

Synthesis and Structure of [6](1,4)Naphthalenophane and [6](1,4)Anthracenophane and Their Peri-Substituted Derivatives

Yoshito Tobe,* Shinji Saiki, Hirokazu Minami, and Koichiro Naemura

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received March 13, 1997)

[6](1,4)Naphthalenophane (**1a**), [6](1,4)anthracenophane (**2a**), and their peri-substituted derivatives **1b**, **1c**, and **2b** were synthesized from 8-bromo[6]paracyclophane (**4**) by a benzoannulation method. The ^1H NMR spectral properties of **1b**, **1c**, and **2b** as well as the X-ray crystallographic structure analysis of **1b** indicate that their bridged aromatic rings are more distorted than those of the corresponding parent systems, **1a** and **2a**. Thermally reversible photochemical isomerization of **1b** and **2b** took place readily, giving the corresponding Dewar valence isomers, **10b** and **11b**.

While the chemistry of small $[n]$ paracyclophanes has been extensively explored during the last decade,¹⁾ little has been learned about the $[n]$ cyclophanes of condensed benzenoid aromatics.²⁾ We synthesized the smallest 1,4-bridged cyclophanes having a naphthalene or anthracene core,³⁾ [6](1,4)-naphthalenophane (**1a**) and [6](1,4)anthracenophane (**2a**), and studied their structure and unusual reactivity.⁴⁾ Recently, the lower homologue in the naphthalene series, a [5](1,4)-naphthalenophane derivative, was characterized below room temperature by Bickelhaupt.⁵⁾ We also succeeded in the synthesis of the 1,4,5,8-tetraphenyl and tetramethyl derivatives **3b** and **3c** of the smallest [6](9,10)anthracenophane and the spectroscopic characterization of the unstable parent hydrocarbon **3a** (Chart 1).⁶⁾ We found that the introduction of peri substituents remarkably enhanced the kinetic stability of this system, which is otherwise extremely unstable. On the other hand, the peri-substituted **3b** and **3a** are thermodynamically

less stable than the parent **3c**, because the out-of-plane deformation of the aromatic rings of **3b** and **3c** is more severe than that of **3a**, due to the steric repulsion. In this context, we report here on the syntheses of [6](1,4)naphthaleno- and anthracenophanes **1b**, **1c**, and **2b**, having phenyl or methyl groups at the peri positions from 8-bromo[6]paracyclophane (**4**),⁷⁾ by using the benzoannulation method.⁸⁾ This synthetic procedure was applied for the preparation of the parent systems, **1a** and **2a**, furnishing an alternative way for their synthesis.⁹⁾ We also report on the spectral properties of **1b**, **1c**, and **2b** and an X-ray crystallographic analysis of **1b**, which reveal that their bridged aromatic rings are more distorted than the corresponding parent systems, **1a** and **2a**, and the thermally reversible photochemical isomerization of **1b** and **2b** to the corresponding Dewar isomers, **10b** and **11b**.

The treatment of bromocyclophane **4** with a mixed strong base¹⁰⁾ comprising sodium amide and sodium *t*-butoxide in THF in the presence of furan afforded two isomeric [4+2] adducts, *syn*-**5a** and *anti*-**6a**, in a ratio of 6:1 (41% yield) (Scheme 1). A similar reaction with 2,5-dimethylfuran gave *syn*-**5c** and *anti*-**6c** (3:4; 28% yield). The reaction of **4** with 2,5-diphenylfuran¹¹⁾ was undertaken in refluxing toluene using potassium *t*-butoxide as the base, to yield *syn*-**5b** (19%). The corresponding *anti* isomer **6b** was not detected. Similarly, the treatment of **4** with $\text{NaNH}_2/\text{NaO}^t\text{Bu}$ in the presence of in situ prepared isobenzofuran¹²⁾ yielded the [4+2] adducts *syn*-**7a** and *anti*-**8a** in a ratio of 1:2 (66% yield). The major isomer **8a** was also obtained by desilylation of **8c** (88%), which was prepared by the reaction of **4** with in situ generated 1,3-bis(trimethylsilyl)isobenzofuran¹³⁾ using lithium tetramethylpiperidide as the base in 50% yield. The reaction of **4** with 1,3-diphenylisobenzofuran was undertaken using the mixed-base $\text{NaNH}_2/\text{NaO}^t\text{Bu}$ to afford *anti*-**8b** in 30% yield. A small amount of *syn* isomer **7b** was also obtained in another run. The orientation of the oxygen atoms of the epoxynaphthalenophanes and epoxyanthracenophanes was deduced on the basis of the ^1H NMR chemical shifts of the

