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Novel Naphthacenequinone Derivatives Undergoing Photovalence Isomerization: A New Photochromic Molecule

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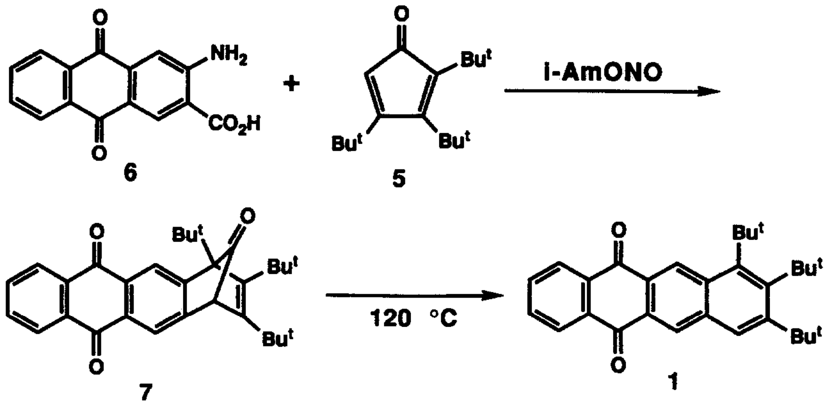
Abstract: 7,8,9-Tri-t-butyl-5,12-naphthacenequinone (**1**) and 1,2,3-tri-t-butyl-5,12-naphthacenequinone (**2**) were synthesized. The lowest excited singlet states of both **1** and **2** possess $\pi\pi^*$ nature strongly. Correspondingly, upon irradiation , **1** and **2** undergo photovalence isomerization to give the *valene* isomer of **1** and the *Dewar* isomer of **2**, respectively. The interconversions between the naphthacenequinones and their valence isomers were reversible photochemically.

Pairs of valence isomers which can interconvert photochemically have received considerable attention because of their potential for wide range of molecular devices. The exciting possibility of using these materials in optical memory media has caught the imagination of several research groups.[1] In the course of our study on overcrowded annelated arenes, we have found out the photochemical interconversion between poly-t-butylnaphthalene and anthracene and their valence isomers.[2] These systems can be considered to be a preliminary model of photoresponsive compounds for use in optical memory media. In this context, we have been trying to develop polyacenequinones which undergo photovalence isomerization, because the molecules possess some desired features, i.e., their inherent spectral sensitivity at visible region as well as their resistibility toward destructive reactions such as photooxidation. Previously we reported anthraquinone derivatives which undergo photodriven reversible isomerization between Dewar-anthraquinones.[3] Although they showed fundamental behavior as a photochromic molecule, there remained problems to be solved, that is, spectral sensitivity at longer wavelength region and kinetic stability of the Dewar-type valence isomers. With an aim to develop more ideal photoresponsive system in mind, we have synthesized 7,8,9-tri-t-butyl-5,12-naphthacenequinone (**1**) and 1,2,3-tri-t-butyl-5,12-naphthacenequinone (**2**) with poly-t-butyl substitutional modification which we have employed to make photoinert arenes photoreactive.

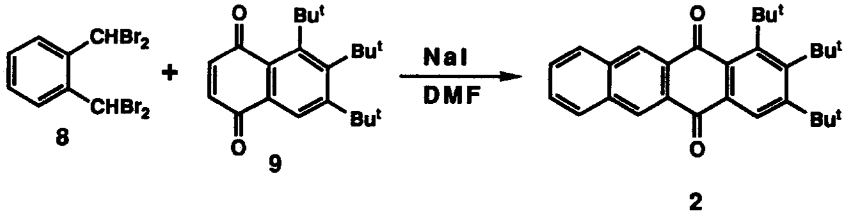
RESULTS AND DISCUSSION

7,8,9-Tri-t-butyl-5,12-naphthacenequinone (**1**) was synthesized by the reaction of 2,3-dehydroanthraquinone with 2,3,4-tri-t-butylcyclopentadienone (**5**)[4] followed by thermal decarbonylation of the Diels-Alder adduct (**7**) (Scheme 1). 2-Amino-3-anthraquinonecarboxylic acid (**6**)[5] was used as a precursor of 2,3-dehydroanthraquinone. 1,2,3-Tri-t-butyl-5,12-naphthacenequinone (**2**) was synthesized according to Scheme 2.

