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π-Extended *o*-quinoidal tropone derivatives: experimental and theoretical studies of naphtho[2,3-*c*]tropone and anthro[2,3-*c*]tropone

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Received 5th January 2004, Accepted 16th February 2004
First published as an Advance Article on the web 5th March 2004

π-Extended *o*-quinoidal tropone derivatives, naphtho[2,3-*c*]tropone (**3**) and anthro[2,3-*c*]tropone (**4**), have been investigated theoretically as well as experimentally. The geometrical optimization of **3**, **4**, and related compounds at the B3LYP level employing 6-31G* basis set as well as the GIAO calculations at the RHF level employing the 6-31+G* basis set have been performed to evaluate the contributions of the polarized resonance forms to these molecules. The GIAO calculated NICS(1) values indicate that the aromaticities of the tropone rings of *o*-quinoidal **3** and **4** are significantly increased as compared with that of parent tropone (**1**) at the expense of the fused benzenoid rings, consistent with the significant electronic polarization of these molecules in the ground state. On the other hand, the fusion of a benzene or naphthalene ring to the 2,3- or 4,5-position of tropone leads to diminution of aromaticity in the resulting tropone moiety. Experimentally, irradiation of 6,7-(2′,3′-naphtho)bicyclo[3.2.0]hepta-3,6-dien-2-one (**10**) in a rigid glass at −196 °C leads to the formation of **3**, which exhibits a characteristic UV-Vis absorption extending to 700 nm and undergoes rapid [π12 + π14] dimerization upon thawing the glass. In contrast, 6,7-(2′,3′-anthro)bicyclo[3.2.0]hepta-3,6-dien-2-one (**11**) showed no sign of isomerization to **4** under the same reaction conditions.

Introduction

Tropone (**1**) has been considered to be a representative example of nonbenzenoid aromatic compounds since aromaticity is expected in this molecule when the 6π-electron polar resonance structure **1b** (Scheme 1) contributes significantly to it. However, it has been shown[1] that the ground state of tropone is adequately described as polyenone **1a**, though the contribution from **1b** should also be considered to some extent. It is, therefore, of particular interest to alter the electronic structure of the tropone system based on its structural modification. As reported previously,[2] annelation of the benzo group at the 3,4-position of tropone to generate *o*-quinoidal 3,4-benzotropone (**2**) leads to increased polarization of the C=O bond, suggesting the enhancement of aromaticity at least in the tropone moiety. These findings prompted us to investigate the chemistry of next higher homologues of this series, *i.e.* naphtho[2,3-*c*]tropone (**3**) and anthro[2,3-*c*]tropone (**4**). Extension of the π-electron system to **3** and **4** is expected to produce substantial π-delocalization and to modify the electronic structure of the tropone system more dramatically. In fact, theoretical calculations suggest significant electronic polarization of these molecules in the ground state, *viz.*, a substantial contribution of the polar resonance structures **3b** and **4b**.[3] Herein we report the details of the computational and experimental investigation of these *o*-quinoidal molecules, including the successful generation of **3** as a kinetically labile species.

Results and discussion

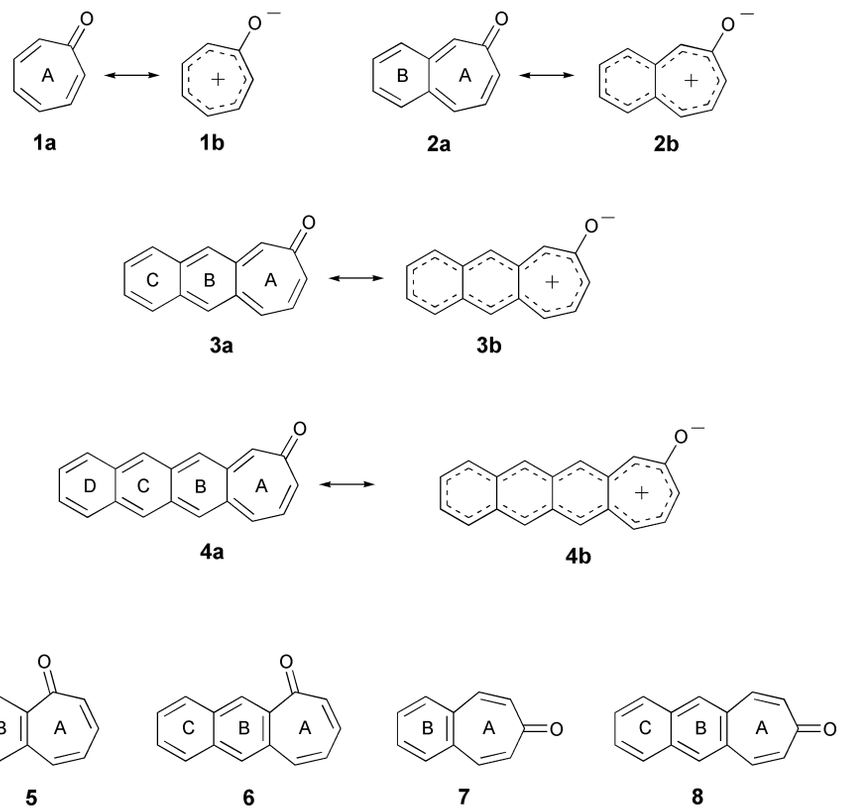
Computational analysis: geometry optimization for compounds 1–4