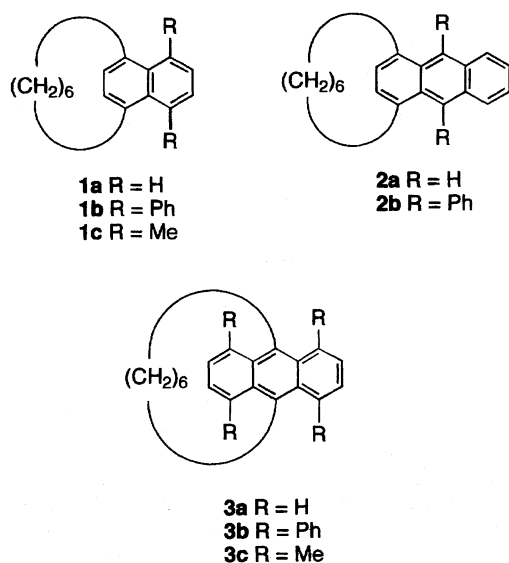
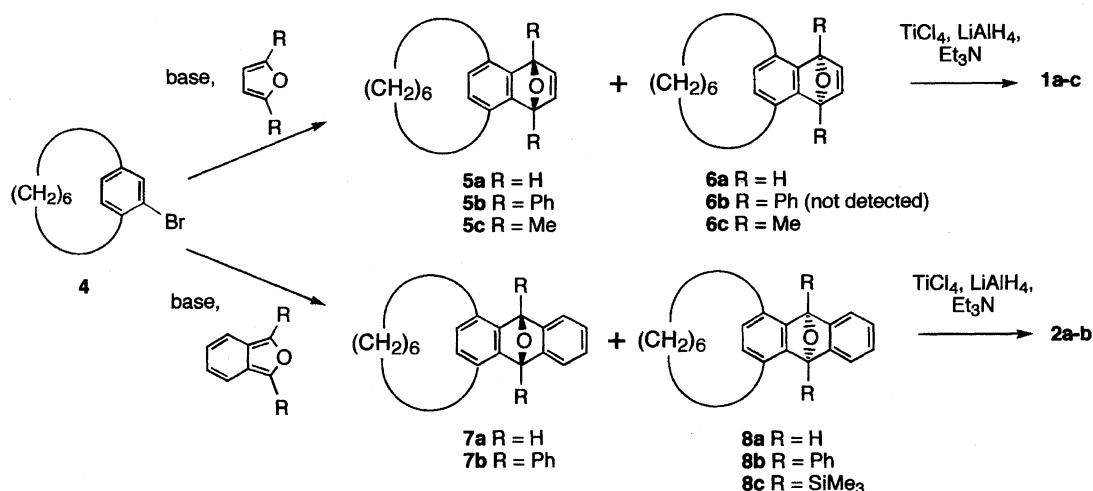


Chart 1.



Scheme 1.

bridge methylene protons (H_k) (Chart 2). Namely, H_k of the *anti* isomers should suffer from a shielding effect of the double bond of the oxanorbornadiene unit (for **6a** and **6c**) or the benzene ring of the benzoxanorbornadiene unit (for **8a–c**). Accordingly, the isomers which exhibit the methylene signal for H_k (**6a** $\delta = -1.05$, **6c** $\delta = -0.92$, **8a** $\delta = -2.76$, **8b** $\delta = -2.80$, **8c** $\delta = -2.81$) at a higher field than that of the reference compound, [6]paracyclophane (**9** $\delta = -0.62$),¹⁴ are assigned to those having an *anti* oxygen bridge (Chart 3). The assignment of *syn*-**5b** having phenyl groups at the peri positions is more equivocal; it was deduced on the basis of the absence of signals for the benzylic protons, H_a and H_d , at a low-field region (2.7–3.0 ppm), because these protons should suffer from a shielding effect of the peri-attached phenyl groups if the structure has a *syn* orientation of the oxygen atom.

The reductive deoxygenation of *syn*-**5a** with a low-valent titanium reagent prepared from titanium(IV) chloride, lithium aluminum hydride, and triethylamine (7:2.5:1)¹⁵ in THF gave naphthalenophane **1a** in 52% isolated yield.