By the modification of the method of Cava and his co-workers,[6] Diels-Alder reaction between 5,6,7-tri-t-butylnaphthoquinone (**9**) and dibromo-o-xylylene generated *in situ* from α,α,α',α'-tetrabromo-o-xylene (**8**) followed by elimination of two molecules of hydrogen bromide from the primary adduct afforded **2**.



Scheme 1.



Scheme 2

Electronic spectra of **1** and **2** are shown in Fig. 1 and Fig. 2. One characteristic feature of the electronic spectra of **1** and **2** is the bathochromic shifts of their longest absorption bands compared with that of parent naphthacenequinone. Especially, **1** reveals its spectral sensitivity up to 540 nm. Secondly, in each of the spectra for **1** and **2**, the longest wavelength absorption band reveals a large extinction coefficient ($\varepsilon > 5000$), in contrast to the parent molecule whose longest wavelength band possesses a small coefficient below $\varepsilon = 100$.[7] This indicates that the bands are due to a $\pi\pi^*$ electronic transition instead of weak $n\pi^*$ transition, and consequently the lowest excited singlet states (S_1) of **1** and **2** bear $\pi\pi^*$ nature strongly, in contrast to the parent molecule whose S_1 is known to be $n\pi^*$.[8] In the case of **1**, fluorescence was observed,[9] also indicating the $\pi\pi^*$ nature of its S_1 state. The similar change in electronic configuration of excited state from $n\pi^*$ to $\pi\pi^*$ accompanying the substitutional modification has been observed in the case of anthraquinone, and we have attributed the phenomenon to the molecular deformation caused by the substitution.[3,10] The $\pi\pi^*$ characters of S_1 of **1** and **2** are of importance for them to undergo photovalence isomerization as following. Photovalence isomerizations of aromatic compounds generally involve singlet state and not triplet states,[11] and therefore, their S_1 states should be responsible for the reactions in solution. If the S_1 state is $n\pi^*$ photovalence isomerizations, at least those of endoergic type, should be not efficient because the initial excited state is localized on the carbonyl moiety whereas the key bond rearrangement process is located on the aromatic rings. Thus, the change of the electronic configuration of S_1 of **1**

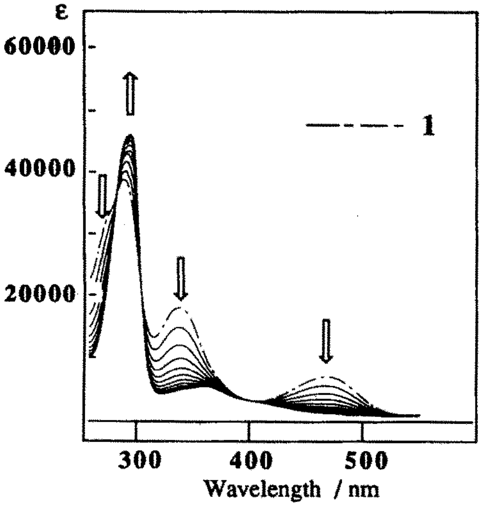


Figure 1. Electronic spectrum of **1** in chloroform and the spectral change occurring upon irradiating the solution at 480 nm. The final curve is the spectrum for **3**.