To gain insights into the structural changes induced by the 3,4-annelation of a tropone ring with naphthalene (to form **3**) and anthracene (to form **4**), geometrical optimizations of **3** and **4** were carried out at the density functional B3LYP level[4] employing the 6-31G* basis set implemented in the Gaussian 98 program package.[5] The structures of the lower homologues, **1** and **2**, were also optimized at the same level for comparison. The optimized geometries of **1**–**4** are shown in Fig. 1. Particularly interesting are the findings that the C=O bond length is increased as the number of annelated benzene rings increases, though the effect is more prominent in the first annelation compared to further ones: 1.235, 1.240, 1.242, and 1.243 Å for **1**, **2**, **3**, and **4**, respectively. A similar trend is also found for changes in the length of the skeletal C–C bond. Thus, as the number of annelated benzene rings increases, the double bonds become longer while the single bonds become shorter except for the joint bonds including the C(3)–C(4) bond in the tropone moiety. The elongation of the C=O bond as well as the decrease of peripheral bond alternation would be attributable to the increased contribution of polarized resonance forms and thus suggests that the higher homologues are electronically more polarized than the lower homologues.

Nucleus-independent chemical shifts (NICS) for compounds 1–8

The increased contribution of polarized resonance forms **2b**–**4b** in the annelated derivatives is expected to provide a substantial aromatic character to these molecules. Nucleus-independent chemical shifts (NICS) proposed by Schleyer *et al*.[6] have proven to be a simple and efficient probe of aromaticity:[7] large negative NICS values denote aromaticity and the large positive values denote antiaromaticity while small NICS values indicate non-aromaticity. Accordingly, NICS(1) values were calculated for a series of troponoid compounds **1**–**8** (Scheme 1) with the GIAO method at the RHF/6-31+G* level for B3LYP/6-31G* opti-

DOI: 10.1039/b400080n



Scheme 1

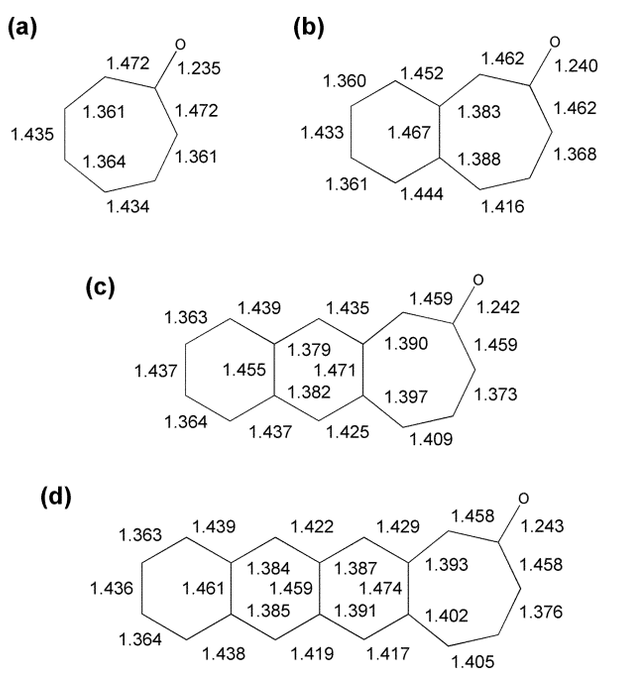


Fig. 1 Optimized geometries of tropone derivatives (a) **1**, (b) **2**, (c) **3**, and (d) **4** computed at the B3LYP/6-31G* level: bond lengths are shown in Å.

mized geometries. All the NICS values were calculated at points 1 Å above the ring centroids to minimize interference from the local magnetic anisotropy due to the carbonyl group. The results are summarized in Table 1. Parent tropone **1** shows the NICS(1) value of −2.9, indicating little resonance stabilization in this system. Interestingly, the NICS(1) value of the tropone ring becomes more negative (more aromatic) when a tropone ring is fused at the 3,4-position to benzene (to form **2**) or naphthalene (to form **3**), or anthracene (to form **4**), whereas those of the fused benzenoid rings become more positive relative to the parent compounds. Thus, it seems that the aromaticity of the

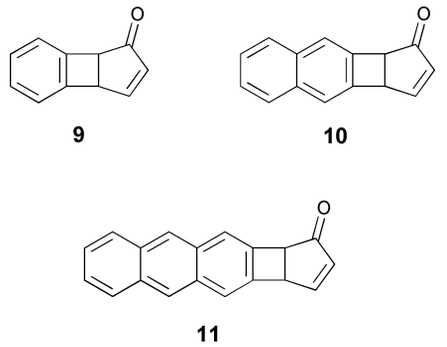
Table 1 The NICS(1) values computed in the geometrical centers of individual rings for compounds **1**–**8** (GIAO-RHF/6-31+G*//B3LYP/6-31G*)

Compound	Ring-A	Ring-B	Ring-C	Ring-D
1	−2.9	—	—	—
2	−5.7	−5.5	—	—
3	−7.4	−8.6	−5.3	—
4	−8.5	−10.3	−8.6	−5.4
5	−1.4	−12.0	—	—
6	−0.5	−12.8	−11.5	—
7	−1.7	−11.2	—	—
8	−0.6	−12.0	−11.4	—

tropone rings of **2**, **3**, and **4** is increased at the expense of that of the fused benzenoid rings. Particularly interesting is the finding that the NICS(1) value of the tropone ring in **3** (−7.4) and **4** (−8.5) approach to that of benzene (−11.2), suggesting increased contribution of polarized resonance forms **3b** and **4b**. The closely attended elongation of the C=O bonds of **1** (1.235 Å), **2** (1.240 Å), **3** (1.242 Å), and **4** (1.243 Å) with the enhancement in their negative NICS(1) values attests that the NICS(1) values properly reflect the contributions of the polarized resonance forms. In sharp contrast, the NICS(1) value of the tropone ring in **5**-**8**[8,9] become more positive (less aromatic) and are closer to zero.