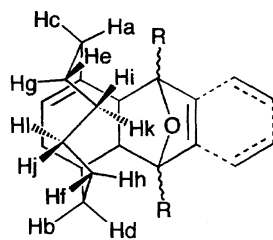


Chart 2.

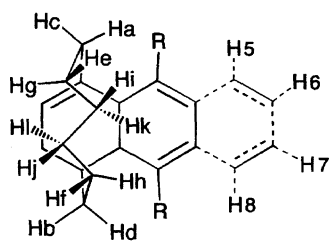


Chart 3.

The deoxygenation of **8a** under similar conditions gave anthracenophane **2a** in 51% yield. This provides an alternative way for the synthesis of **1a** and **2a**. The present method is as convenient as the previous method^{4a} with respect to the total steps and yields from commercially available starting materials. However, this route has an advantage in view of the fact that: (i) both **1a** and **2a** are prepared from the common advanced intermediate **4**, and (ii) the peri-substituted derivatives, such as **1b**, **1c**, and **2b**, are prepared as described below. Thus, the deoxygenation of a mixture of **5b** and **6b** or **5c** with the titanium reducing agent yielded the 5,8-disubstituted naphthalenophanes **1b** (87%) or **1c** (60%). Moreover, the reduction of **8b** under similar conditions furnished 9,10-diphenylanthracenophane **2b** in 59% yield.

As in the case of the parent hydrocarbons, **1a** and **2a**,^{4c} the peri-substituted derivatives **1b**, **1c**, and **2b** exhibit a temperature-dependent ¹H NMR behavior due to the flipping of the methylene bridge. The barriers of the flipping were determined by either a line-shape analysis or from the coalescence temperature (Table 1). As shown in Table 1, the barriers for **1b**, **1c**, and **2b** are smaller than those of the corresponding parent compound by about 1.5 kcal mol⁻¹. The decrease in the energy barrier implies that the out-of-plane distortion of the bridged aromatic rings of the peri-substituted compounds

Table 1. Barriers for the Flipping of the Methylene Bridges of Naphthalenophanes **1a–c** and Anthracenophanes **2a–b**

Compd	$\Delta G^\ddagger$ /kcal mol ⁻¹ (temp/K)
1a	13.6 (273) ^{a,b}
1b	12.2 (283) ^a
1c	12.1 (298) ^c
2a	13.4 (268) ^{a,b}
2b	12.0 (298) ^d

a) Determined from the coalescence temperature and $\Delta\nu$. b) Ref. 4a. c) Determined by the line shape analysis of the signals of the methyl protons. d) Determined by the line shape analysis of the signals of the aromatic protons H5 and H8 which were decoupled by irradiation of the signals of H6 and H7.

Table 2. ^1H NMR Chemical Shifts of Naphthalenophanes **1a—c** and Anthracenophanes **2a—b**^{a)}

Proton	Compd				
	1a ^{b)}	1b ^{c)}	1c ^{d)}	2a ^{b)}	2b ^{c,e)}
H _a	2.86	1.68	2.54	3.00	1.69
H _b	2.27	1.82	2.19	2.36	1.69
H _c	3.01	2.48	2.97	3.08	2.25
H _d	3.49	2.09	3.50	3.58	1.69
H _e	1.74	1.33	1.56	1.77	1.36
H _f	1.58	1.14	1.56	1.60	1.17
H _g	0.71	0.53	0.66	0.80	0.61
H _h	0.34	-0.04	0.10	0.38	0.17
H _i	0.79	0.53	0.66	0.71	0.61
H _j	1.11	1.01	1.16	1.14	1.17
H _k	-1.84	-1.92	-1.87	-1.81	-1.60
H _l	-0.47	-0.51	-0.36	-0.31	-0.29

a) Chemical shifts are in δ ppm. b) Measured at -50°C in CDCl_3 (Ref. 3a). c) Measured in CD_2Cl_2 at -80°C . d) Measured in CD_2Cl_2 at -85°C . e) The signals are still broader than those of the other compounds measured at the same temperature presumably because of the hindered rotation of the peri-substituted phenyl groups.

is greater than that of the parent systems. A similar, but more distinct, difference was observed for the 9,10-bridged anthracenophanes **3a—c**.^{6b,6c)}

At low temperatures (-50 to -85°C) the conformation of the methylenes is frozen on the NMR time scale. The signals of the methylene protons were assigned on the basis of the H-H COSY experiment, as listed in Table 2 and Chart 3. There is not much difference between the chemical shifts of the methylene protons of **1a** and those of **1c**, except for H_a,