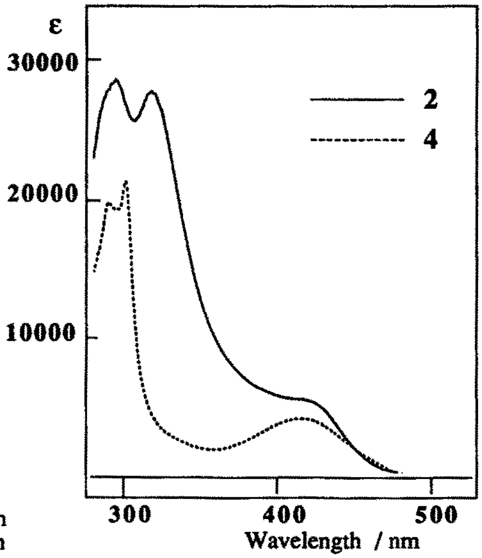
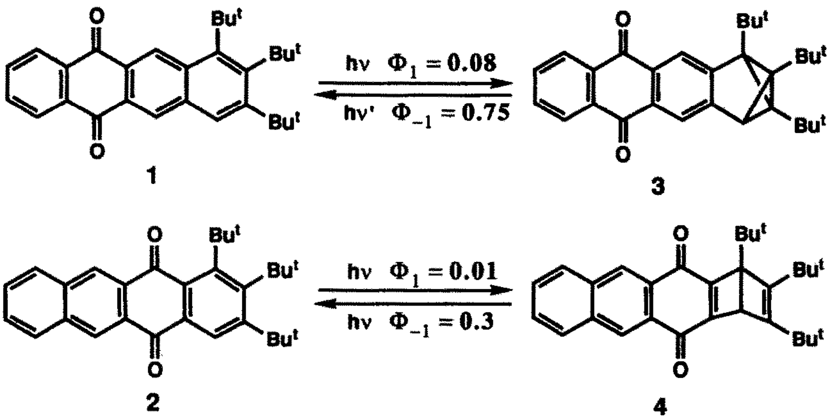


Figure 2. Electronic spectra of **2** and **4** in chloroform.



Scheme 3

and **2** would facilitates their photovalence isomerizations.

Degassed solutions of **2** in $CDCl_3$ sealed in NMR sample tubes were irradiated with a high pressure Hg-lamp by using various glass filters, and the photolyzed solutions were analyzed by ^{1}H-NMR directly. When irradiations were performed through Toshiba L-42 ($\lambda > 400$ nm), L-39 ($\lambda > 360$ nm), UV-37 ($\lambda > 340$ nm) and Pyrex ($\lambda > 300$ nm), no obvious changes were detected by ^{1}H-NMR analysis. The photochemical inertness of **2** seemed strange judging from the fact that all of arenes and anthraquinone with the same type of substitution undergo photovalence isomerization. After many trials, when the irradiation was performed with a high pressure Hg-lamp through a combination of filters, Toshiba UV-36A and Pyrex (300 nm < λ < 400 nm), new signals appeared at 1.22, 1.20 and 1.16 ppm in the ^{1}H-NMR following the reaction. Preparative scale irradiation under the same condition followed by the product analysis revealed that the photoreaction of **2** gave 1,2,3-tri-t-butyl-

1,4-Dewar-naphthacenequinone (4) as shown in Scheme 3. This reaction is photochemically reversible. Quantum yields for the forward and the reverse processes were determined as written in Experimental section and are shown in Scheme 3. Figure 2 shows that the absorption bands for 2 and 4 at wavelength region longer than 400 nm are similar to each other with respect to their shape as well as extinction coefficients. This means that photostationary composition ([4]/[2]) obtained by the irradiation with the light of the wavelength longer than 400 nm would be close to the ratio of the quantum yields for the reverse and the forward reactions (Φ_1/Φ_{-1}). As shown in Scheme 3, the quantum yield for the cycloreversion is 30 times larger than that for the forward reaction. This is the reason why observable amounts of 4 were not produced under irradiation conditions where Hg-lamp spectral lines of 404 nm and 436 nm were not cut off. Because of this photochemical feature, the pair of valence isomers 2/4 is worthless in view of photochromism.