Preparation of precursors 10 and 11

We next turned our attention to the experimental studies of **3** and **4** to gain a better understanding of these intriguing molecules. On the basis of our previous successful generation of **2** from the corresponding benzocyclobutene valence-bond isomer **9**,[2] we envisaged **10** and **11** (Scheme 2) as promising precursors for **3** and **4**. Although compound **9** has been prepared *via* the addition of benzyne to 2-cyclopentenone acetal, the yield of the benzyne adduct is disappointingly low (4%).[2] Therefore, modification of the synthetic route was required for the efficient preparation of **10** and **11**, which were finally carried out



Scheme 2

as outlined in Scheme 3.[10] Photocycloaddition of 2-cyclopentenone with (*E*)-1,4-dichloro-2-butene followed by protection of the carbonyl group and subsequent two-fold dehydrochlorination produced diene **14**. The Diels–Alder reaction of **14** with benzyne followed by dehydrogenation with DDQ gave naphthalene derivative **15**. Bromination of **15** followed by dehydrobromination and hydrolysis afforded enone **10**. Anthracene derivative **11** was also obtained from **14** *via* the similar reaction sequence indicated.

Photochemical generation and characterization of 3

o-Quinoidal **3** is expected to be a kinetically labile, highly reactive species, so that the photochemicl generation of **3** from **10** (Scheme 4) was examined under matrix isolation conditions at low temperature. When a degassed EPA solution of **10** (a 5 : 5 : 2 mixture of ether, isopentane, and ethanol) in a Pyrex tube was irradiated with a high-pressure mercury lamp at liquid nitrogen temperature (−196 °C), development of an intense absorption was observed in the range of 520–700 nm (Fig. 2). The generated blue–green species was stable in the frozen EPA glass but was consumed rapidly even below −100 °C when the glass was thawed. HPLC analysis of the resultant photolysate indicated clean formation of two products (*ca.* 1 : 1), which were isolated and unambiguously characterized as *syn*-[π12 + π14] dimers **19** and **20** by X-ray crystallography.[3] Thus we concluded that **3** was successfully generated photochemically from **10**. It is interesting to note that **3** afforded regioisomeric

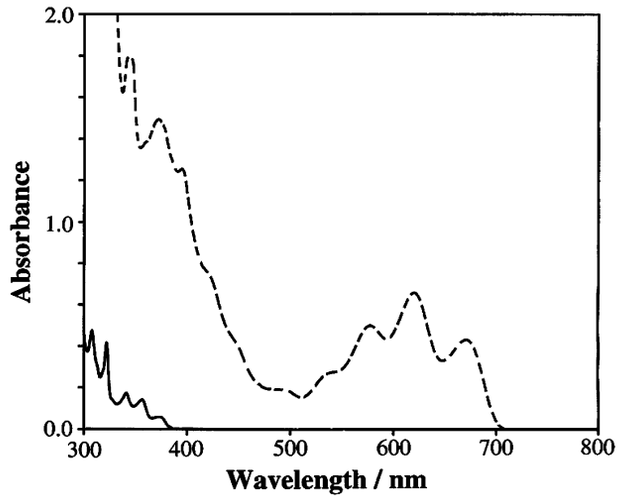
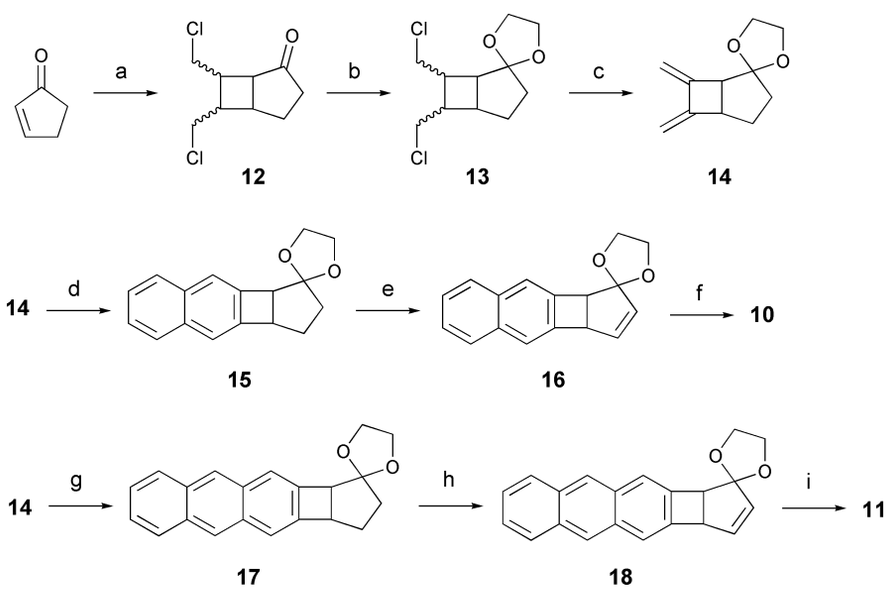