Table 3. Observed and AM1-Calculated Out-of-Plane Deformation Angles of Naphthalenophanes **1a—b** and Anthracenophanes **2a—b**

Compd		α (deg) ^{a)}	β (deg) ^{b)}	$\alpha + \beta$ (deg)
1a	Calcd	24.5	16.7	41.2
1b	Calcd	25.8	16.0	41.8
	Exptl ^{c)}	20.8	20.3	41.1
2a	Calcd	25.4	16.0	41.4
	Exptl ^{d)}	21.0	19.5	40.5
2b	Calcd	27.2	14.8	42.0

a) Average out-of-plane bending angle of the para carbons. b) Average out-of-plane bending angle of the benzylic carbons. c) This work. d) Ref. 4a.

which exhibited an upfield shift of 0.32 ppm. On the other hand, the benzylic protons (H_a—H_d) and homobenzylic protons (H_e—H_h) of **1b** and **2b** exhibit a remarkable upfield shift relative to those of **1a** and **2a**, due to an anisotropic shielding effect of the peri-substituted phenyl groups. In particular, the proximate benzylic proton (H_a) shows an upfield shift of 1.18 (for **1b**) and 1.31 (for **2b**) ppm and H_d exhibits a 1.40 (for **1b**) and 1.89 (for **2b**) ppm upfield shift.

In order to assess the effect of the phenyl groups on the structure of the [6](1,4)naphthalenophane system, an X-

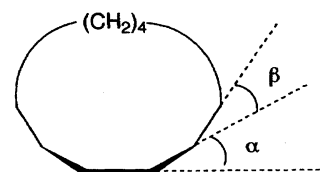
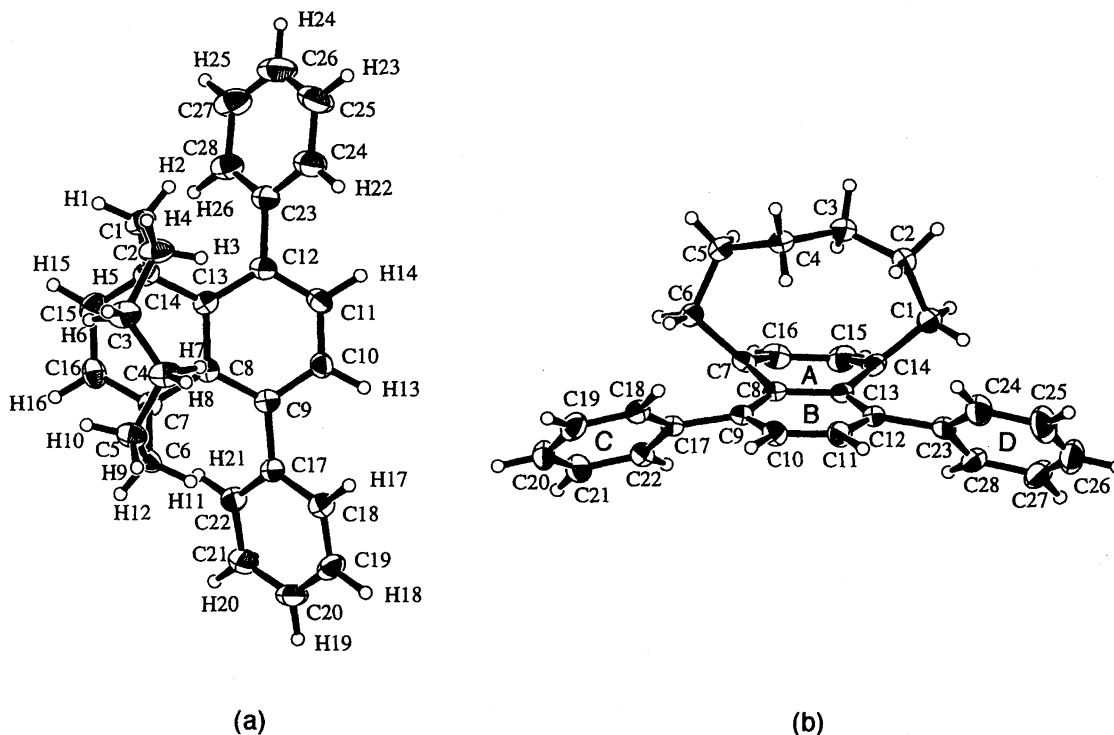
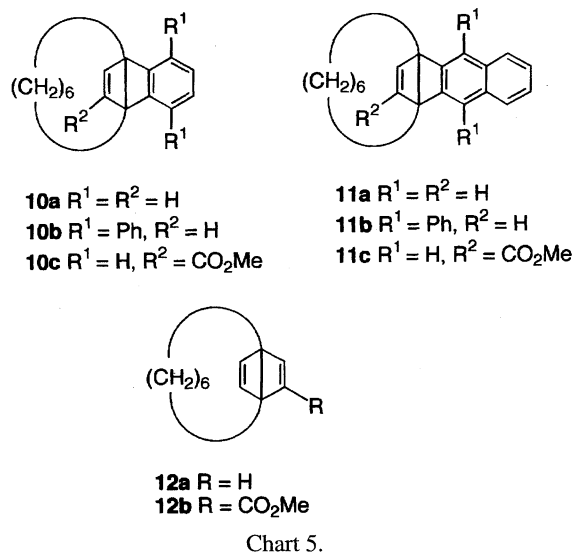