In contrast to 2, 7,8,9-tri-t-butyl-5,12-naphthacenequinone (1) revealed some desirable properties for photochromic molecule of present interest. Upon irradiation with a high-pressure Hg-lamp through a Toshiba L-42 filter ($\lambda > 400$ nm), 1 isomerized to the corresponding valene isomer 3 (Scheme 3). As shown in Fig.1, the electronic spectra following the photoreaction in $CHCl_3$ revealed isosbestic points at 280 nm and 303 nm indicating that the reaction was chemically quantitative. Interconversion between 1 and 3 was photochemically reversible, and the irradiation (high-pressure Hg-lamp, filter: L-42) afforded a photostationary state with the composition of 1 : 3 = 1 : 22. Quantum yields for the reactions were measured for 313 nm irradiation, to be Φ (1 to 3) = 0.08 and Φ (3 to 1) = 0.75. Although quantum yield for the forward reaction is much smaller than the reverse, the photostationary state (high-pressure Hg-lamp, filter: L-42) lies far to valene isomer (3). It is due to a large difference between 1 and 3 in their extinction coefficients at the wavelength region above 400 nm (Fig. 1). Triplet quenchers, 2,5-dimethyl-2,4-hexadiene (ET = 58.7 kcal, 0.15 M), trans-stilbene (ET = 50 kcal, 0.15 M), anthracene (ET = 42.0 kcal, 0.15 M) and molecular oxygen, were of no effect on the photovalence isomerization of 1. On the other hand, the fluorescence of 1 was quenched by N,N-dimethylaniline with $k_q\tau = 2.5$ M^{-1}, and correspondingly the reaction was quenched in the same condition. Thus, it seems likely that the photovalence isomerization of 1 is an electrocyclic reaction involving only singlet states. The reaction feature might be favorable for photochromism, because concerted electrocyclic reactions do not involve intermediates such as ions and radicals, which cause irreversible side reactions.[12]

It might be noteworthy that 1 gave the *valene* isomer 3 in contrast to that 2 and anthraquinone derivatives with the same type of substitution [3] give their *Dewar*-isomers. This is presumably because the substituted ring of 1 possesses an out-of-plane ring deformation of zigzag form, which facilitates the formation of bicyclobutane skeleton, whereas 2 and 1,2,3-tri-t-butylanthraquinone would take a skew conformation by the repulsive interaction between t-butyl group at C_1 and the adjacent carbonyl oxygen, which leads to 1,4-bond formation. Generally, valene isomers are thermally much more stable than the corresponding Dewar isomers. In the present case also, 3 showed remarkable kinetic stability, and no change was observed after heating its solution in methylcyclohexane at 100 °C for 20 hr, whereas 4 reverted to 2 with a half life of 4 hr at 55°C..

In summary, 7,8,9-tri-t-butyl-5,12-naphthacenequinone (1) and 1,2,3-tri-t-butylnaphthacenequinone (2) were synthesized. They showed photochromic behavior between their valence isomers. Especially, phtochromism of 1/3 pair is thermally irreversible. Spectral sensitivity of 1 reaches up to 540 nm, but this value is still not enough and the problem remained to be solved. The naphthacenequinones, 1 and 2, are the first example of naphthacenequinone derivative which undergoes photovalence isomerization.

EXPERIMENTAL

^{1}H-NMR spectra were obtained on a JEOL JNM FX90Q FT NMR spectrometer or a JEOL JNM GX400 spectrometer, and chemical shifts are reported in δ value. IR spectra were recorded on a JASCO A-100 infrared spectrophotometer. Mass spectra were obtained with a JEOL JMS-DX 300 mass spectrometer. Electronic spectra were measured with a Hitachi U-3410 spectrophotometer. Fluorescence spectra were measured with a Shimadzu RF-502A spectrofluorophotometer. Melting points were determined on a Yanaco micro melting point apparatus and are not corrected.

