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Adamantane-2,4-bis(*p*-quinone methide) and -2,6-bis(*p*-quinone methide) as New Models for Intramolecular Interactions between Spatially Separated Redox Systems

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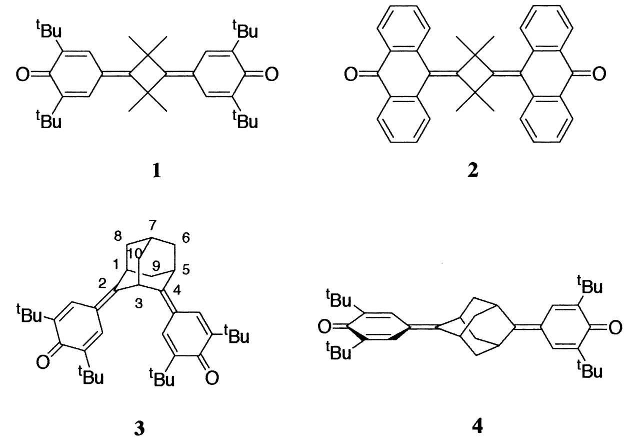
Adamantane-2,4-bis(*p*-quinone methide) and -2,6-bis(*p*-quinone methide) were synthesized by the reaction of adamantane-2,4-dione and -2,6-dione, respectively, with lithium 4-lithio-2,6-di-*t*-butylphenoxide, followed by dehydration. Their structures were established by spectroscopic and X-ray crystallographic analyses. Having a distance (2.47 Å) between C2 and C4 longer than that (ca. 1.9 Å) between C1 and C3 of cyclobutane-1,3-bis(*p*-quinone methide)s, adamantane-2,4-bis(*p*-quinone methide) was found to show a clear through-space interaction (homoconjugation) and to form a σ-bond at its bis(anion radical) stage upon both chemical and electrochemical reduction. On the other hand, adamantane-2,6-bis(*p*-quinone methide), which has a long distance and near orthogonal arrangement between the quinone methide chromophores, shows a through-bond interaction, though it is weak.

Quinones and quinone methides (quinomethides) are important members in organic electrochemistry owing to their multistep redox properties.[1] These quinonoid systems form anion radicals and dianions upon electronic reduction with good reversibility. When a molecule contains more than one quinomethide group, there can be intramolecular interaction between or among the quinomethide groups or their anion radicals depending on their spatial relationship. As such systems, Hünig et al. studied cyclobutane-1,3-bisquinomethides, **1** and **2**, which formed dynamic multistep redox systems involving σ-bonds formation.[2] In these compounds, two quinomethide groups are spatially close enough to form σ-bond in their bis(anion radical)s. Such intramolecular bis(anion radical)s would either form a σ-bond or remain unbonded, depending on the spatial arrangement of radical centers, and at a proper arrangement a molecule could show dynamic behaviors sensitive to external conditions. In order to find electrochemically highly dynamic multi-quinomethide systems, we examined the properties of adamantane derivatives incorporated with two quinomethide groups. Because of the rigid and distinct molecular geometry, adamantane would be an ideal compound of molecular framework for assessing intramolecular interactions between incorporated redox systems. Although the intramolecular interactions in adamantane derivatives have been studied to some extent,[3–5] no studies on adamantanes incorporated with good redox systems have been described. Here we report on the synthesis, structures, and properties, in particular redox behaviors, of adamantane-2,4-bis-*p*-quinomethide **3** [2,4-bis(4-oxo-3,5-di-*t*-butylcyclohexa-2,5-dienylidene)adamantane] and adamantane-2,6-bis-*p*-quinomethide **4** [2,6-bis(4-oxo-3,5-di-*t*-butylcyclohexa-2,5-dienylidene)adamantane] (Chart 1).

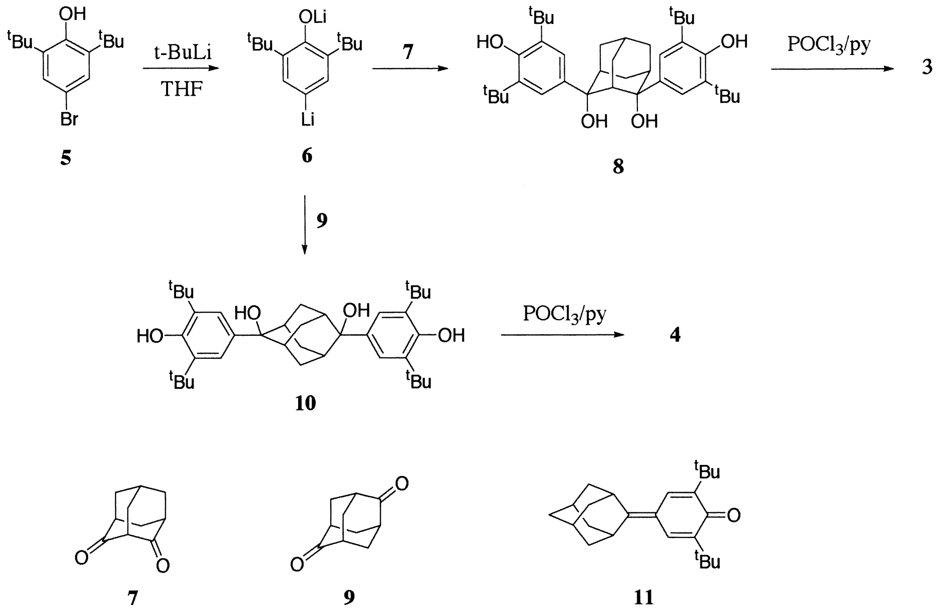


1 **2** **3** **4**

Chart 1.