Chart 4.

Fig. 1. Molecular structure of naphthalenophane **1b**. (a) Top view, (b) Side view.

ray crystallographic structure analysis of **1b** was undertaken (Fig. 1). Table 3 lists the out-of-plane deformation angles (α and β ; Chart 4) of the bridged aromatic ring A of **1b** together with those of **2a**, determined by an X-ray analysis and those estimated from the calculated geometries for **1a—b** and **2a—b** using the semiempirical AM1 method.¹⁶⁾ The calculated deformation angles are qualitatively in good agreement with the observed values, though this semiempirical method tends to overestimate the angle α . The bending angles, particularly those of the para carbons (α), of the peri-substituted derivatives, **1b** and **2b**, are slightly larger than those of the corresponding parent systems, **1a** and **2a**. However, the difference is smaller than those observed for the 9,10-bridged anthracenophanes **3a—c**,^{6c)} in accord with observations in the dynamic NMR. Short nonbonded distances are observed between the benzylic hydrogens and the phenyl carbons of **1b** ($H2 \cdots C23 = 2.48 \text{ \AA}$, $H11 \cdots C17 = 2.47 \text{ \AA}$), indicating that the small increase in the distortion of the ring A is due to a steric repulsion. The twist angles between ring B and the peri-attached phenyl rings (C and D) are 45.3° and 42.1° , respectively.

It has been well documented that [6]paracyclophane (**9**) and its derivatives undergo a thermally reversible photochemical valence isomerization to their corresponding Dewar isomers.^{14,17)} Previously, we reported that the photoisomerization of naphthalenophane **1a** to its Dewar isomer **10a** and its thermal cycloreversion took place readily.^{4b)} It is therefore not surprising that a similar photoisomerization occurred upon the irradiation ($\lambda > 350 \text{ nm}$) of the diphenyl derivative **1b**, giving the Dewar isomer **10b** (quantitative by ¹H NMR spectrum) (Chart 5). On the other hand, we also reported that the irradiation of anthracenophane **2a** did not lead to the Dewar isomer **11a**, but, instead, to the cyclobutane dimers resulting from a [2+2] cycloaddition at the 1,2-bond of the anthracene core, presumably through its triplet excited state.^{4c)} Since it has been known that the introduction of phenyl groups at the 9,10-positions of the anthracene core



suppress the intersystem crossing efficiency from its singlet excited state,¹⁸⁾ it is reasonable to assume that 9,10-diphenylanthracenophane **2b** would undergo valence isomerization from the singlet excited state rather than cycloaddition from the triplet state. Indeed, the irradiation ($\lambda > 350 \text{ nm}$) of **2b** resulted in the quantitative (by NMR) formation of the Dewar isomer **11b**. The structures of **10b** and **11b** were readily assigned on the basis of the NMR spectra, particularly by the presence of signals due to the quaternary carbons in the ¹³C NMR spectra (**10b** $\delta = 65.1$, **11b** $\delta = 65.2$).

