A NOVEL [3]RADIALENE DERIVATIVE WITH AN AMPHOTERIC REDOX PROPERTY. A DIHYDROTHIOPHENEDIYLIDENE-EXTENDED TRISBENZOQUINOCYCLOPROPANE

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Abstract: 1,2-Bis(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-[5-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophen-2-ylidene]cyclopropane, a new near-infrared dye, has been synthesized and characterized as the first radialene derivative exhibiting an amphoteric multi-stage redox property.

Creation of novel multistage redox systems has been keenly desired in order to build up multi- or singlecomponent organic metals or other functional materials such as chromotropic devices, catalysts for electron transfer reactions, and so on. The [3]radialene skeleton appears to be advantageous to development of the conjugation-extended type of redox systems because of its coplanar and relatively rigid conformation, and several π -acceptors¹ and a π -donor² incorporating the [3]radialene framework have been synthesized so far However, there have never been reported any [n]radialene derivatives ($n \ge 3$) exhibiting an amphoteric redox property³ in which both anodic oxidation and cathodic reduction are detected We have previously synthesized thenoquinonoid (dihydrothiophenediylidene) -extended diphenoquinone 1^{3c,4} as a novel amphoteric three-stage one-electron redox system and clarified that the central sulfur atom plays a key role in developing its amphoteric property. Thus, the thienoquinonoid-extention method could be applicable more widely for the molecular design strategies to synthesize amphoteric compounds, if thienoquinonoid-extended compound 3 would show the amphotericity, because the mother compound 2^5 is not amphoteric and moreover its electron-accepting ability is as strong as chloranil.^{1b} The synthesis of **4**, a benzologue of **3**, has been unsuccessful.⁶ The physical and chemical properties of 4 which have remained unknown may be revealed on referring to those of 3 In the present paper, we report the successful synthesis and electrochemical properties of 3, the first radialene exhibiting the amphoteric redox property. Moreover, 3 exhibits a very intense absorption maximum in the near-infrared region, so that it ranks as a new near-infrared dye.7



The synthesis of **3** was achieved via the route depicted in Scheme 1. 1,2-Bis(hydroxyphenyl)chlorocyclopropenium ion **5**, obtained by the reaction of trichlorocyclopropenium ion with di-*t*-butylphenol,⁸ was allowed to react with an equimolar amount of thenylphenol 6^{3c} in chloroform at room temperature, and then the resulting mixture was refluxed for 2 h. After the usual work-up, the crude product was purified by silica-gel column chromatography to give a quinarenone-type⁹ compound 7^{10} in 20 % yield based on the trichlorocyclopropenium ion. The IR spectrum of 7 showed a characteristic cyclopropene C=C stretching band at 1830 cm⁻¹ together with a C=O and an OH band at 1610 and 3610 cm⁻¹, respectively. However, 7 was revealed to exist as an equilibrium mixture of **7a** and **7b** in a chloroform solution, because in the ¹H NMR spectrum the benzenoid ring protons appeared as a sharp two-proton singlet (C ring protons) and a broad four-proton signal resonating at a lower field (A and B ring protons). In addition, a sharp OH singlet corresponds to one proton and the vicinal coupling constant of the thienyl ring protons (*J*=4.0 Hz) is too small to be assigned to that for **7c**.¹¹ A benzene solution of **7** was treated with excess potassium ferricyanide dissolved in 0 1 M KOH solution at room temperature, followed by column chromatography of the crude product on silica gel with hexane-AcOEt (9:1), to afford a desired compound **3** as greenish-black needles.¹² It is noticeable that 3 is stable in the solid state at room temperature, while **4** dimerizes with ease.⁶