Results and Discussion

We have reported the good utility of lithium 4-lithio-2,6-di-*t*-butylphenoxide **6**, generated by treatment of 4-bromo-2,6-di-*t*-butylphenol **5** with three equivalents of *t*-BuLi,[6] for the synthesis of the corresponding quinomethides by reaction with ketones.[7] Here dianion **6** was applied to the synthesis of **3** and **4**. Thus, the reaction of **6** with adamantane-2,4-dione **7**[8] afforded the 2,4-bisadduct **8** in 64% yield. Although there can be three stereo isomers [*endo-endo*, *exo-exo*, *endo-exo* (racemate)] for **8**, ^{1}H and ^{13}C NMR spectra suggest an overwhelming formation of one isomer. The product was assigned to be 2-*exo*-4-*exo* isomer based on the observation of seven ^{13}C signals for the adamantane skeleton (C_{2V} symmetry) and steric consideration for the approach of nucleophile **6**. Dehydration of **8** with POCl$_3$ in pyridine gave the desired compound **3** in 74% yield (Scheme 1). In a similar way, 2,6-bisquinomethide **4** was synthesized from adamantane-2,6-dione **9**[9] via bis-adduct **10** in 30% yield. Mono-*p*-quinomethide **11** was also prepared simi-



Scheme 1. Synthesis of adamantane-quinomethides **3**, **4**, and **11**.

larly from adamantanone for comparisons (83% yield).

Bisquinomethides **3** and **4** are yellow substances with good air and thermal stabilities. Single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from ethyl acetate–hexane (for **3**) or benzene–hexane (for **4**). The latter crystals include hexane molecules in 1 : 1 ratio. Figure 1a shows the ORTEP drawings of **3**. The quinomethide groups are essentially planar. The distance between C2 and C4 is 2.47 Å, and the dihedral angle between two quinomethide groups is 111.0°. The distance and angle are suitable enough for through-space interaction (homoconjugation) between the p-orbitals at C2 and C4. In the crystal, two molecules form a pair so as to fill their molecular concaves [Fig. 1b]. Figure 2 shows the ORTEP drawings of **4**. Although the crystal of **4** showed relatively poor diffractions because of slow evaporation of included hexane molecules during the measurement, allowable data were obtained for the determination of the structure of **4**. The distance between C2 and C6 is 3.52 Å, which is about 1 Å longer than that of **3**, and the planes of the two quinomethide groups are twisted by 74.6° each other. In theory, the two quinomethide groups should be in orthogonal arrangement. Since the quinomethide group having two *t*-butyl groups is bulky, some packing force in the crystal could be a reason for the deviation from the orthogonal arrangement.

UV-vis absorptions of 2,4-bisquinomethide **3** exhibits split absorption maxima at 312 and 350 nm to indicate considerable interaction (homoconjugation) between the two chromophores. The X-ray structure of **3** is compatible with this observation. On the other hand, 2,6-bisquinomethide **4** ($\lambda_{\max}$ = 341 nm) shows a single peak absorption similar to monoquinomethide **11** ($\lambda_{\max}$ = 334 nm in CH_2Cl_2) with almost doubled absorption coefficient and slightly longer wavelength absorption than **11** (Fig. 3). The small bathochromic shift and single absorption maximum indicate that interaction between the quinomethide groups of **4** is weak, if any.

Upon cyclic voltammetry, 2,4-bisquinomethide **3** shows one set of quasi-reversible redox waves which have a large difference (hysteresis) between the reduction and re-oxidation potentials (ΔE = 0.65 V at room temperature, Table 1, Fig. 4). The difference became larger when the measurement temperature was lowered (ΔE = 1.02 V at −40 °C, Fig. 4). The equivalency of the two quinomethide groups in the redox behavior agrees with the homoconjugation, and the temperature-dependent voltammogram indicates that the electronic reduction of **3** involves a substantial structural change, probably σ-bond formation between C2 and C4 to give bisphenoxide **12** that has a 2,4-didehydroadamantane skeleton (Scheme 2). On the other hand, 2,6-bisquinomethide **4** exhibits two sets of reversible redox waves in a narrow range ($\Delta E_{1/2}$ = 0.11 V). The first reduction potential (−1.47 V) is slightly lower than that of monoquinomethide **11** (−1.55 V). The marginal non-equivalency of the two quinomethide groups in **4** suggests a weak interaction between them in spite of the long distance of C2–C6 and the near-orthogonal arrangement. These results coupled with those of electronic absorption point to the existence of a strong through-space interaction for **3** and a weak through-bond interaction for **4**.