The thermal cycloreversion of **10b** and **11b** took place quantitatively to afford the corresponding cyclophanes, **1b** and **2b**. The rates of cycloreversion of **10b** (in toluene) and **11b** (in cyclohexane) were measured; the kinetic parameters are listed in Table 4 and Chart 5, together with those of related Dewar naphthalenophanes, **10a** and **10c**, Dewar anthracenophane **11c**, and Dewar isomers of [6]paracyclophane, **12a** and **12b**. As can be seen from a comparison of the kinetic data for the isomerization of **10a** and those of

Table 4. Kinetic Data for the Thermal Valence Isomerization of Dewar Paracyclophanes **12a—b**, Dewar Naphthalenophanes **10a—c**, and Dewar Anthracenophanes **11b—c**^{a)}

Compd	Temp/ $^\circ\text{C}$	k/s^{-1}	k_{rel}	$E_a/\text{kcal mol}^{-1}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{cal deg}^{-1} \text{ mol}^{-1}$
12a ^{b)}	25.0 ^{c)}	1.07×10^{-6}	1.0	21.7	21.1	-15.3
12b ^{d)}	25.0 ^{c)}	3.34×10^{-6}	3.1	24.9	24.3	-2.0
10a ^{e)}	25.0 ^{c)}	4.33×10^{-5}	41	19.5	18.9	-15.3
10b ^{f,g)}	25.0 ^{c)}	7.48×10^{-7}	0.69	25.2 ± 0.2	24.7 ± 0.2	-4.0 ± 0.5
	39.9	$(5.69 \pm 0.08) \times 10^{-6}$				
	49.8	$(2.00 \pm 0.01) \times 10^{-5}$				
	62.3	$(8.63 \pm 0.01) \times 10^{-5}$				
10c ^{e)}	25.0	6.18×10^{-5}	58	23.8	23.2	0.0
11b ^{f)}	25.0 ^{c)}	2.27×10^{-5}	21	23.4 ± 0.3	22.8 ± 0.3	-3.4 ± 1.0
	28.4	$(3.54 \pm 0.10) \times 10^{-5}$				
	37.6	$(1.14 \pm 0.01) \times 10^{-4}$				
	46.9	$(3.41 \pm 0.00) \times 10^{-4}$				
11c ^{e)}	25.0	4.23×10^{-4}	400	21.8	21.2	-2.8

a) Measured in cyclohexane unless otherwise stated. b) Ref. 19. c) Extrapolated from higher temperatures. d) Ref. 14c. e) Ref. 4b. f) This work. g) Measured in toluene.

10b, the introduction of peri-attached phenyl groups brings about a considerable deceleration of the isomerization rate. A substantial increase in the activation enthalpy for isomerization of **10b** relative to that of **10a** (6 kcal mol⁻¹) is ascribed to a steric repulsion in the transition state between the methylene bridge and the phenyl groups. A similar, but less distinct, effect of the substituent was observed in a series of Dewar isomers bearing a methoxycarbonyl group (**12a** vs. **12b** and **10a** vs. **10c**).^{4b} As reported for esters **12b**, **10c**, and **11c** previously,^{4b} the activation energy decreases by 1–2 kcal mol⁻¹ with increasing size of the aromatic rings that are formed after cycloreversion, i.e., benzene, naphthalene, and anthracene. This trend was also observed not only for the unsubstituted systems, **12a** and **10a**, but also for the diphenyl derivatives, **10b** and **11b**. By extrapolating this tendency, one can estimate the activation free energy of isomerization of the unknown Dewar anthracenophane **11a** to be 12–13 kcal mol⁻¹ ($\Delta H^\ddagger = 17$ kcal mol⁻¹, $\Delta S^\ddagger = -15$ cal deg⁻¹ mol⁻¹) at room temperature. This implies that **11a** would not be isolated (or hardly detected), even if it were formed, because of the fast cycloreversion to **2b**.

In summary, a new synthetic route to **1a**, **2a**, and their peri-substituted derivatives **1b**, **1c**, and **2b** was developed based on the benzoannulation method. The ¹H NMR spectral properties, X-ray crystallographic structure analysis, and semiempirical AM1 calculations indicate that the bridged aromatic rings of the peri-substituted derivatives are more distorted than those of the corresponding parent systems, **1a** and **2a**. Thermally reversible photochemical isomerization of **1b** and **2b** took place readily, giving the corresponding Dewar isomers, **10b** and **11b**.

Experimental

¹H and ¹³C NMR (270 and 67.5 MHz, respectively), IR, UV-vis, and mass spectra were taken with JEOL JNM-MH-270, Hitachi 260-10, Hitachi 220A, and JEOL JMS-DX-303-HF spectrometers, respectively. X-Ray diffraction data were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). GLC was conducted with a Shimadzu GC-14B gas chromatograph equipped with a CBP1 column. Analytical HPLC was carried out with a Shimadzu LC-10AS chromatograph equipped with a Inertsil ODS column, and preparative HPLC separations were performed with a JAILC-908 chromatograph equipped with JAIGEL 1H and 2H.