The redox property of **3** was evidenced by its cyclic voltammogram (CV) shown in Figure 1. The two reversible one-electron couples appear in the cathodic region and more interestingly one-electron wave at 1.23 V in an anodic region. The one-electron nature of each of the three waves was supposed from their equal height. Thus the amphoteric three-stage one-electron redox reaction of **3** was proved to proceed in the sequence shown in equation (1). 2^{++} $+^{++}$ 2^{-+} $+^{++}$ 2^{-+} $+^{++}$ $2^{2^{--}}$ (1)

$$3^{+*} \xrightarrow{+e}_{-e} 3 \xrightarrow{+e}_{-e} 3^{-*} \xrightarrow{+e}_{-e} 3^{2-}$$
 (1)

No oxidation was observed for 2 within the potential range readily accessible for electrochemical studies, therefore such a relatively easier oxidation ability of 3 should be attributable to the thienoquinonoid-extention, e.g., the radical cation 3^{+*} can be effectively stabilized by participation of sulfur $3p\pi$ orbitals. Although the anodic wave is irreversible, the formation of the radical cation 3^{+*} by the electrochemical oxidation of 3 was



Figure 1. Cyclic voltammogram of 3, 1.0 mM in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at room temperature (scan rate: 50 mV / sec, reference electrode⁻ SCE). demonstrated by its EPR spectrum composed of nine lines with g=2.0046. The EPR spectrum composed of symmetrical eight lines (a pentet of doublets) due to the radical anion 3⁻⁺, obtained under the electrochemical reduction of 3, appeared at g=2.0041.¹³

The electrochemical data of 3 obtained by the CV are listed in Table 1 together with those of $1^{3c,4}$ and 2.^{1b} The E₁^{red} value of 3 is much more positive by 0.45–0.5 V than that of 1 and is almost equal to that of 2, indicating that the electron-accepting ability is not so weakened in 3 on comparing with 2, so that 3 can be used as an acceptor molecule. The negative charge in 3^{2-} should be delocalized over the oxygen atoms of the A and B and also of the C rings, since the ΔE^{red} (= $E_2^{red} - E_1^{red}$) value, a measure to estimate the Coulomb repulsion in a diamon state, is a little smaller by 0.1 V for 3 than for 2. However, it is worth noting that the ΔE^{red} value for 3 is larger than that for 1, whereas 3 exhibits a longer conjugation than 1. The [3]radialene molety is thus shown to be an excellent extending areno π -system for stabilizing thermodynamically the radical amon, which results from the contribution of the aromatic stabilization participated by the twofold [3.6]- and onefold [3.5.6]quinarenonetype resonance structures,⁹ while the participating extent of each resonance structure may not be equivalent. The 13]radialene π -system appears to be also favorable to increase the electron-donating ability, since the E_{pa}^{0x} value for 3 is lower by about 0.1 V than that for 1, whereas the former involves one more quinonoid carbonyl group than the latter. Thus, the E_1^{sum} value³ found for 3 is smaller by 0.56–0 59 V than that for 1, indicating a significantly higher amphotericity for 3 than for 1

Table 1. Electrochemical properties of 3 and its related compounds 1 and 2. V vs. SCE^a)

Compound	Solvent	E1red	E2red	ΔEred	log K _{sem}	Epaox	E1ox	E_1^{sum}
3	EtCN	+0.04	-0.26	0.30	5.08	+1.14	+1.11b)	1.07
3	CH ₂ Cl ₂	-0.01	0.29	0.28	4.75	+1.23	+1.20b)	1 21
2 ^c)	CH ₂ Cl ₂	+0.05	-0 33	0.38	6.44		·	
$1(R=t-Bu)^{d}$	MeCN	-0.46	-0.60	0.14	2.37	+1.24	+1.20	1.66
$1(R=t-Bu)^{d}$	CH_2Cl_2	-0.51	-0.61	0.10	1.69	+1.32	+1.26	1 77

a) Obtained under the conditions given in the caption to Figure. 1. b) Deduced 30 mV from E_{pa} ox.

c) Reference 1b d) Reference 3c, 4.