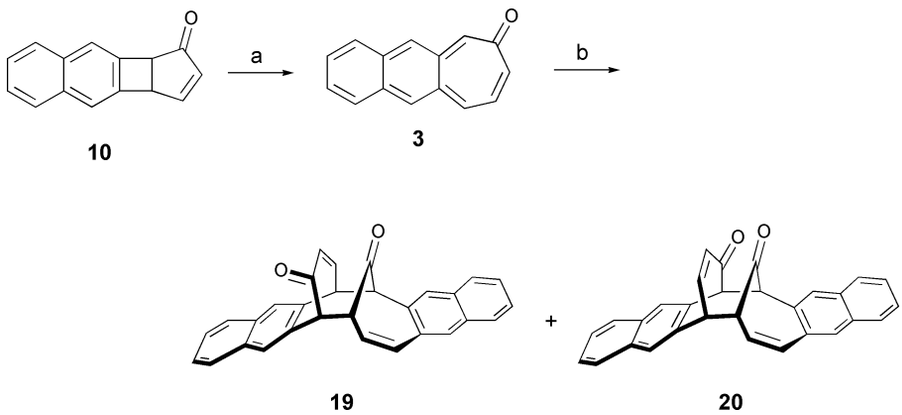
Fig. 2 Absorption spectral changes observed upon irradiation of **10** with a high-pressure mercury lamp through Pyrex in an EPA glass at −196 °C: before (solid line) and after irradiation (dashed line; λ_{max}/nm 533sh, 577, 621, 674).

syn-[π12 + π14] dimers **19** and **20** while **2** gave stereoisomeric *syn*- and *anti*-[π8 + π10] dimers.

The frontier molecular orbitals of **3**, together with those of **2** for comparison, are shown in Fig. 3. The preferential *syn*-dimerization observed for **3** may be rationalized by the extended secondary orbital interactions in the transition states characteristic to this naphtho-fused system. Coefficients for the frontier molecular orbitals of **3** are also consistent with the periselectivities observed the thermal dimerization reaction of this molecule. As reported previously, compound **2** is relatively stable at −78 °C ($t_{1/2}$ > 300 s at a concentration comparable to that of **3** in the present investigation) and undergoes dimerization with a rate constant of 12 ± 3 M^{-1} s^{-1} in EPA at −78 °C, whereas compound **3** was too unstable to determine the rate constant for dimerization under the same conditions. Thus, **3** was proven to be kinetically less stable than **2**, presumably reflecting the smaller HOMO–LUMO gap in **3**.[11] Photochemically, compound **3** appeared to be stable, at least in the EPA glass matrix at −196 °C, and showed no tendency to revert to **10**.



Scheme 3 *Reagents and conditions*: (a) (*E*)-1,4-dichloro-2-butene, *hv*, 12 °C, 12 h, 58%; (b) ethylene glycol, TsOH, refluxing benzene, 2 h, 94%; (c) *t*-BuOK, 18-crown-6, THF, room temperature, 3 h, 94%; (d) *o*-dibromobenzene, *n*-BuLi, toluene, room temperature, 22 h, then DDQ, benzene, room temperature, 2 h, 46%; (e) $PyHBr_3$, dichloromethane, room temperature, 35 h, then *t*-BuOK, 18-crown-6, refluxing THF, 5 h, 48%; (f) aqueous 1N HCl, THF, 50 °C, 5 h, 80%; (g) 2,3-dibromonaphthalene, *n*-BuLi, toluene, room temperature, 40 h, then DDQ, benzene, room temperature, 2 h, 60%; (h) $PyHBr_3$, dichloromethane, room temperature, 16 h, then *t*-BuOK, 18-crown-6, refluxing THF, 60%; (i) aqueous HCl, refluxing THF, 50 °C, 10 h, 55%.



Scheme 4 *Reagents and conditions*: (a) *hν*/Pyrex, EPA, −196 °C; (b) < −100 °C.

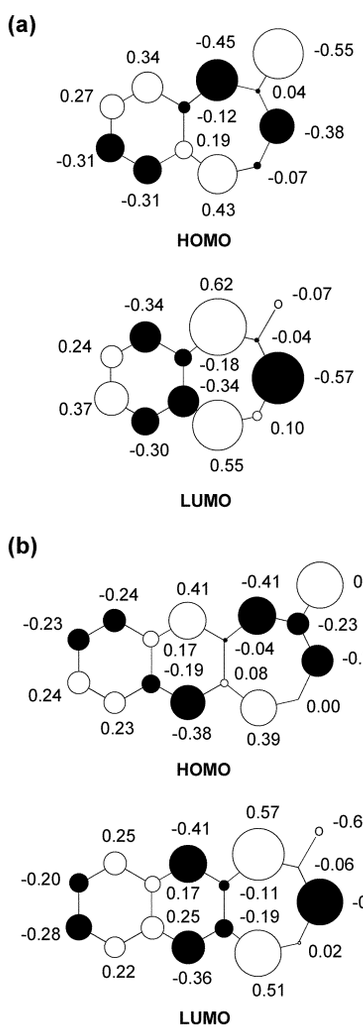
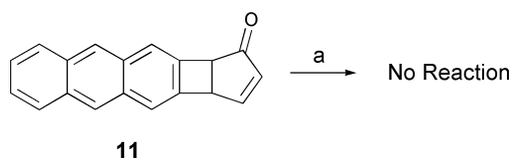


Fig. 3 Frontier molecular orbitals of (a) **2** and (b) **3** (B3LYP/6-31G*).