5,8-Dihydro-5,8-epoxy[6](1,4)naphthalenophanes (5a) and (6a). To a suspension of 472 mg (12.1 mmol) of sodium amide in 1.0 mL of THF was added dropwise 286 mg (3.86 mmol) of *t*-butyl alcohol in 0.7 mL of THF under a nitrogen atmosphere; the mixture was then heated at 40 °C for 2 h. After the mixture was cooled in an ice bath, a solution of bromocyclophane **4**⁷⁾ (128 mg, 0.536 mmol) in 0.96 mL (13 mmol) of furan and 0.5 mL of THF was added dropwise. The mixture was allowed to warm to room temperature and was then stirred for 1 h before being poured into ice-water. The mixture was extracted with ether:dichloromethane (2:1). The extract was washed with 10% HCl, dried (MgSO₄), and evaporated. The products were separated by flash chromatography on silica gel to afford 42 mg (35%) of **5a** and 7 mg (6%) of **6a**.

syn-5a: Colorless oil; ¹H NMR (CD₂Cl₂, -50 °C) $\delta = 7.05$ (1H, dd, $J = 5.6, 1.4$ Hz), 7.01 (1H, dd, $J = 5.6, 1.4$ Hz), 6.80 (1H,

d, $J = 8.4$ Hz), 6.75 (1H, d, $J = 8.4$ Hz), 5.79 (1H, br s), 5.72 (1H, br s), 3.03 (1H, dd, $J = 12.8, 5.8$ Hz), 2.71 (1H, dd, $J = 12.6, 5.9$ Hz), 2.35 (1H, dd, $J = 12.4, 5.5$ Hz), 2.04 (1H, dd, $J = 12.4, 5.5$ Hz), 1.5–1.8 (2H, m), 1.0–1.3 (2H, m), 0.81 (1H, tt, $J = 13.0, 6.5$ Hz), 0.67 (1H, tt, $J = 12.9, 6.3$ Hz), -0.4 to -0.1 (2H, m); ¹³C NMR (CD₂Cl₂, -40 °C) $\delta = 153.4$ (s), 149.3 (s), 142.7 (d), 142.3 (d), 137.1 (s), 136.7 (s), 132.6 (d), 127.7 (d), 80.8 (d), 80.6 (d), 35.1 (t), 33.5 (t), 33.4 (t), 33.3 (t), 26.5 (t), 24.8 (t); IR (neat) 1290, 1050, 1010, 870, 830, 760, 720 cm⁻¹; MS m/z (rel intensity) 226 (M⁺; 86), 141 (100). HRMS Calcd for C₁₆H₁₈O: M, 226.1358. Found: m/z 226.1367.

anti-6a: Colorless oil; ¹H NMR (CD₂Cl₂, -50 °C) $\delta = 7.03$ (1H, dd, $J = 5.4, 1.7$ Hz), 6.90 (1H, d, $J = 8.6$ Hz), 6.87 (1H, dd, $J = 5.4, 1.7$ Hz), 6.81 (1H, d, $J = 8.2$ Hz), 5.81 (1H, br s), 5.64 (1H, br s), 2.79 (1H, dd, $J = 11.6, 6.0$ Hz), 2.75 (1H, dd, $J = 12.1, 6.4$ Hz), 2.16 (1H, ddd, $J = 12.0, 12.0, 6.4$ Hz), 1.86 (1H, ddd, $J = 12.4, 12.4, 5.4$ Hz), 0.6–1.6 (5H, m), 0.1–0.3 (1H, m), -0.03 (1H, dt, $J = 14.6, 8.2$ Hz), -1.05 (1H, m); ¹³C NMR (CD₂Cl₂, -40 °C) $\delta = 151.5$ (s), 146.2 (s), 142.3 (d), 140.4 (d), 138.9 (s), 137.6 (s), 132.3 (d), 127.8 (d), 81.9 (d), 81.5 (d), 34.8 (t), 33.6 (t), 33.3 (t), 33.1 (t), 26.4 (t), 22.2 (t); IR (neat) 1280, 1020, 870, 850, 830, 740, 720 cm⁻¹; MS m/z (rel intensity) 226 (M⁺; 100). HRMS Calcd for C₁₆H₁₈O: M, 226.1358. Found: m/z 226.1373.