In order to make the redox behavior clearer, alkali-metal reductions of **3** and **4** were carried out. A yellow solution of **3** changed to a colorless solution upon contact with sodium in THF; the UV-vis spectral change is shown in Fig. 5. The appearance of an isosbestic point at 282 nm indicates a clean transformation. The final reduction product which had UV absorptions at 266 and 319 nm was assigned to bisphenoxide **12** by detailed ^{1}H- and ^{13}C-NMR analysis (see Experimental Section for signal assignments) as well as its trapping as bis(trimethylsilyl) ether **13** by reaction with chlorotrimethylsilane (87% yield; Scheme 2). Both ^{1}H and ^{13}C NMR spectra of **12** and **13** agree with C_{2V} symmetry of the molecules. The parent 2,4-didehydroadamantane **14** has been known,[10] and its most characteristic NMR result is a very low field appearance of C9 (δ 52.5) which is situated directly across from cyclopropane ring.[11] Compounds **12** and **13** also show such a low field sp^3 carbon at δ 50.61 and 50.59, respectively, consonant with the

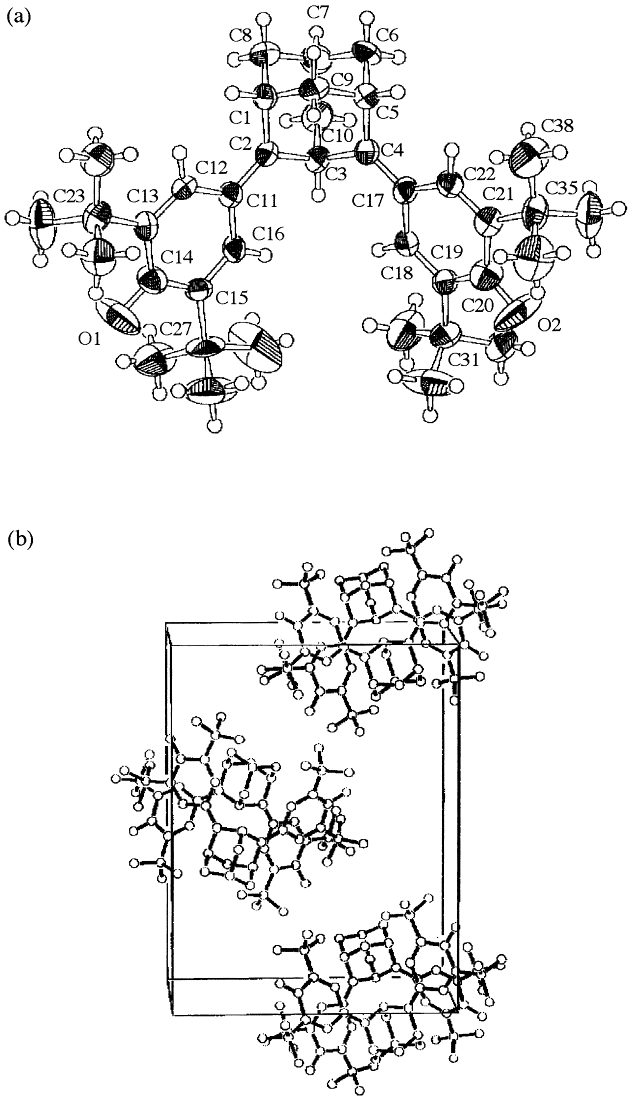


Fig. 1. Molecular and crystal structure of **3**: (a) An ORTEP drawing (50% thermal ellipsoids), (b) viewed along the *c* axis. Selected structural parameters: C(1)–C(2) 1.513(8), C(2)–C(3) 1.533(8), C(2)–C(11) 1.359(8), C(11)–C(12) 1.432(8), C(12)–C(13) 1.343(8), C(14)–O(1) 1.229(8), C(1)–C(2)–C(3) 108.8(5), C(3)–C(2)–C(11) 124.9(6), C(2)–C(3)–C(4) 107.7(5), C(2)–C(11)–C(12) 122.3(6), C(13)–C(14)–O(1) 120.9(6).