5,6,7-Tri-t-butyl-1,4-naphthoquinone (9)

To a suspension of 1-amino-4,7-dihydroxybenzotriazole[13] (477 mg, 2.88 mmol) and 2,3,4-tri-t-butylcyclopentadienone (5)[4] (648 mg, 2.61 mmol) in dry methylene chloride (50 mL) was added lead tetraacetate (5.22 g, 11.8 mmol) in portions, and the mixture was stirred for 3 hr under Ar. The reaction mixture was poured into 90 mL of 15% KOH aq and the brown precipitate was filtered off. Enough amount of ether was added to the filtrate and extracted. The organic layer was washed with water and dried over Na_2SO_4. Removal of organic solvents afforded a orange oily residue. Heating the residue at 80 °C for 1 hr and successive chromatography on silica-gel with benzene gave 5,6,7-tri-t-butyl-1,4-naphthoquinone in 76% yield. **9**: mp 43°; ^{1}H-NMR ($CDCl_3$) δ 7.70 (s, 1H), 6.73 (s, 2H), 1.47 (s, 9H), 1.45 (s, 9H), 1.40 (s, 9H); IR (KBr) 1740, 1660, 1610, 1420, 840 cm^{-1}; UV ($CHCl_3$) λ nm (ε) 425 (3400) 309 (8100) , 223 (22000); Exact Mass Calcd for $C_{22}H_{30}O_2$: 326.22447. Found: 326.21987.

1,2,3-Tri-t-butyl-5,12-naphthcenequinone (2)

To a solution of 5,6,7-tri-t-butyl-1,4-naphthoquinone **9** (202 mg, 0.62 mmol) and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-o-xylene **8** (404 mg, 0.96 mmol) in dry DMF (50 mL) was added NaI (1.01 g, 6.73 mmol) with vigorous stirring at 80 °C under Ar. After 3 hr, the reaction mixture was poured into 15% $Na_2S_2O_4$ and extracted with ether. The organic layer was dried over Na_2SO_4, and evaporated. The residue was purified with a silica-gel chromatography to give **2** in 32% yield. Further purification was performed by recrystallization from MeOH. **2** : mp 214-215°; ^{1}H-NMR ($CDCl_3$) δ 8.71 (s, 1H), 8.65 (s, 1H), 8.15-7.96 (m, 2H), 7.68-7.57 (m, 2H), 1.53 (s, 9H), 1.52 (s, 9H), 1.47 (s, 9H); IR (KBr) 3040, 3020, 2970, 2930, 2870, 1670, 762 cm^{-1}; UV ($CHCl_3$) λ nm (ε) 423 (5600) 319 (27000) , 296 (28500); Exact Mass Calcd for $C_{30}H_{34}O_2$: 426.25602. Found: 426.25330.

7,8,9-Tri-t-butyl-5,12-naphthacenequinone (1)

To a solution of 2,3,4-tri-t-butylcyclopentadienone **5** (308 mg, 1.24 mmol) and isoamyl nitrite (0.38 mL, 2.83 mmol) in dry dioxane (dried over Na, 15 mL) was added a suspension of 2-amino-3-anthracenecarboxylic acid **6** (498 mg, 1.87 mmol) in the same solvent (15 mL) at room temperature. After heating at 100 °C for 1 hr, the reaction mixture was poured into 15% NaOH aq and extracted with ether. The organic layer was concentrated, and the residual material was purified with a silica-gel column with benzene to afford the Diels-Alder adduct (**7**). Heating the adduct at 120 °C for 4 hr and successive recrystallization from MeOH gave **1** in 53% yield. mp 221-223°; ^{1}H-NMR ($CDCl_3$) δ 9.26 (s, 1H), 8.56 (s, 1H), 8.41-8.31 (m, 2H), 7.86-7.72 (m, 2H), 7.65 (s, 1H), 1.73 (s, 9H), 1.51 (s, 9H), 1.40 (s, 9H); IR (KBr) 3060, 3040, 3010, 2985, 2930, 2890, 1675, 795, 720 cm^{-1}; UV ($CHCl_3$) λ nm (ε) 457 (7300), 331 (19000), 282 (36900) ; Exact Mass Calcd for $C_{30}H_{34}O_2$: 426.25602. Found: 426.25313.

