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Synthesis of 1,2,3-Tri-t-butyl-6,13- and 8,9,10-Tri-t-butyl-5,14-pentacenequinones and Their Photochromic Behaviors : New Photochromic Molecules

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Abstract: 1,2,3-Tri-t-butyl-6,13-pentacenequinone (**1a**) and 8,9,10-tri-t-butyl-5,14-pentacenequinone (**1b**) were synthesized. The lowest excited singlet states of both **1a,b** bear $\pi\pi^*$ nature strongly. Correspondingly **1a** and **1b** undergo photovalence isomerization to give the corresponding *valene* type isomers. The interconversion between the naphtacenequinones and their *valene* isomers were reversible photochemically.

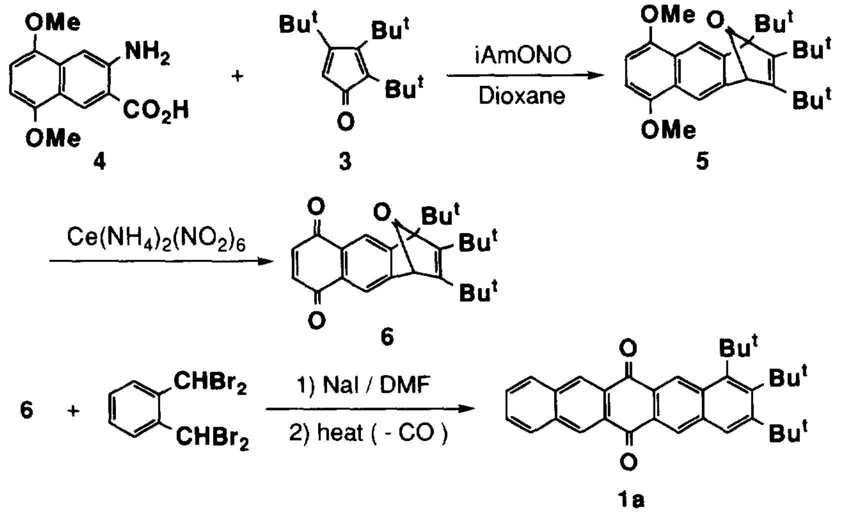
INTRODUCTION

Pairs of valence isomers that show photochemical interconversion have been a subject of much recent interests because of their potentiality 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 this context, we have been continuing the study on the derivatization of polyacenes [2] and polyacenequinones [3] to make the molecules to undergo reversible photo-isomerization. Although the derivatives developed by us so far showed some desirable properties as a photochromic molecule, for example remarkable kinetic stabilities of both the chemical binary states, clean forward and reverse photochemical reactions and so on, there still remained a problem to be solved, that is, spectral sensitivity of the molecules at longer wavelength region. In this aspect, the most excellent photochromic molecule in our study so far was 7,8,9-tri-t-butyl-5,12-naphthacenequinone which showed an absorption band with a maximum at 457 nm and its absorption edge of around 530 nm.[2b] One of the criteria for photochromic molecules of actual use is that their photochromism can be operative at the wavelength regions of semiconductor lasers (780-1600 nm) or at least their second harmonic. With the aim to improve the spectral sensitivity at longer wavelength region, we have synthesized 1,2,3-Tri-t-butyl-6,13-pentacenequinone (**1a**) and 8,9,10-tri-t-butyl-5,14-pentacenequinone (**1b**), and their photochromic behaviors were examined.