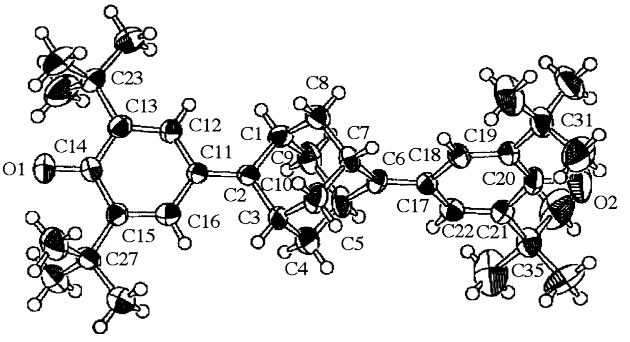


Fig. 2. An ORTEP drawing (50% thermal ellipsoids) of **4**. Included solvents (hexane) are omitted for simplicity. Selected structural parameters: C(1)–C(2) 1.505(9), C(1)–C(8) 1.529(10), C(1)–C(9) 1.54(1), C(2)–C(11) 1.379(9), C(11)–C(12) 1.443(9), C(12)–C(13) 1.362(9), C(13)–C(14) 1.475(9), C(14)–O(1) 1.245(8), C(2)–C(1)–C(8) 110.8(6), C(2)–C(1)–C(9) 109.2(6), C(1)–C(2)–C(3) 110.7(6), C(1)–C(2)–C(11) 125.5(6), C(2)–C(11)–C(12) 121.2(7), C(13)–C(14)–O(1) 120.0(7).

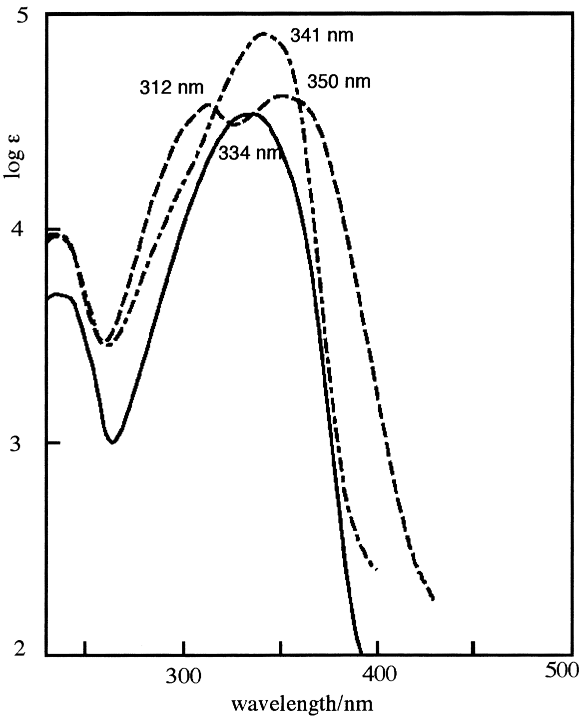


Fig. 3. Electronic spectra of **3** (– – –), **4** (– - – -), and **11** (— —) in CH_2Cl_2.

2,4-didehydroadamantane structure. The one of the methylene protons at C9 (δ 2.75; NOE with the aromatic protons) is also at the lowest field among the protons on the didehydroadamantane framework. On the other hand, a yellow solution of **4** changed to a pale orange solution upon contact with sodium in THF (λ_{max} = 266, 318 nm tailing to visible region). Exposure of this solution to air reproduced **4** in 80% yield. While the re-

Table 1. Reduction Potentials of **3**, **4**, and **11**

Compound	Temp/°C	Reduction potentials/V[a)]		$\Delta E(E_{pa} - E_{pc})$/V
3	25	$E_{pc} = -1.27$	$E_{pa} = -0.62$	0.65
	−40	$E_{pc} = -1.31$	$E_{pa} = -0.29$	1.02
4	25	${}^1E_{1/2} = -1.47$	${}^2E_{1/2} = -1.58$	
11	25	${}^1E_{1/2} = -1.55$		

a) V vs Ag/AgCl in 0.1 M Bu_4NClO_4/DMF (ferrocene/ferrocene$^+$ = 0.48 V), sweep rate 100 mV s^{-1}.