Attempted photochemical generation of 4

In contrast to the smooth photochemical generation of **2** and **3** from the corresponding benzocyclobutene and naphthocyclobutene valence-bond isomers **9** and **10**, respectively, anthrocyclobutene derivative **11** failed to give ring-opened **4** (Scheme 5). Thus, when a degassed EPA solution of **11** in a Pyrex tube was irradiated with a high-pressure mercury lamp at −196 °C, no development of absorption was observed in the long-wavelength region expected for **4** and the starting **11** was recovered quantitatively. The low excitation energy of anthrocyclobutene derivative **11** might be responsible for the lack of its reactivity to rearrange into **4** and result in the efficient fluorescent emission observed.



Scheme 5 *Reagents and conditions*: (a) *hν*/Pyrex, EPA, −196 °C.

Conclusions

The B3LYP/6-31G* optimized geometries of a series of tropones **1**–**4** suggest that the degree of electronic polarization would be further enhanced in naphtho-fused **3** and anthro-fused **4** as compared to that in benzo-fused **2**. Consistently, the GIAO calculated NICS(1) values indicate that the aromaticities of the tropone rings in **3** and **4** are significantly increased at the expense of the fused benzenoid rings to exceed that of not only **1** but also **2**, consistent with the greater electronic polarization in the ground state, namely, a substantial contribution of polar resonance structures to these molecules. This polarization effect of tropone ring is unique for the 3,4-annelation, and the fusion of benzene or naphthalene ring to the 2,3- or 4,5-position of tropone leads to the diminution of aromaticity in the resulting tropone moiety. Experimentally, the photochemical isomerization of **10** under matrix isolation conditions allowed the first generation and spectroscopic characterization of **3**, which exhibits a characteristic UV-vis absorption extending to 700 nm. *o*-Quinoidal **3** was proven to be a kinetically labile species which shows high propensity for undergoing [π12 + π14] dimerization even below −100 °C in a dilute solution. In contrast to the successful generation of **3** from **10**, however, a higher homologue **11** showed no sign of isomerization to **4** under the same reaction conditions. The photochemical rearrangement of **10** to **3**, therefore, would represent a limiting case of the present methodology for the generation of *o*-quinoidal tropone derivatives.

Experimental

General methods

^{1}H NMR spectra were recorded on JEOL EX-300 spectrometers at 300 MHz; chemical shifts are given in ppm using tetramethylsilane as a reference. ^{13}C NMR spectra were recorded on a JEOL EX-300 spectrometer in $CDCl_3$ at 75 MHz; chemical shifts are given in ppm using solvent peak as reference. IR spectra were taken on a Hitachi 270–30 infrared spectrometer. Electronic absorption spectra were measured on a Hitachi U-3500 spectrophotometer. Mass spectra were recorded on a JEOL JMS-SX102A spectrometer. GLC work was done on Hitachi 163 gas chromatographs. Preparative chromatography was performed on Merck Kieselgel 60 (70–230 mesh). The light source for photochemistry was a Halos

(Eiko-sha, Japan) 450 W high-pressure Hg lamp. 2,3-Dibromonaphthalene[12] was prepared following the known procedure. Other reagents and solvents were obtained from commercial sources and purified prior to use.

Synthesis

6,7-Bis(chloromethyl)bicyclo[3.2.0]heptan-2-one (12). A degassed solution of 2-cyclopentenone (10.6 g, 0.13 mol) and (*E*)-1,4-dichloro-2-butene (140 mL) in dichloromethane (140 mL) was irradiated with a 450 W high-pressure mercury lamp through Pyrex at 12 °C. The reaction was monitored by GLC (5% Silicon SE30, 0.5 m, 100–270 °C) and the irradiation was terminated after 12 h (70% GLC conversion). After evaporation of the reaction mixture, the residue was subjected to chromatography on silica gel eluted with ether–hexane (40 : 60). The eluent was concentrated and distilled to give **12** (15.5 g, 58%) as a mixture of stereoisomers; bp 115–120 °C (0.5 mmHg); (Found 206.0272, $C_9H_{12}OCl_2$ requires 206.0265); ν_{max} (film)/cm^{-1} 1730; δ_H (300 MHz; $CDCl_3$) 2.02–2.09 (m, 2 H), 2.22–2.44 (m, 2 H), 2.51–2.60 (m, 3 H), 2.80–2.86 (m, 1 H) and 3.61–3.78 (m, 4 H); *m*/*z* (FD) 210 (M^+ + 4, 11.6%), 208 (M^+ + 2, 64.2) and 206 (M^+, 100).

6,7-Bis(chloromethyl)bicyclo[3.2.0]heptan-2-one ethylene acetal (13). A mixture of **12** (5.20 g, 25 mmol), ethylene glycol (3.12 g, 50 mmol), and *p*-toluenesulfonic acid monohydrate (0.48 g, 2.5 mmol) in benzene (400 mL) was heated under reflux for 2 h while water was removed with a Dean–Stark trap. The mixture was cooled, diluted with ether (400 mL), washed successively with aqueous $NaHCO_3$ (400 mL), water (400 mL), and brine (400 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 20) to give **13** (5.90 g, 94%) as a mixture of stereoisomers; (Found 250.0524, $C_{11}H_{16}O_2Cl_2$ requires 250.0528); ν_{max} (film)/cm^{-1} 1100; δ_H (300 MHz; $CDCl_3$) 1.49–1.56 (m, 1 H), 1.72–1.97 (m, 3 H), 2.03–2.11 (m, 3 H), 2.46–2.49 (m, 1 H), 3.46–3.72 (m, 4 H) and 3.88–3.95 (m, 4 H); *m*/*z* (FD) 254 (M^+ + 4, 13.4%), 252 (M^+ + 2, 67.4) and 250 (M^+, 100).