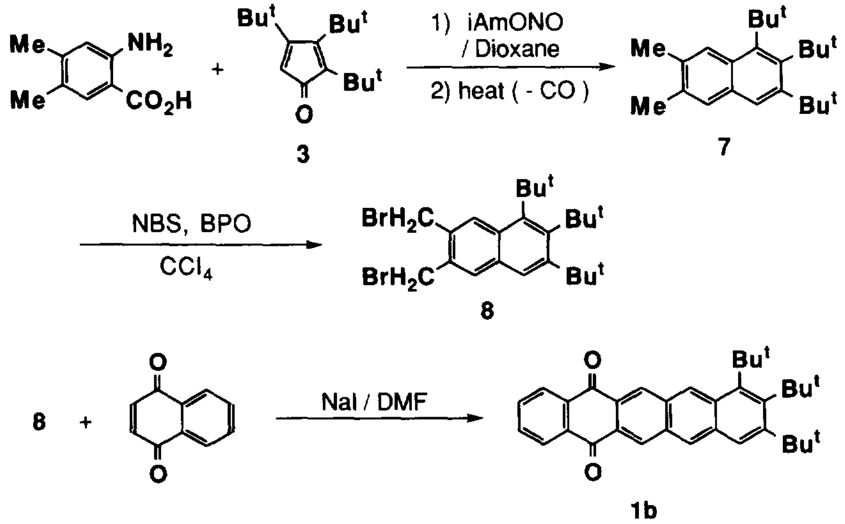
RESULTS AND DISCUSSION

1,2,3-Tri-t-butyl-6,13-pentacenequinone (**1a**) and 8,9,10-tri-t-butyl-5,14-pentacenequinone (**1b**) were synthesized according to Scheme 1 and Scheme 2, respectively, by using 2,3,4-tri-t-butylcyclopenta-2,4-dien-

1-one (**3**) [4] as a building block for the tri-t-butyl aromatic ring in the products. In the synthetic scheme for both the molecules, Cava's method [5] was employed for the elongation of aromatic rings. In the synthetic scheme, the Cava's reaction for the condensation of 2,3-bis(bromomethyl)-5,6,7-tri-t-butylnaphthalene (**8**) with naphthoquinone proceeded successfully, though the reaction is not applicable to the condensation of 2,3-bis(bromomethyl)naphthalene. For example, the reaction of 2,3-bis(bromomethyl)naphthalene with naphthoquinone did not afford parent pentacenequinone or its dihydro derivative. The reason for the unusual reactivity of **8** toward Cava's reaction is presumably as followed. The Cava's reaction is considered to proceed



Scheme 1



Scheme 2

by the Diels-Alder reaction between dienophiles and o-quinoid polyofefinic intermediates generated by the debromination of the bis(bromomethyl)benzenes. The formation of the o-quinoidal molecule from the bis(bromomethyl)naphthalenes would require a larger energy than the case of bis(bromomethyl)benzenes corresponding to the difference in aromatic stabilization energy between naphthalene and benzene. In the case of **8**, however, the loss of aromatic stabilization energy should be relatively small compared with that for usual planar derivatives because aromaticity of **8** is destroyed partially because of the out-of-plane bending deformation of the π-structure of the molecule caused by the repulsion between the bulky t-butyl groups.

The electronic spectrum of **1a** in acetonitrile is shown in Fig. 1. A longest wavelength absorption band is revealed in a visible region with a maxima at 451 nm. The band shows bathochromic shift by 47 nm in comparison with the longest ππ* absorption of parent pentacenequione.[6] Similarly, bathochromic shifts of the longest absorption bands of polyacenes and polyacene quinones have been observed when the molecules were furnished with tri-t-butyl substitution.[2,3] The effect can be attributed to the destabilization of the ground states of the aromatic molecules due to the out-of-plane bending deformation of their π structure caused by the steric repulsion between t-butyl groups. In fact, the first ionization potential of 1,2,3-tri-t-butylnaphthalene (7.19 eV) is small in comparison with that (7.64 eV) of 1,2,3-trimethylnaphthalene indicating that steric congestion destabilize the HOMO-π-MO of the aromatic molecule. Correspondingly, the longest absorption band for the former appears at the longer wavelength (365 nm) compared with that (320 nm) for the latter derivative.