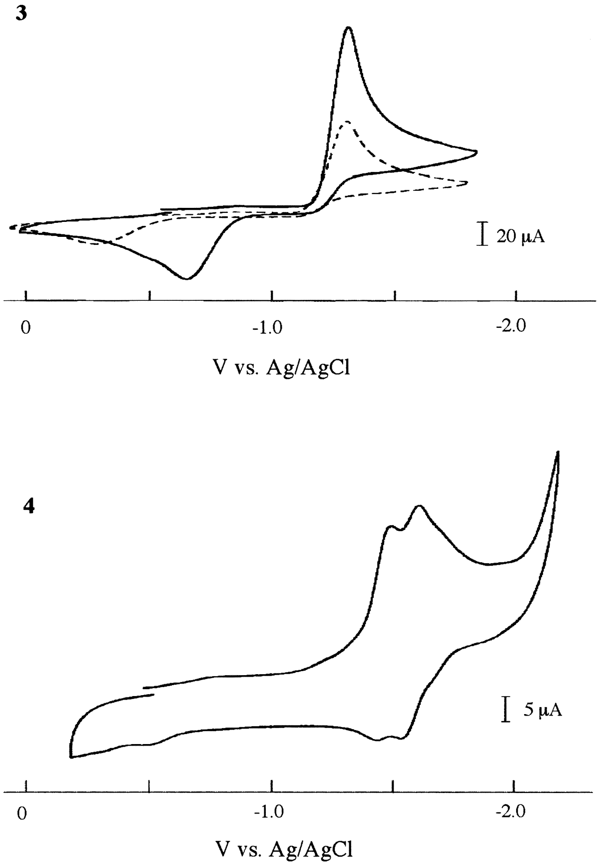
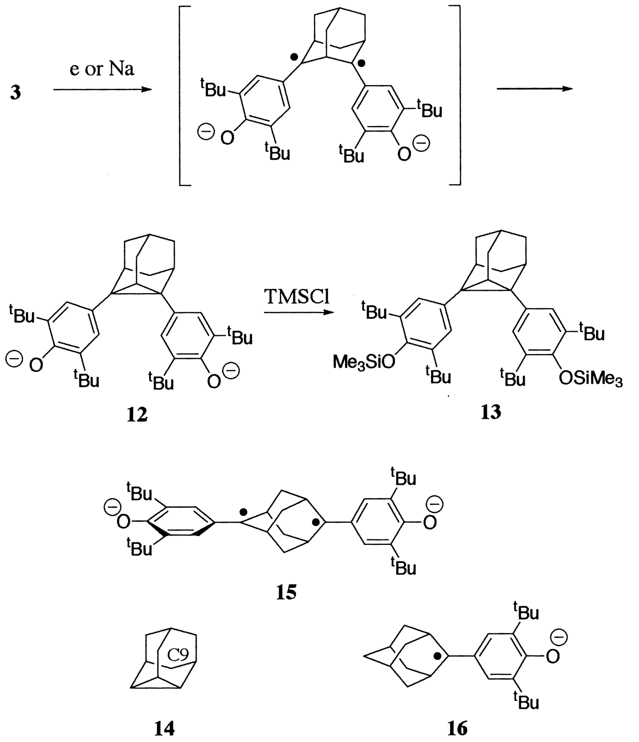


Fig. 4. Cyclic voltammograms of **3** and **4** (solid line at 25 °C; dotted line at −40 °C).



Scheme 2. Electronic reductions of adamantane-quinomethides.

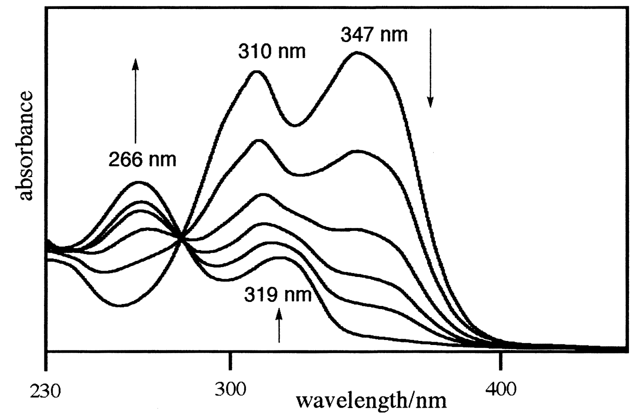


Fig. 5. UV-vis spectral change of **3** upon reduction with Na in THF.

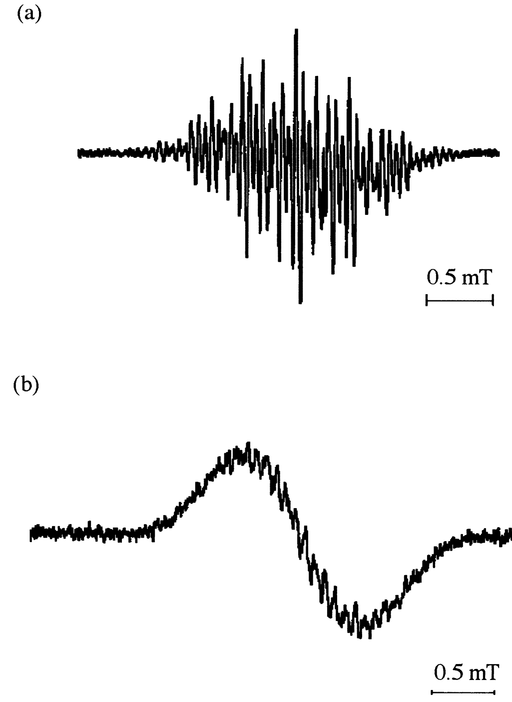


Fig. 6. ESR spectra of **16** (a) and **15** (b) in 2-methyl THF at 25 °C.

duced solution of **3** was ESR-silent in agreement with the σ-bond formation, the reduced solution of **4** was ESR-active. The ESR spectrum of the solution exhibits broad absorptions probably of bis(anion radical) **15** [Fig. 6b]. In contrast, the anion radical **16** obtained from monoquinomethide **11** by a similar reduction shows complicated signals but with sharp hyperfine-structure (due to coupling with aromatic protons and fourteen protons on the adamantane skeleton) [Fig. 6a]. Similar broad ESR absorption in solutions due to a dipole-dipole interaction has been reported for a *p*-quarterphenyl biradical/quinone system.[12]