6,7-Bismethylenebicyclo[3.2.0]heptan-2-one ethylene acetal (14). To a solution of the ethylene acetal (5.90 g, 2.4 mmol) in dry THF (200 mL) was added dropwise a solution of potassium *tert*-butoxide (7.90 g, 7.1 mmol) in dry THF (200 mL) under argon. The mixture was stirred at room temperature for 3 h and then evaporated. Water (200 mL) was added to the residue and the mixture was extracted with ether (3 × 200 mL). The extracts were combined, washed with brine (300 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 20) to give diene **14** (3.91 g, 94%) as a pale yellow oil; (Found 178.0982, $C_{11}H_{14}O_2$ requires 178.0994); ν_{max} (film)/cm^{-1} 1098; δ_H (300 MHz; $CDCl_3$) 1.70–1.77 (m, 2 H), 1.83–1.96 (m, 1 H), 2.03–2.14 (m, 1 H), 3.01 (d, *J* = 6.3 Hz, 1 H), 3.27 (d, *J* = 6.9 and 6.3 Hz, 1 H), 3.96 (br s, 4 H), 4.78 (br s, 1 H), 4.86 (br s, 1 H), 5.19 (br s, 1 H) and 5.25 (br s, 1 H); δ_C (75 MHz, $CDCl_3$) 29.20, 32.67, 43.85, 50.33, 63.90, 65.09, 103.61, 105.88, 117.71, 146.65 and 151.57; *m*/*z* (FD) 178 (M^+, 100%).

6,7-(2′,3′-Naphtho)bicyclo[3.2.0]hept-6-en-2-one ethylene acetal (15). To a solution of **14** (1.98 g, 11.1 mmol) and *o*-dibromobenzene (5.25 g, 22.2 mmol) in toluene (60 mL) was added 1.6 M *n*-butyllithium in hexane (13.9 mL, 22.2 mmol) over 5 min under ice cooling. The mixture was allowed to warm to room temperature, stirred for 22 h, diluted with ether (100 mL), washed with water (100 mL), dried with Na_2SO_4, and concentrated. The residue was dissolved in 500 mL of benzene and used for the next reaction. To the benzene solution was added dichlorodicyano-*p*-benzoquinone (3.39 g, 14.9 mmol) in portions. The mixture was stired at room temperature for 2 h, diluted with ether (500 mL), washed successively with 10% aqueous NaOH (500 mL) and brine (500 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 20) to give **15** (2.66 g, 46%) as a viscous oil; (Found 252.1143, $C_{17}H_{16}O_2$ requires 252.1150); ν_{max} (film)/cm^{-1} 1092; δ_H (300 MHz; $CDCl_3$) 1.69–1.74 (m, 2 H), 1.92–2.10 (m, 2 H), 3.75 (d, *J* = 4.4 Hz, 1 H), 3.99–4.13 (m, 5 H), 7.37–7.40 (m, 2 H), 7.47 (s, 1 H), 7.55 (s, 1 H) and 7.77–7.82 (m, 2 H); δ_C (75 MHz, $CDCl_3$) 26.86, 32.25, 45.99, 52.39, 64.02, 65.11, 116.14, 119.79, 121.06, 124.55, 124.70, 127.95, 128.29, 134.14, 134.43, 142.16 and 145.65; *m*/*z* (FD) 252 (M^+, 100%).

6,7-(2′,3′-Naphtho)bicyclo[3.2.0]hepta-3,6-dien-2-one ethylene acetal (16). To a solution of **15** (2.5 g, 9.9 mmol) in dichloromethane (180 mL) was added pyridinium tribromide (3.5 g, 11 mmol) in one portion, and the mixture was stirred at room temperature for 35 h and then poured into 10% aqueous $Na_2S_2O_3$ (200 mL). The organic layer was separated, washed with brine (150 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 9) to give 1.88 g of bromide as a mixture of stereoisomers, which was dissolved in 500 mL of dry THF and used for the next reaction. To the THF solution was added 18-crown-6 (2.25 g, 8.5 mmol) and potassium *tert*-butoxide (0.96 g, 8.5 mmol) and the mixture was refluxed for 20 h, cooled to room temperature, and evaporated. Water (200 mL) was added to the residue and the mixture was extracted with chloroform (3 × 100 mL). The extracts were combined, washed with brine (200 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 9) to give **16** (1.18 g, 48%) as a viscous oil; (Found 250.0990, $C_{17}H_{14}O_2$ requires 250.0994); ν_{max} (film)/cm^{-1} 1150, 1072, 1022 and 994; δ_H (300 MHz; $CDCl_3$) 4.02–4.21 (m, 5 H), 4.60 (dd, *J* = 3.8 and 2.5 Hz, 1 H), 5.61 (br d, *J* = 5.8 Hz, 1 H), 6.40 (dd, *J* = 5.8 and 2.5 Hz, 1 H), 7.35–7.41 (m, 2 H), 7.44 (s, 1 H), 7.63 (s, 1 H) and 7.71–7.80 (m, 2 H); δ_C (75 MHz, $CDCl_3$) 52.14, 52.93, 64.46, 65.49, 116.09, 119.32, 123.54, 124.80, 125.04, 128.10, 128.30, 130.75, 133.90, 133.94, 138.12, 141.48 and 147.04; *m*/*z* (FD) 250 (M^+, 100%).