In the ¹H NMR spectrum of 3, each of the two ring protons on the A, B, and C rings showed different chemical shifts, suggesting that the five rings in 3 should be fixed and not rotate around the intercyclic bonds in solution. The C ring is a little more magnetically shielded than A or B ring, because the chemical shift of H_g on C ring is higher by 0.1–0.2 ppm than those of H_d, H_c, and H_b on B and A rings. Thus the band at lower frequency of the two carbonyl bands (1578 and 1590 cm⁻¹) in the IR spectrum of 3 can be assigned to that of C ring.

The electronic spectrum of **3** showed a characteristic 1st excitation band in the near-infrared region of 820 nm (Figure 2) which is more bathochromic by 400 and 51 nm compared with those of **7** and **2**, respectively. The very high absorption intensity of the maximum reveals the nearly coplanar conformation of **3**.

In the preceding paper dealing with an attempted synthesis of 4,⁶ the absorption band temporarily observed at 1300 nm was assigned to that of 4. Based on the electronic spectral data of 3, however, it is now suggested that 4 should show its absorption maximum at a shorter wave-length region, since the 1st excitation band of benzoquinonoid-extended tropone^{9b} showed a red shift by only 50 nm from that of thienoquinonoid-extended one.^{11b}



Figure 2. Electronic spectrum of 3.

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- 10. 7: Reddish brown needles, mp 256–258 °C, FAB-MS: m/z (%) 734 (M⁺+2, 55), 733 (M⁺+1, 97), 732 (M⁺. 10); ¹H NMR (400 MHz, CDCl₃) δ 1.518 (18H, s, *t*-Bu-C), 1.535 (36H, s, *t*-Bu-A,B), 5.540 (1H, s, OH-C), 7.510 (1H, d, J=4.0 Hz, H_t), 7.572 (2H, s, H_{h,g}), 7.865 (1H, d, J=4.0 Hz, H_e), 7.880 (4H, br s, H_{a-d}); IR (KBr) 3610, 2970–2880, 1838, 1610, 1525, 1490, 1420, 1360, 1330, 1092, 923, 906 cm⁻¹; UV/VIS (MeCN) λ max (log ε) 257 (4.18), 267 (4.19), 382 (4.54), 403 (4 69), 425 (4.86), 508 nm (4.16).
- The J_{e,f} value for 7c is expected to be around 5.3-6.0 Hz, see: (a) K. Takahashi, K. Nishijima, K. Takase, and S. Katagiri, *Tetrahedron Lett.*, 1983, 24, 205, (b) K. Takahashi, T. Sakae, and K. Takase, *Chem. Lett.*, 1980, 179.
- 12 3· Green-black needles, mp 230–232 °C, DEI-MS: m/z (%) 732 (M++2, 8), 730 (M+, 100), ¹H NMR (400 MHz, CDCl₃) δ 1.364 (18H, s, *t*-Bu-C), 1 396 (18H, s, *t*-Bu-A,B), 1.410 (9H, s, *t*-Bu-B), 1.455 (9H, s, *t*-Bu-A), 7.480 (1H, d, *J*=2.5 Hz, H_h), 7.342 (1H, d, *J*=2.5 Hz, H_g), 7.879 (1H, d, *J*=5.5 Hz, H_f), 7.675 (1H, d, *J*=5.5 Hz, H_e), 7.442 (1H, d, *J*=2.25 Hz, H_d), 7.521 (2H, d, *J*=2.25 Hz, H_{b,c}), 7.755 (1H, d, *J*=2.25 Hz, H_a); IR (KBr) 2960 (m), 1590 (vs), 1578 (vs), 1455 (m), 1386 (m), 1360 (m), 1253 (w), 1098 (s), 1082 (m), 893 (m) cm⁻¹; UV/VIS/NIR (MeCN) λ max (log ε) 245 (4.13), 287 (4.08), 323 (4.19), 356 (4.25), 380 (4.39 sh), 408 (4.55), 446 (4.45), 650 (4.41 sh), 740 (4.59 sh), 820 (4.66), 940 nm (4 23 sh)
- 13. The EPR measurment was carried out by Prof Y. Ikegami and Dr. K. Akiyama to whom we are indebted (Received in Japan 19 February 1991)