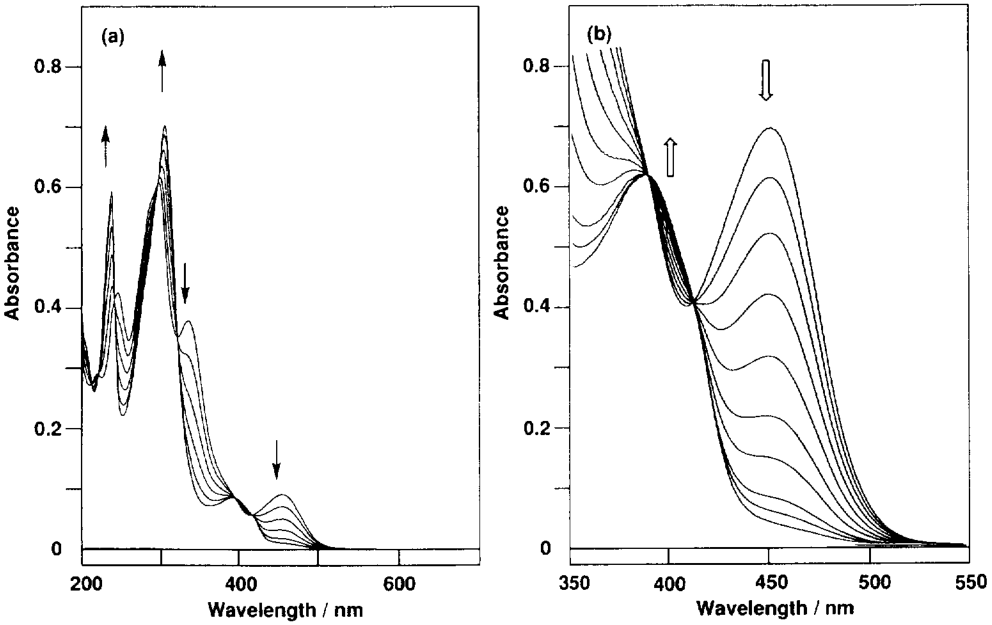


Figure 1. The spectral changes occurring upon irradiating a solution of **1a** in acetonitrile. (a) Initial concentration of **1a** was $[\mathbf{1a}]_{init.} = 1.3 \times 10^{-5}$ M , and (b) $[\mathbf{1a}]_{init.} = 9.0 \times 10^{-5}$ M. The initial curve is the spectrum for **1a**. and the final one corresponds to the spectrum for **2a**

The longest absorption band of **1a** reveals a large extinction coefficient of 6700 indicating that the lowest singlet state (S_1) of **1a** bears ππ* character strongly, whereas S_1 state of parent 6,13-pentacenequinone is known [6] to be $n\pi^*$ in nature. The spectral feature of **1a** is very close to that of 7,8,9-tri-t-butyl-5,12-naphthacenequinone (**9**) [2b] which shows the longest absorption band with a maximum at 457 nm (ε = 7300). The increment of the number of the aromatic rings by this way from **9** to **1a** does not give rise to any improvement in view of the spectral sensitivity of the molecule at longer wavelength region. As shown in Fig. 2, on the other hand, the longest band of the absorption spectrum of **1b** appears at λ_{max} = 496 nm with the extinction coefficient ε = 8100, and the absorption edge of the band reaches up to around 580 nm. Thus, the spectral sensitivity of the molecule was improved by the increment of the number of aromatic rings in unsymmetric manner as from **9** to **1b**. In the case of **1b** also, the large extinction coefficient indicates that the S_1 state of **1b** bears $\pi\pi^*$ nature. The $\pi\pi^*$ nature of S_1 states of **1a** and **1b** is prerequisite for the molecules to undergo photovalence isomerization.[2]