6,7-(2′,3′-Naphtho)bicyclo[3.2.0]hept-3,6-dien-2-one (10). To a solution of **16** (1.18 g, 4.72 mmol) in THF (50 mL) was added 10% aqueous HCl (5 mL) and the mixture was heated at 50 °C for 5 h. The mixture was cooled to room temperature, diluted with chloroform (300 mL), washed successively with 10% aqueous $NaHCO_3$ (100 mL) and brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 9) to give **10** (0.77 g, 80%) as colorless solids; mp 213–215 °C (ether); (Found 206.0740, $C_{15}H_{10}O$ requires 206.0732); λ_{max} (EtOH)/nm 270 (ε/dm^3 mol^{-1} cm^{-1} 13000), 278.5 (13000), 287.5 (8400sh), 309 (960), 322 (880) and 343 nm (330); ν_{max} (KBr)/cm^{-1} 1692; δ_H (300 MHz; $CDCl_3$) 4.30 (d, *J* = 3.3 Hz, 1 H), 4.78 (dd, *J* = 3.3 and 3.0 Hz, 1 H), 6.09 (d, *J* = 6.0 Hz, 1 H), 7.40–7.46 (m, 2 H), 7.56 (s, 1 H), 7.70 (s, 1 H), 7.75–7.80 (m, 2 H) and 7.85 (dd, *J* = 6.0 and 3.0 Hz, 1 H); δ_C (75 MHz, $CDCl_3$) 51.16, 53.21, 121.32, 122.77, 126.02, 126.09, 128.60, 128.88, 134.13, 134.23, 134.29, 138.99, 144.03, 162.11 and 205.47; *m*/*z* (FD) 206 (M^+, 100%).

6,7-(2′,3′-Anthro)bicyclo[3.2.0]hept-6-en-2-one ethylene acetal (17). To a solution of **14** (0.50 g, 2.8 mmol) and 2,3-dibromonaphthalene[12] (1.60 g, 5.6 mmol) in toluene (20 mL) was added 1.6 M butyllithium in hexane (3.6 mL, 5.6 mmol) over 1 min under ice cooling. The mixture was allowed to warm to room temperature, stirred for 40 h, diluted with benzene (200 mL), washed successively with water (200 mL) and brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was dissolved in benzene (70 mL) and dichlorodicyano-*p*-benzoquinone (0.49 g, 2.2 mmol) was added to the solution in

portions. The mixture was stired at room temperature for 2 h, diluted with benzene (200 mL), washed successively with 10% aqueous NaOH (100 mL), water (100 mL), and brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (2 : 8) to give **17** (0.58 g, 60%) as colorless solids; mp 173–175 °C (ether); (Found 302.1312, $C_{21}H_{18}O_2$ requires 302.1307); ν_{max} (film)/cm^{-1} 1324, 1092, 936 and 744; δ_H (300 MHz; $CDCl_3$) 1.56–1.81 (m, 2 H), 2.01–2.10 (m, 2 H), 3.80 (d, J = 4.6 Hz, 1 H), 4.01–4.17 (m, 5 H), 7.41–7.45 (m, 2 H), 7.60 (s, 1 H), 7.68 (s, 1 H), 7.95–7.98 (m, 2 H), 8.35 (s, 1 H) and 8.37 (s, 1 H); δ_C (75 MHz, $CDCl_3$) 27.41, 32.56, 46.16, 52.59, 64.16, 65.26, 116.52, 119.38, 120.71, 124.87, 124.97, 126.04, 126.48, 127.85, 127.97, 130.88, 130.96, 132.71, 132.93, 142.00 and 145.78; *m*/*z* (FD) 302 (M$^+$, 100%).

6,7-(2′,3′-Anthro)bicyclo[3.2.0]hepta-3,6-dien-2-one ethylene acetal (18). To a solution of **17** (0.65 g, 2.2 mmol) in dichloromethane (150 mL) was added pyridinium tribromide (0.76 g, 2.4 mmol) in one portion. The mixture was stirred at room temperature for 16 h and then poured into 10% aqueous $Na_2S_2O_3$ (100 mL). The organic layer was separated, washed with brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was dissolubed in dry THF (40 mL) and used for the next reaction. To the THF solution was added potassium *tert*-butoxide (40 mg, 0.35 mmol) and 18-crown-6 (95 mg, 0.35 mmol) and the mixture was refluxed for 5 h under argon, cooled to room temperature, and evaporated. Water (50 mL) was added to the residue and the mixture was extracted with chloroform (3 × 50 mL). The extracts were combined, washed with brine (50 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether–hexane (1 : 9) to give **18** (42 mg, 60%) as colorless solids; mp 185–187 °C (ether); (Found 300.1142, $C_{21}H_{16}O_2$ requires 300.1150); ν_{max} (KBr)/cm^{-1} 1148, 1070 and 1022; δ_H (300 MHz; $CDCl_3$) 4.05–4.17 (m, 4 H), 4.25 (d, J = 3.8 Hz, 1 H), 4.66 (dd, J = 3.8 and 2.4 Hz, 1 H), 5.67 (d, J = 5.7 Hz, 1 H), 6.43 (dd, J = 5.7 and 2.4 Hz, 1 H), 7.58 (s, 1H), 7.40–7.46 (m, 2 H), 7.77 (s, 1 H), 7.94–7.97 (m, 2 H), 8.32 (s, 1 H) and 8.36 (s, 1 H); *m*/*z* (FD) 300 (M$^+$, 100%).

