J=7.5, 7.5, 1.5 Hz, H-4,7), 7.59 (2H, dd, J=7.5, 1.5 Hz, H-5,6), 7.94 (2H, dd, J=7.5, 1.5 Hz, H-2,9), 8.26 (4H, s, H-12, 16, 18, 22); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 135.94 (C-25,26), 142.13 (C-24), 115.90 (C-11), 135.94 (C-17, 23), 132.49 (C-12, 16, 18, 22), 136.76 (C-13, 15, 19, 21), 158.72 (C-14, 20), 191.65 (C-1, 10); IR (KBr) 3600 (w), 2950 (m), 1820 (w), 1590 (s), 1550 (s), 1380 (vs), 1370 (vs), 1330 (m), 930 (m), 740 (s) cm^{-1}; UV/VIS (MeCN) λ max nm (log ε) 237 (4.34), 295 (4.08), 372 (4.37).

12) **3**: Blue-black needles, mp 220 °C (decomp), 96% yield, FD-MS (664, M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (18H, s, *t*-Bu), 1.56 (18H, s, *t*-Bu), 7.51 (2H, ddd, J=7.5, 7.5, 1.3 Hz, H-3,8), 7.54 (2H, dd, J=7.5, 1.3 Hz, H-5,6), 7.56 (2H, d, J=2.0 Hz, H-16, 18), 7.63 (2H, ddd, J=7.5, 7.5, 1.3 Hz, H-4,7), 7.67 (2H, dd, J=7.5, 1.3 Hz, H-2,9), 8.30 (2H, d, J=2.0 Hz, H-12, 22); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 150.75 (C-25, 26), 152.36 (C-24), 122.89 (C-11), 134.52 (C-17, 23), 133.09 (C-12, 22), 130.77 (C-16, 18), 128.54 (C-13, 21), 128.17 (C-15, 19), 187.12 (C-14, 20), 193.84 (C-1, 10); IR (KBr) 2850~2980 (m), 1716 (m), 1589 (s), 1481 (m), 1456 (m), 1385 (m), 1363 (m), 1282 (m), 1254 (m), 1092 (m), 914 (s), 748 (m) cm^{-1}; UV/VIS (MeCN) λ max nm (log ε) 235 (4.50), 327 (4.24), 374 (4.15), 478sh (3.72), 570sh (4.46), 619 (4.79).

13) The assignments were made by comparison with the signals of **6**, **7**, and **8**.

14) Of the two carbonyl bands at 1716 and 1590 cm^{-1} in the IR of **3**, the former can be assigned to the seven-membered ring carbonyl stretching, since it is unplausible for **3** to exhibit a low or a similar seven-membered ring carbonyl frequency compared with those of the intramolecular pull-push type compounds **8** or **6**.

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