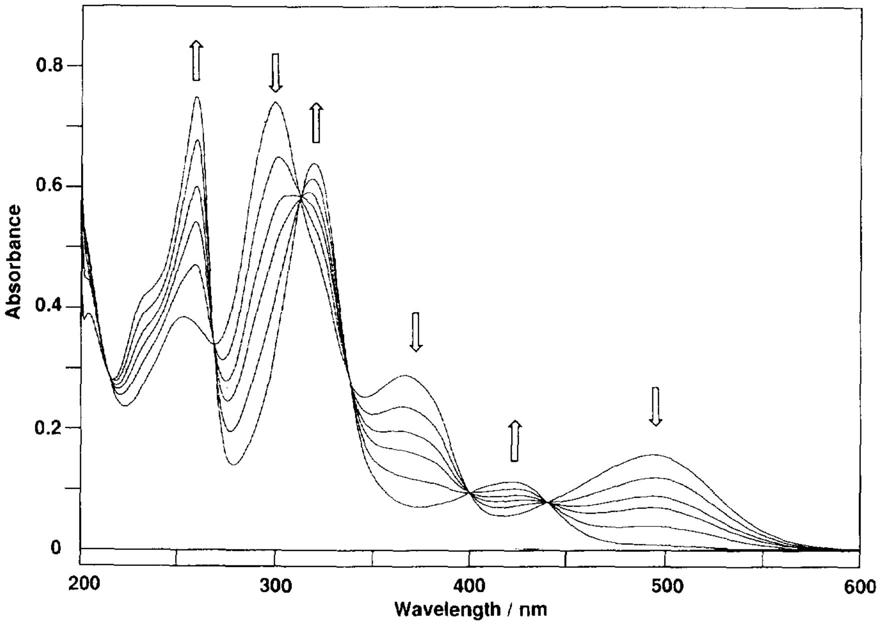
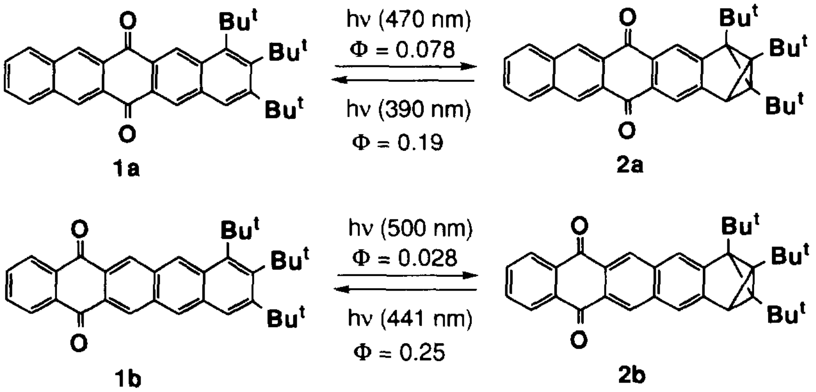


Figure 2. The spectral changes occurring upon irradiating a solution of **1b** in acetonitrile. Initial concentration of **1b** was $[\mathbf{1b}]_{init.}$ = 1.9 x 10^{-5} M. The initial curve is the spectrum for **1b** the final one corresponds to the spectrum for **2b**.

Steady state photolysis of **1a** was performed with a degassed solution of **1a** (1.3 x 10^{-5} M, 4 ml) in acetonitrile charged in a quartz cell with an optical path of 1 cm. The solution was irradiated at 470 nm at room temperature by using an excitation beam of a Shimadzu RF 502 spectrofluorometer, which was adjusted at 470 nm with a band width of 5 nm. The reaction was followed by electronic spectra measured at appropriate time intervals. As shown in Fig. 1, the steady state photolysis of **1a** revealed spectral changes accompanied by several isosbestic points indicating that the photochemical process accompanies no formation of observable amount of side product(s). Photolysis of **1b** was performed in the same manner at 500 nm to give the spectral changes shown in Fig. 2. In this case also, clear isosbestic points were observed. The analysis of the photoproduct was based on ^{1}H-NMR of the products obtained with the larger scale photolyses. In the case of the large scale photolyses, irradiations were performed with a high pressure mercury lamp coupled with appropriate glass filters, i.e., the mercury resonance spectrum of 436 nm was selected for the photolysis of **1a** by using a Toshiba Y 44 filter ($\lambda > 410$ nm) and that of 546 nm for **1b** by using a Toshiba Y 52 filter ($\lambda > 505$ nm). The ^{1}H-NMR spectrum of the product of the photolysis of **1a** indicated the formation of the corresponding tri-t-butylpentacenequinovalene (**2a**) as a sole product. The ^{1}H-NMR spectrum of aliphatic proton region was composed of the proton resonance signals at δ 1.24 (s, two t-butyl), 1.56 (s, t-butyl) and 2.41 (s, bridge head) with an intensity ratio of 18 : 9 : 1 which compares well with those of the related compounds.[2,3,7] The other signals for the aromatic protons (AA'BB' appeared at around δ 8.10 and 7.65, and singlets at δ 7.95, 8.24 and 8.79 with a ratio of 2 : 2 : 1 : 1 : 2) are well compatible with the structure of **2a**. The photolysis of **1b** also gave the corresponding *valene* isomer (**2b**) as a sole product. The set of ^{1}H-NMR signals for the product [δ 1.25 (s, 18 H), 1.59 (s, 9H), 2.45 (s, 1H), 7.56 (s, 1H), 7.83 (s, 1H), 8.57(s, 1H), 8.63(s, 1H), AA'BB' at 7.77 (2H) and 8.38 (2H)] is consistent with the structure of **2b**.