Conclusion

Although adamantane-2,4-bisquinomethide **3** has a longer distance (2.47 Å) between C2 and C4 than that (1.9 Å) between C1 and C3 of cyclobutane-1,3-bisquinomethides **1** and **2**, it shows a strong through-space interaction (homoconjugation) between the redox chromophores and forms σ-bond when reduced to its bis(anion raidcal). On the other hand, adamantane-2,6-bisquinomethide **4**, which has about 1 Å longer distance (3.52 Å) and near orthogonal arrangement between the chromophores, exhibits a weak but detectable through-bond interaction. Therefore, a dynamic system based on bis-redox systems as here initially desired will be found in a bis-redox system having a spatial arrangement between those of **3** and **4**. In addition, the ready σ-bond formation of **3** to a strained didehydroadamantane derivative **12** upon electronic reduction makes adamantane-2,4,9-trisquinomethide an interesting target molecule because its electronic reduction would form a degenerative trianion radical. It is also noteworthy that introduction of the dye chromophores with good redox properties in carbon frameworks like **3** and **4** seems advantageous in observing intramolecular interactions more clearly than the introduction of ordinary chromophores such as carbonyl groups.

Experimental

Melting points were measured on a Yanaco MP 500D and were uncorrected. Mass spectra were recorded with a JEOL SX-102 by EI or FAB method. Infrared spectra were recorded on a Perkin Elmer 1650 FT-IR spectrophotometer in KBr disks and only significant absorption bands are reported. UV-vis absorption spectra were obtained on a Jasco V-570 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on Varian UNITY plus 600 (600 MHz), JEOL GSX-400 (400 MHz), or JEOL EX-270 (270 MHz) spectrometer, and recorded in δ value from tetramethysilane as an internal standard. The ^{1}H and ^{13}C NMR spectra of **3** and **12** were measured at 600 MHz and assigned by combination of H-H COSY, NOESY, HMQC, and HMBC techniques. Cyclic voltammetry was performed on a Yanaco Model P-1100 voltammetric analyzer. ESR spectra were measured on a JEOL JES-RE1X spectrometer. Adamantane-2,4-dione and -2,6-dione, **7** and **9**, were prepared by oxidation of 2-adamantanone according to the literature.[8] 4-Bromo-2,6-di-*t*-butylphenol **5** was prepared according to the literature with modifications.[13]

2,4-Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)adamantane-2,4-diol (8): To a solution of **5** (1.71 g, 6.0 mmol) in tetrahydrofuran (THF; 20 mL) was added dropwise a 1.64 M (1 M = 1 mol dm^{-3}) solution of *t*-butyllithium in pentane (11.0 mL, 18.0 mmol) at −78 °C. The mixture was stirred at 0 °C for 1 h. To the resulting colorless suspension of dianion **6** was added dropwise a solution of **7** (328 mg, 2.0 mol) in THF (20 mL) at −78 °C; the mixture was stirred at 0 °C for 3 h, and then at room temperature for 3 h. After hydrolysis with saturated ammonium chloride solution, the mixture was extracted with ethyl acetate/benzene (1 : 1, 70 mL × 3), washed with water and brine, and dried (Na_2SO_4). The solvent was evaporated in vacuo, and the residue was washed with a small amount of cold benzene to give 2,4-diol **8** (744 mg, 64%): colorless needles (from dichloromethane–hexane); mp 281–282 °C (decomp); MS (FAB) *m*/*z* 569 [$(M-OH)^+$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 36H), 1.57–1.79 (m, 7H), 1.91 (dt, J = 13.5, 2.8 Hz, 1H), 2.70 (s, 2H), 2.82 (d, 13.5, 1H), 3.43 (s, 1H), 4.30 (s, 2H), 5.18 (s, 2H), 7.44 (s, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 26.46, 29.35, 30.34, 32.28, 34.67, 35.21, 35.48, 40.94, 79.30, 121.98, 135.08, 135.73, 152.87; IR 880, 1060, 1121, 1159, 1208, 1241, 1360, 1441, 2952, 3389, 3640 cm^{-1}; Found: C, 78.70; H, 9.73%. Calcd for $C_{38}H_{56}O_4$: C, 79.12; H, 9.78%.