6,7-(2′,3′-Anthro)bicyclo[3.2.0]hepta-3,6-dien-2-one (11). To a solution of **18** (42 mg, 14 mmol) in THF (20 mL) was added 10% aqueous HCl (2 mL) and the mixture was heated at 50 °C for 10 h. The mixture was cooled to room temperature, diluted with chloroform (100 mL), washed successively with 10% aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried with Na_2SO_4, and concentrated. The residue was purified by preparative TLC (chloroform) to give **11** (20 mg, 55%) as colorless solids; mp >250 °C (ether); (Found 256.0895, $C_{19}H_{12}O$ requires 256.0888); ν_{max} (KBr)/cm^{-1} 1692; δ_H (300 MHz; $CDCl_3$) 4.36 (d, J = 2.9 Hz, 1 H), 4.84 (dd, J = 3.1 and 2.9 Hz, 1 H), 6.16 (d, J = 5.7 Hz, 1 H), 7.43–7.48 (m, 2 H), 7.70 (s, 1 H), 7.85 (s, 1 H), 7.90 (dd, J = 5.7 and 3.1 Hz, 1 H), 7.95–8.00 (m, 2 H), 8.35 (s, 1 H) and 8.36 (s, 1 H); *m*/*z* (FD) 256 (M$^+$, 100%).

Thermal [π12 + π14] dimerization of 3. A solution of 50 mg (0.24 mmol) of **10** in 500 mL of EPA (4.9 × 10^{-3} M) was distributed among 70 Pyrex ampules and degassed by freeze-pump-thaw cycles. The solution in each sealed ampule was frozen in liquid N_2, irradiated with a 450 W high-pressure Hg lamp for 10 min, and then warmed to room temperature. This freeze-irradiation-thaw cycle was repeated four times for each sample before the irradiation was discontinued. TLC analysis (chloroform) of the resultant photolyzate indicated the exclusive formation of two products. The mixture was concentrated and the residue purified by preparative TLC (chloroform) to give recovered **10** (29 mg, 58%), **19** (8 mg, 16%) and **20** (8 mg, 16%).

*For **19***. Mp >250 °C (ether); (Found 512.1765, $C_{38}H_{24}O_2$ requires 512.1776); ν_{max} (KBr)/cm^{-1} 1704 and 1660; δ_H (300 MHz; $CDCl_3$) 4.13 (ddd, J = 6.8, 5.8, and 2,5 Hz, 1 H), 4.28 (dd, J = 9.1 and 4.9 Hz, 1 H), 4.37 (dd, J = 5.8 and 1.7 Hz, 1 H), 4.68 (dd, J = 4.9 and 2.5 Hz, 1 H), 5.48 (dd, J = 12.4 and 6.8 Hz, 1 H), 6.15 (dd, J = 11.8 and 1.7 Hz, 1 H), 6.18 (d, J = 12.4 Hz, 1 H), 7.04 (s, 1 H), 7.21–7.34 (m, 2 H), 7.28 (s, 1 H), 7.38–7.44 (m, 3 H), 7.49 (ddd, J = 8.0, 6.9, and 1.4 Hz, 1 H), 7.60 (d, J = 8.0 Hz, 1 H), 7.62 (s, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.82 (s, 1 H) and 7.83 (d, J = 8.0 Hz, 1 H); *m*/*z* (FD) 512 (M$^+$, 100%).

*For **20***. Mp >250 °C (ether); (Found 512.1767, $C_{38}H_{24}O_2$ requires 512.1776); ν_{max} (KBr)/cm^{-1} 1702 and 1660; δ_H (300 MHz; $CDCl_3$) 4.10 (ddd, J = 6.9, 5.8, and 2.8 Hz, 1 H), 4.32 (dd, J = 8.8 and 5.8 Hz, 1 H), 4.34 (dd, J = 4.4 and 1.4 Hz, 1 H), 4.66 (dd, J = 4.4 and 2.8 Hz, 1 H), 5.52 (dd, J = 12.1 and 6.6 Hz, 1 H), 6.15 (d, J = 12.1 Hz, 1 H), 6.16 (dd, J = 11.8 and 1.4 Hz, 1 H), 7.15 (s, 1 H), 7.20–7.50 (m, 6 H), 7.56 (s, 1 H), 7.61 (s, 1 H), 7.63 (d, J = 8.0 Hz, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.83 (d, J = 8.0 Hz, 1 H) and 7.88 (s, 1 H); *m*/*z* (FD) 512 (M$^+$, 100%).

Irradiation of 10 in an EPA glass matrix at −196 °C: measurement of the electronic absorption spectrum of 3

A solution of **10** in 7 mL of EPA (4.9 × 10^{-3} M) was placed in a Pyrex tube, degassed by freeze-thaw cycles, and sealed. The sealed tube was immersed in liquid N_2 in a Dewar having two parallel windows facing each other and irradiated through the window. When the solution of **10** in EPA was irradiated with a 450 W high-pressure Hg lamp at −196 °C, development of absorptions with λ_{max} at 533sh, 577, 621, and 674 nm were observed. Absorbances at 621 nm after 10, 20, 40, and 60 min of irradiation were 0.20, 0.35, 0.53, and 0.64, respectively, and it was increased upon further irradiation.

Acknowledgements

We thank Professor Tamotsu Inabe (Hokkaido University) for the use of X-ray analytical facilities. M. O. gratefully acknowledges financial support from the Tokuyama Science Foundation and the Shorai Foundation for Science and Technology.

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