Dewar 1,2,3-tri-t-butyl-5,12-naphthacenequinone (4)

A solution of 1,2,3-tri-t-butyl-5,12-naphthacenequinone **2** (500 mg, 1.17 mmol) in acetonitrile (20 mL) was deaerated by passing argon gas and was irradiated with a 400W high pressure Hg-lamp through a Toshiba UV-36A filter (300 nm < λ < 400 nm). After 20 hr irradiation, the solvent was removed under reduced pressure. The residue was developed on a preparative silica-gel TLC plates at -15°C (n-pentane : CH_2Cl_2 = 1 : 1) to afford Dewar-1,2,3-tri-t-butyl-5,12-naphthacenequinone **4** (45 mg) together with a recovery of **2** (390 mg). Recrystallized from MeOH / CH_2Cl_2 gave yellow crystals of **4** : mp (dec) 215-216°; ^{1}H-NMR ($CDCl_3$) δ 8.54 (s, 2H), 8.07-7.96 (m, 2H), 7.68-7.58(m, 2H), 3.89 (s, 1H), 1.22 (s, 9H), 1.20 (s, 9H), 1.16 (s, 9H); IR (KBr) 3050, 2955, 2905, 2860, 1665, 1620, 1605, 760 cm^{-1}; UV ($CHCl_3$) λ nm (ε) 420 (4000) 301 (21300) 289 (19600); Exact Mass Calcd for $C_{30}H_{34}O_2$: 426.25602. Found: 426.25379.

Photoreaction of 7,8,9-tri-t-butyl-5,12-naphthacenequinone (1)

A solution of 7,8,9-tri-t-butyl-5,12-naphthacenequinone (**1**) (200 mg, 0.47 mmol) in $CHCl_3$ (50 mL) was deaerated by passing an argon flow and was irradiated with a 400W high pressure Hg-lamp through a Toshiba L-42 filter (λ>400 nm). After 15 hr irradiation, removal of the solvent and successive chromatography (silica-gel) afforded the powder of valene isomer (**3**) (140 mg). Recrystallization from MeOH gave pale yellow crystals of **3** :

mp 218° (dec) ; IR (KBr) 2850, 1665, 1590, 1323, 1290, 703 cm^{-1}.; ^{1}H-NMR ($CDCl_3$) δ 8.38-8.23 (m, 2H), 8.14 (s, 1H), 7.81-7.70 (m, 2H), 7.85 (s, 1H), 2.38 (s, 1H), 1.56 (br.s, 9H), 1.23 (s, 18H).; UV ($CHCl_3$) λ nm (ε) 358 (4090) 290 (45000); Exact Mass Calcd for $C_{30}H_{34}O_2$: 426.25602. Found: 426.25650.

Quantum yield for the photoreactions of 1 and 2.

A solution of 7,8,9-tri-t-butyl-5,12-naphthoquinone (**1**) in $CHCl_3$ (2.96×10^{-4} M, 4 mL) in a quartz cell was deaerated by freeze-pump-thaw cycles and sealed. The sample was irradiated at 313 nm (band width: 10 nm) by using the excitation beam of a Shimadzu RF-502A fluorometer, and the electronic spectra were measured at appropriate time intervals. Conversions were determined based on the electronic spectra. Light intensity was determined based on a chemical actinometry using potassium ferrioxalate. Quantum yields for the forward and the reverse processes, Φ_1 and Φ_{-1}, were evaluated according to the eq. 1 ;

$$\frac{d[V]}{dt} = I\frac{\varepsilon_q[Q]}{(\varepsilon_q[Q] + \varepsilon_v[V])}\Phi_1 - I\frac{\varepsilon_v[V]}{(\varepsilon_q[Q] + \varepsilon_v[V])}\Phi_{-1} \qquad (1)$$

where [Q] = concentration of quinone, [V] = concentration of valence isomer, ε_q = extinction coefficient of quinone at wavelength of the light used for the quantum yield measurement, ε_v = extinction coefficient of valence isomer at the same wavelength, Φ_1 = quantum yield for the formation of the valence isomer, Φ_{-1} = quantum yield for the cycloreversion, I = intensity of light.

Quantum yield for the photoreaction of 1,2,3-tri-t-butyl-5,12-naphthacenequinone (**2**) was obtained by a similar manner on a irradiation at 366 nm (band width: 10 nm).

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