The photovalence isomerization of **1a** was photochemically reversible. Upon irradiation of the solution of **2a** with 390 nm light (one of the isosbestic points), the band at 451 nm for **1a** was recovered to an extent for a photostationary state with a composition of **1a** : **2a** = 2.4 : 1. It was also the case for **1b**/**2b** interconversion, and irradiation of a solution of **2b** at 441 nm (one of the isosbestic points) gave a photostationary mixture with a composition of **1b** : **2b** = 9 : 1. No observable amount of side product was formed in the reverse reactions, **2a** to **1a** and **2b** to **1b**, and the spectral changes for the reactions were exactly same in feature to Fig. 1 and Fig. 2 except for the direction of the change.

The quantum yields for the photovalence isomerizations of **1a** and **1b** were determined. In the present case, the photochemical isomerizations are reversible, and therefore, actinometry should be performed at the wavelength region longer enough where the products reveal no absorption. One difficulty was a lack of conventional chemical actinometer for the wavelength region above 450 nm.[8] Here, the color bleaching reaction of the ring closed form of fulgide [10] was employed as an actinometer according to the recommendation of Horspool.[9] Irradiations were performed by using an excitation beam of a Shimazdu RF 502 A spectrofulorometer adjusted at an appropriate wavelength with a band width of 5 nm. It was comfirmed that the intensity of the beam was stable enough during the irradiation time. Thus, the quantum yield for the reaction of **1a** to **2a** was determined to be Φ = 0.079 (470 nm) and Φ = 0.028 (500 nm) for **1b** to **2b**. As mentioned above, the compositions of the photostationary states were **1a**/**2a** = 2.4/1 and **1b**/**2b** = 9/1 when the solutions were irradiated at the isosbestic points, 390 nm and 441 nm, respectively. Assuming that there is no significant dependence of the quantum yields on the excitation wavelength, quantum yields for the cycloreversions were estimated to be Φ = 0.19 for **2a** to **1a**, and Φ = 0.25 for **2b** to **1b**, based on the forward quantum yield and the composition of **1**/**2** in the photostationary state. Actually, the photostationary mixture with the same composition (**1b**/**2b** = 9/1) was obtained when the solution of **1b** was irradiated at the other isosbestic point (400 nm) indicating that there is no significant dependence of the quantum yields on the excitation wavelength.

The photochromism of **1b** in a solid film of methyl methacrylate polymer (PMMA) was examined. The PMMA film incorporating with **1b** was prepared as followed. PMMA (Wako Pure Chemical LTD., mean value of n = 1200 for $(C_5H_8O_2)_n$) of 1.2 g amount was added to a solution of **1b** (5 mg, 0.0105 mmol) in 6 ml chloroform, and the mixture was sonificated to afford a homogeneous viscous liquid. The liquid was casted on an optical quartz plate so that a homogeneous thin film was obtained. The liquid film was dried at ambient temperature in the dark followed by under vacuo by using an oil diffusion pump. The absorption spectrum of **1b** in the PMMA film was very much similar to that in acetonitrile solution. A typical sample of the thin film showed an absorption band at λ_{max} = 498 nm with its absorbance of 0.4. Irradiation of the film at 500 nm caused the spectral changes similar to that in acetonitrile accompanying isosbestic points at 403 nm and 440 nm, and the band at 498 nm disappeared completely. Upon irradiation at 440 nm, the band recovered again up to the photostationary state, i.e., 89 % of the initial absorbance ($A_1 = 0.89A_0$).

The fatigue of **1b** in the PMMA film upon a number of cycles of the photoreactions was examined in an anaerobic condition. One cycle was composed of the irradiation at 500 nm till the complete disappearance of the band at 498 nm and the irradiation at 440 nm to recover **1b** reaching photostationary state. The amount of **1b** alive after n times of the cycle was estimated by the value of A_n/A_1, where A_n was the absorbance at 498 nm after the n times of the cycle. After 170 times of the cycle, 68.1 % of **1b** was alive, which corresponded to 99.8 % per one cycle in average. The fatigue of **1b** in benzene solution (5.0×10^{-5} mol/L) in degassed condition was examined in a similar manner. In this case, 46.6 % of **1b** was alive after 170 times of the cycle. These results indicate that non-fluid media might be effective for suppressing side reaction(s) though we could not specify the reaction(s) responsible for the fatigue.