2,6-Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)adamantane-2,6-diol (10): To a suspension of dianion **6** prepared from **8** (975 mg, 3.4 mmol) in 10 mL of THF and 1.64 M *t*-butyllithium in pentane (6.3 mL, 10.3 mmol) was added a solution of **9** (187 mg, 1.1 mmol) in THF (5 mL), and the mixture was worked up as described above. The crude product was purified by column chromatography (Al_2O_3, eluent; benzene) to give 2,6-diol **10** (327 mg, 50%): colorless powder (benzene-hexane); mp 219–220 °C (decomp); MS (FAB) *m*/*z* 559 [$(M-OH)^+$]; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (s, 36H), 1.69 (quasi-d, 2H), 2.38–2.40 (quasi-d, 6H), 2.53 (br. s, 2H), 5.17 (s, 2H), 7.34 (s, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 28.09, 29.92, 30.41, 30.91, 34.61, 34.90, 35.21, 75.06, 122.16, 135.29, 135.64, 152.81; IR 885, 952, 999, 1020, 1109, 1122, 1157, 1211, 1241, 1317, 1361, 1441, 2954, 3443, 3640 cm^{-1}; Found: C, 79.22; H, 9.76%. Calcd for $C_{38}H_{56}O_4$: C, 79.12; H, 9.78%.

Adamantane-2,4-bis(*p*-quinone methide) (3): To a solution of **8** (105 mg, 0.18 mmol) in pyridine (5 mL) was added phosphoryl chloride (0.1 mL, 1.0 mmol) at 0 °C. The mixture was allowed to warm to room temperature, stirred for 4 h, and then poured into ice-water (20 mL). The mixture was extracted with benzene (50 mL × 3), and the combined organic phase was washed with 2 M hydrochloric acid, water and brine, and dried (Na_2SO_4). After evaporation of solvent in vacuo, the residue was purified by coloumn chromatography (Al_2O_3, 50 g, eluent; hexane/benzene = 1 : 1) to give **3** (73 mg, 74%): yellow needles (benzene–hexane); mp 318–319 °C; MS (FAB) *m*/*z* 541.5 [$(M+H)^+$]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (s, 18H, CH_3), 1.34 (s, 18H, CH_3), 2.01 (br. d, J = 12.4 Hz, 1H, C9 eq-H), 2.09 (br. d, J = 12.6 Hz, 2H, C6,8 ax-H), 2.21 (narrow quintet, 1H, C9-H), 2.25 (br. s, 2H, C10-methylene), 2.26 (br. d, J = 12.6 Hz, 2H, C6,8 eq-H), 2.34 (dt, J = 12.4, 2.6 Hz, 1H, C9 ax-H), 3.64 (br. s, 2H, C1,5-H), 5.03 (br. s, 1H, C3-H), 7.37 (d, J = 2.8 Hz, 2H, C2′ or C6′-H), 7.45 (d, J = 2.8 Hz, 2H, C2′ or C6′-H) (The designations, ax and eq, are based on the cyclohexane ring bearing the quinomethide group(s)); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.86 (C7), 29.52 (CH_3), 29.68 (CH_3), 34.14 (C1,5), 35.37 (benzyl), 35.38 (benzyl), 39.41 (C6,8), 39.99 (C9), 40.66 (C3), 43.54 (C10), 123.47 (C1′), 125.32 (C2′ or C6′), 126.82 (C2′ or C6′), 147.30 (C3′ or C5′), 147.64 (C3′ or C5′), 163.90 (C2,4), 186.97 (carbonyl); UV-vis (CH_2Cl_2) λ_{max} (log ε) 312 (4.58), 350 nm (4.62); IR 1090, 1256, 1364, 1387, 1456, 1551, 1614, 2955 cm^{-1}; Found: C, 84.33; H, 9.79%. Calcd for $C_{38}H_{52}O_2$: C, 84.39; H, 9.69%.

Adamantane-2,6-bis(*p*-quinone methide) (4): 2,6-Diol **10** (200 mg, 0.35 mmol) and phosphoryl chloride (0.2 mL, 0.2 mmol) in pyridine (8 mL) were reacted as described above. The crude product was purified by column chromatography (Al_2O_3, eluent; hexane/benzene = 1 : 1) to give **4** (110 mg, 59%): yellow prisms (benzene–hexane); mp 360 °C (decomp); MS (FAB) *m*/*z* 541.5 [$(M+H)^+$]; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.34 (s, 36H), 2.24 (s, 8H), 3.63 (br 4H), 7.44 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.59, 33.91, 35.42, 41.96, 123.18, 126.28, 147.15, 164.77, 187.10; UV-vis (CH_2Cl_2) λ_{max} (log ε) 341 nm (4.90); IR 900, 918, 1103, 1264, 1352, 1451, 1484, 1558, 1612, 2955 cm^{-1}; Found: C, 84.11, H, 10.58%. Calcd for $C_{38}H_{52}O_2 \cdot C_6H_{14}$: C, 84.29; H, 10.61%.