In summary, new derivatives of pentacenequinone, 1,2,3-Tri-t-butyl-6,13-pentacene-quinone (**1a**) and 8,9,10-tri-t-butyl-5,14-pentacenequinone (**1b**), were synthesized. They showed photochromic behavior between their *valene* type isomers (**2**). In each case, both the isomers were kinetically stable, and no change was observed after heating the *valene* isomers in methylcyclohexane at 100 °C for 20 h. The spectral sensitivity of **1b** reaches up to 580 nm, the value is comparable to that of the colored form of fulgide.[1a]

EXPERIMENTAL

General

^{1}H-NMR spectra were measured on a GE QE-300 or a JEOL FX-90Q spectrometer, and chemical shifts are reported in δ scale. IR spectra were recorded on a Nicolet 205 Ft infrared spectrophotometer. Electronic spectra were obtained by using a HITACHI U-3410 spectrophotometer. Melting points were measured with a Yanagimoto micro melting point apparatus and were not corrected. Solvents for measuring electronic spectra were commercially available spectral grade and were used without further purification. Reagents for syntheses were obtained commercially and were used without further treatment without otherwise noted.

Diels-Alder reaction of 5,8-dimethoxy-2,3-dehydronaphthalene generated from 4 with 2,3,4-tri-t-butyl-2,4-cyclopentadienone (3).
The cyclopentadienone (**3**) (152 mg, 0.6 mmol) was dissolved in dry dioxane (50 ml), and to this was added iso-amylnitrite (0.3 ml). The mixture was heated to 60 °C and was added anthranilic acid (**4**) (190 mg, 0.8 mmol) in the same solvent and was stirred for 1 h at 80 °C. Solvent removal and successive chromatography on silica gel (benzene/hexane = 1/1) afforded the adduct (**5**) (0.15 g, 56%). Analytical sample was obtained by recrystallization from ethanol. mp : 172-174 °C.^{1}H-NMR ($CDCl_3$) δ ppm 8.41 (s, 1H), 8.05 (s, 1H), 6.67 (s, 2H), 4.59(s, 1H), 3.95 (s, 6H), 1.95 (br s, 3H), 1.57 (br.s, 3H), 1.39 (s, 9H), 1.29-1.31 (br s, 12H). IR (KBr) 2956, 2832, 1762, 1613, 1466, 1266, 1089 cm^{-1}. HRMS Calcd. for $C_{29}H_{38}O_3$: 434.2821, Found: 434.2870.

Cerium diammonium nitrate oxidation of 4.
The adduct (**5**) obtained above (150 mg, 0.35 mmol) was dissolved in 20 ml of acetone, and the solution was added 1 ml water. Cerium(IV) diammonium nitrate (567 mg) was added to this solution, and the mixture was stirred for 15 min at room temperature. The mixture was poured on to water and extracted with ether. Removal of ether followed by chromatography on silica gel afforded the naphthoquinone derivative (**6**) in 87% (122 mg) yield. Recrystallization from ethanol afforded analytical sample. mp ; 141 °C. ^{1}H-NMR ($CDCl_3$) δ ppm 8.31 (s, 1H), 7.98 (s, 1H), 6.94 (s, 2H), 4.70(s, 1H), 1.91 (br s, 3H), 1.56 (br s, 3H), 1.38 (s, 9H), 1.23-1.27 (br s, 12H). IR (KBr) 2966, 2928, 1775, 1669, 1597, 1312, 848 cm^{-1}.HRMS Calcd. for $C_{27}H_{32}O_3$: 404.2351, Found: 404.2414.

Cava's reaction of 6 with α, α, α',α'-tetrabromo-o-xylene : 1,2,3-Tri-t-butyl-1,4-dihydro-1,4-oxomethano-6,13-pentacenequinone.
A mixture of **6** (108 mg, 0.27 mmol), α, α, α',α'-tetrabromo-o-xylene (168 mg, 0.4 mmol) and sodium iodide (440 mg) in dry DMF (1.5 ml) was heated at 80 °C for 3 h under argon. The mixture was poured on to aq. NaS_2O_4 and extracted with ether. Removal of the solvent followed by chromatography on silica gel afforded the title compound (70 mg, 52 %). Recrystallization from ethanol afforded pale yellow crystals. mp : 178-179 °C. ^{1}H-NMR ($CDCl_3$) δ ppm 8.84 (s, 2H), 8.63 (s, 1H), 8.29 (s, 1H), 8.09-8.12 (m, 2H), 7.66-7.70 (m, 2H), 4.75 (s, 1H), 1.96 (br s, 3H), 1.59 (br s, 3H), 1.48 (s, 9H), 1.30-1.33 (br s, 12H). IR (KBr) 2960, 1783, 1673, 1456, 1296, 769 cm^{-1}.HRMS Calcd. for $C_{35}H_{36}O_3$: 504.2664, Found: 504.2707

1,2,3-Tri-t-butyl-6,13-pentacenequinone (1a)
The title compound was obtained by thermal decarbonylation as following. A solution of 1,2,3-tri-t-butyl-1,4-dihydro-1,4-oxomethano-6,13-pentacenequinone (62 mg) obtained above in methylene chloride was charged in a test tube and the solvent was removed under reduced pressure. The test tube was filled with argon by using a three way valve and an argon balloon and was heated at 140 °C for 1h in a glass tube oven. The resulting material was developed on a preparative TLC of silica gel with benzene to afford **1a** (58 mg, 96%). Recrystallization was performed with ethanol. mp : 239-240 °C. ^{1}H-NMR ($CDCl_3$) δ ppm 9.36 (s, 1H), 8.91 (s, 2H), 8.66 (s, 1H), 8.10-8.14 (m, 2H), 7.67-7.71 (m, 3H), 1.76 (s, 9H), 1.52 (s, 9H), 1.41 (s, 9H). IR (KBr) 2961, 2925, 1677, 1280, 756 cm^{-1}. HRMS Calcd. for $C_{34}H_{36}O_2$: 476.2715, Found: 476.2705.

1,2,3-Tri-t-butyl-6,7-dimethylnaphthalene (7).
The cyclopentadienone (**3**) (1.5 g, 6 mmol) was dissolved in dry dioxane (30 ml), and to this was added iso-amylnitrite (0.75 ml). The mixture was heated to 60 °C and was added 4,5-dimethyl anthranilic acid (1.0 g, 6 mmol) in the same solvent and was stirred for 1 h at 80 °C. Solvent removal and successive chromatography on silica gel (hexane/dichloromethane = 1/1) afforded the adduct, 1,2,3-tri-t-butyl-6,7-dimethyl-1,4-dihydro-1,4-oxomethanonaphthalene 1.17 g (55 %). ^{1}H-NMR ($CDCl_3$) δ ppm 7.38 (s, 1H), 7.04 (s, 1H), 4.40 (s, 1H), 2.26(s, 3H), 2.24 (s, 3H), 1.80(s, 3H), 1.52 (s, 6H), 1.38 (s, 9H), 1.28 (s, 9H). IR (KBr) 2956, 1763, 1457, 1365 cm^{-1}.The adduct was dissolved in xylene and the solution was heated at 130 °C for 8 h. Solvent removal and successive chromatography on silica gel (hexane) afforded **7** (0.87 g, 81 %). mp : 101-102 °C.^{1}H-NMR ($CDCl_3$) δ ppm 7.98 (s, 1H), 7.38 (s, 1H), 7.31 (s, 2H), 2.41 (s, 3H), 2.36 (s, 3H), 1.66(s, 9H),

1.45(s, 9H), 1.37(s, 9H). IR (KBr) 2956, 1580, 1480, 1370, 1230 cm^{-1}. HRMS Calcd. for $C_{24}H_{36}$: 324.2817, Found: 324.2826.

6,7-Dibromomethyl-1,2,3-tri-t-butylnaphthalene (8).
A solution of **7** (0.38 g), N-bromosuccimide (0.49 g) and benzoylperoxide (2 mg) in tetrachloromethane was refluxed for 1 h under argon. Solvent removal and successive chromatography on silica gel (hexane/dichloromethane = 1/1) afforded the solid of **8** 0.4 g (71 %). mp : 105-109 °C. ^{1}H-NMR ($CDCl_3$) δ ppm 8.22 (s, 1H), 7.61 (s, 2H), 7.37 (s, 1H), 4.89 (ABq, 2H, J = 10.2 Hz), 4.84 (ABq, 2H, J = 10.2 Hz),[11] 1.66 (s, 9H), 1.46 (s, 9H), 1.37 (s, 9H). IR (KBr) 2997, 1436, 1396, 1212 cm^{-1}. MS : m/z 482 (M^{+}). The compound was used for the next step without further purification.