Adamantane-2-(*p*-quinone methide) (11): To a suspension of dianion **6** prepared from **5** (342 mg, 1.2 mmol) in 5 mL of THF and 1.64 M *t*-butyllithium in pentane (2.2 mL, 3.6 mmol) as described for the synthesis of **9** was added a solution of 2-adamantanone (150 mg, 1.0 mmol) in THF (5 mL). The crude product was purified by column chromatography (Al_2O_3, eluent; benzene) to give 2-(3,5-di-*t*-4-hydroxybutylphenyl)adamantan-2-ol (299 mg, 84%). The alcohol (86 mg, 0.24 mmol) and phosphoryl chloride (0.5 mL, 5.0 mmol) in pyridine (4 mL) were reacted, and the mixture was worked up as described for the synthesis of **3**. Evaporation of solvent in vacuo gave **11** in satisfactory purity (81 mg, 99%): yellow needles (hexane); mp 227–228 °C; MS (EI) *m*/*z* 338 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 18H), 1.90–1.95 (m, 6H), 2.04–2.12 (m, 6H), 3.51 (s, 2H), 7.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.88, 29.59, 34.86, 35.32, 36.65, 40.15, 122.31, 126.65, 146.35, 170.44, 187.18; UV-vis (CH_2Cl_2) λ_{max} (log ε) 334 nm (4.53); IR 880, 899, 944, 1100, 1259, 1362, 1450, 1548, 1612, 2849, 2915 cm^{-1}; Found: C, 85.05, H, 10.06%; Calcd for $C_{24}H_{34}O$: C, 85.15; H, 10.12%.

Alkali Metal Redution. All reactions were carried out under high-vacuum conditions (10^{-5} mmHg). Sodium was deposited as a mirror on the wall of the reaction vessel. The solvents (THF, THF-d_8, or 2-methyl-THF) were dried by sodium-potassium alloy, and degassed by repeated freeze-pump cycles. The amounts of the quinone methides used for the measurement were ca. 0.5 mg for UV-vis. and ESR, and 5 mg for NMR.

NMR Spectral Data of Dianion 12. ^{1}H NMR (600 MHz, THF-d_8, 30 °C) δ 1.32 (s, 36H, CH_3), 1.48–1.50 (m, 3H, C6,8 quasi-eq and C9 quasi-eq H), 1.59 (br. d, J = 11.5 Hz. 2H, C6,8 quasi-ax-H), 1.90 (br. s, 1H, C7-H), 2.07 (br. s, 2H, C10-methylene), 2.15 (br. s, 1H, C3-H), 2.48 (br., 2H, C1,5-H), 2.75 (br. s, 1H, C9 quasi ax-H, NOE with the aromatic protons), 6.76 (s, 4H, aromatic) (The designations, quasi-ax and -eq, are based on the cyclohexane ring bearing the aromatic ring(s)); ^{13}C NMR (150 MHz, THF-d_8, 40 °C) δ 27.18 (C7), 30.72 (C10), 31.18 (CH_3), 32.32 (C3), 34.23 (C6,8), 35.57 (benzyl C), 43.79 (C1,5), 46.74 (C2,4), 50.61 (C9), 124.08 (C2′,6′), 129.01 (C1′), 135.41 (C3′,5′). Due to poor solubility of the dianion in THF, the measurement was done on a dilute solution and no signal assignable to C4′ was observed.

2,4-Bis(3,5-di-*t*-butyl-4-trimethylsiloxyphenyl)-2,4-didehydroadamantane (13): Colorless powder; mp 172–173 °C (decomp); MS (FAB) *m*/*z* 686.8 [$(M+H)^+$]; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.32 (s, 18H), 1.24 (s, 36H), 1.61–1.66 (m, 5H), 2.04–2.08 (m, 3H), 2.43 (br. s, 1H), 2.71 (br. s, 3H), 6.83 (s, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 3.99, 25.47, 28.86, 30.32, 31.27, 33.05, 34.99, 40.90, 45.79, 50.59, 124.32, 134.38, 139.37, 150.28.

X-ray Crystallography. The diffraction data were collected on a Rigaku AFC7R diffractometer with Mo-$K\alpha$ radiation (λ = 0.71069). Crystal data for **3**: $C_{38}H_{52}O_2$, M = 540.83, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 15.105(5), b = 19.591(3), c = 11.208(3) Å, U = 3316(1) Å^3, Z = 4, Dc = 1.083 Mgm^{-3}, μ = 0.064 mm^{-1}, $F(000)$ = 1184. 4282 reflections measured, 4251 unique (R_{int} = 0.310) used in refinement. R = 0.204, wR = 0.204, $R1$ = 0.065 (1288 with $I > 2.0\sigma(I)$). Crystal data for **4**: $C_{44}H_{66}O_2$, M = 627.00, monoclinic, space group $P2_1/c$ (no. 14), a = 15.583(4), b = 14.516(4), c = 19.241(4) Å, β = 113.45(2)°, U = 3992(1) Å^3, Z = 4, Dc = 1.043 Mgm^{-3}, μ = 0.061 mm^{-1}, $F(000)$ = 1384. 8300 reflections measured, 8022 unique (R_{int} = 0.033) used in refinement. R = 0.078, wR = 0.085 (2468 with $I > 2.0\sigma(I)$). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were introduced at ideal positions. The X-ray analysis data have been deposited as Document No. 74040 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 160441 and 160442.

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