8,9,10-Tri-t-butyl-5,14-pentacenequinone (1b)
A mixture of **8** (0.4 g, 0.27 mmol), naphthoquinone (0.7 g, 0.4 mmol) and potassium iodide (0.3 g) in dry DMF (5 ml) was heated at 110 °C for 9 h under argon. The mixture was poured on to aq. NaS_2O_4 and extracted with ether. Removal of the solvent followed by chromatography on silica gel (benzene) afforded the title compound (70 mg, 18 %). Recrystallization from ethanol afforded deep red crystals of **1b**. mp : 215-217 °C. ^{1}H-NMR ($CDCl_3$) δ ppm 9.00 (s, 2H), 8.92 (s, 2H), 8.42 (m, 2H), 8.35 (s, 1H), 7.81(m, 2H), 7.55 (s, 1H), 1.78 (br s, 3H), 1.52 (s, 9H), 1.39 (s, 9H). IR (KBr) 2929, 1673, 1297, 1259 cm^{-1}. HRMS Calcd. for $C_{34}H_{36}O_2$: 476.2715, Found: 476.2710.

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REFERENCES AND NOTES

1) a) Darcy, P. J. ; Heller, H. G. ; Strydam, P. J. ; Whitall, J., *J. Chem. Soc., Perkin Trans I*, **1981**, 202 ; b) Irie, M.; M. Mohri, M., *J. Org. Chem.*, **1988**, 53,803., Irie, M.; Miyatake, ; Uchida, K.; Eriguchi, T., *J. Am. Chem. Soc.*, **1994**, 116, 9894 and references cited therein.

2) a) Yoshida, Z.,*Jpn Kokai Tokkyo Koho, JP 138349* (1979) ; b) Miki, S.; Ema, T.; Shimizu, R.; Yoshida, Z., *Tetrahedron Lett.*, **1992**, 33, 1619 .c) Yoshida, Z.; Miki, S.; Matsuo, K.; Shiojiri, E., *Jpn Kokai Tokkyo Koho, JP 01238546* (1989) d) El-Shishtawy, R. M.; Fukunishi, K.; Miki, S., *Tetrahedron Lett.*, **1995**, 36, 3177.

3) a) Miki, S.; Matsuo, K.; Yoshida, M.; Yoshida, Z., *Tetrahedron Lett.*, **1988**, 29, 2211. b) Miki, S.; Kagawa, H.; Matsuo, K.; Kobayashi, O.; Yoshida, M.; Yoshida, Z., *Tetahedron*, **1992**, 48, 1567. c) Nakayama, T.; Yamaguchi, T.; Ushida, K.; Hamanoue, K.; Miki, S.; Matsuo, K.; Yoshida, Z., *Chem. Phys. Lett.*, **1988**, 148, 259 .

4) Maier, G.; Pfriem, S., *Chem. Ber.*, **1981**, 114, 3965.

5) Cava, M. P.; Deana, A. A.; Muth, K., *J. Am. Chem. Soc.*,**1959**, 81, 6458.

6) Zander, M., *Ber. Bunsen. Physk. Chem.*, **1967**, 71, 424 .

7) Katz, T. J.; Wang, E. J.; Acton, N., *J. Am. Chem. Soc.*, **1971**, 93, 3782.

8) Murov, S. L., *Handbook of Photochemistry*, Marcel Dekker INC.,New York, 1973

9) Horspool, W. H., *Synthetic Organic Photochemistry*", Plenum Press, New York, 1984); pp. 507-508.

10) Heller, H .G.; Langan, J. R., *J. Chem. Soc., Perkin II*, **1981**, 341.

11) The ^{1}NMR for methylene protons of each bromomethyl group appeared as AB quartet probably due to the magnetic diastereotopics caused by a large out-of-plane deformation of the aromatic ring substituted with the t-butyl groups.

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