5,8-Dihydro-5,8-diphenyl-5,8-epoxy[6](1,4)naphthalenophane (5b). To a suspension of 1.00 g (8.88 mmol) of potassium *t*-butoxide in 2 mL of toluene was added a solution of 1.95 g (8.88 mmol) of 2,5-diphenylfuran¹¹⁾ in 5 mL of toluene followed by 354 mg (1.48 mmol) of bromocyclophane **4** in 3.5 mL of the same solvent. The mixture was heated at 120 °C for 45 h. The mixture was worked up as described above, except that the excess diphenylfuran was removed by sublimation prior to chromatography on silica gel to give 108 mg (19%) of **5b**. The corresponding anti isomer was not detected. Colorless solid, mp 214–219 °C (sealed tube); ¹H NMR (CD₂Cl₂, -80 °C) $\delta = 7.6$ –7.9 (4H, m), 7.2–7.6 (8H, m), 6.70 (1H, d, $J = 8.4$ Hz), 6.64 (1H, d, $J = 8.4$ Hz), 2.07 (1H, m), 1.83 (1H, m), 1.55 (1H, m), 1.11 (5H, m), 0.35 (2H, m), -0.41 (2H, m); ¹³C NMR (CD₂Cl₂, -80 °C) $\delta = 154.5$ (s), 149.6 (s), 147.4 (d), 146.0 (d), 137.1 (s), 137.0 (s), 136.3 (s), 136.0 (s), 133.0 (d), 128.6 (d), 128.5 (d), 128.1 (d), 127.9 (d), 127.8 (d), 127.3 (2C, d), 126.2 (d), 125.7 (d), 124.7 (d), 124.4 (d), 93.0 (s), 92.4 (s), 34.4 (t), 34.3 (t), 32.8 (t), 30.1 (t), 27.2 (t), 24.1 (t); UV $\lambda_{\max}$ (CHCl₃) 316 (log ϵ 2.87), 247 (4.22) nm; IR (KBr) 1310, 1020, 1010, 770, 760, 725, 695 cm⁻¹; MS m/z (rel intensity) 378 (M⁺; 79), 105 (100). HRMS Calcd for C₂₈H₂₆O: M, 378.1984. Found: m/z 378.1983.

5,8-Dihydro-5,8-dimethyl-5,8-epoxy[6](1,4)naphthalenophanes (5c) and (6c). The reaction of bromocyclophane **4** (160 mg, 0.669 mmol) and 0.712 mL (6.69 mmol) of 2,5-dimethylfuran was carried out as described for the reaction with furan using 390 mg (10.0 mmol) of sodium amide and 248 mg (3.35 mmol) of *t*-butyl alcohol in 3.1 mL of THF. The flash chromatography on silica gel afforded 48 mg (28%) of a mixture of **5c** and **6c** (3:4 by GLC), which were separated by preparative HPLC.

syn-5c: Colorless solid, mp 92–94 °C; ¹H NMR (CDCl₃, -50 °C) $\delta = 6.86$ (2H, s), 6.81 (1H, d, $J = 8.4$ Hz), 6.75 (1H, d, $J = 8.4$ Hz), 3.18 (1H, dd, $J = 12.2, 5.1$ Hz), 2.26 (2H, m), 2.07 (3H, s), 2.02 (1H, m), 1.96 (3H, s), 1.71 (2H, m), 1.24 (2H, m), 0.84 (1H, m), 0.71 (1H, m), -0.15 (1H, m), -0.39 (1H, m); ¹³C NMR (CDCl₃, -40 °C) $\delta = 154.3$ (s), 150.0 (s), 148.0 (d), 147.4 (d), 135.7 (s), 135.2 (s), 133.1 (d), 128.4 (d), 90.3 (s), 89.4 (s), 35.0 (t), 34.8 (t), 33.9 (t), 31.4 (t), 27.7 (t), 24.7 (t), 18.5 (q), 17.2 (q); UV $\lambda_{\max}$ (CHCl₃) 314 (log ϵ 2.46), 245 (4.11) nm; IR (KBr) 1300, 1155, 890, 865, 770, 740 cm⁻¹; MS m/z (rel intensity) 254 (M⁺;

99), 211 (100), 155 (75). HRMS Calcd for $C_{18}H_{22}O$: M, 254.1671. Found: m/z 254.1658.

anti-6c: Colorless solid, mp 79–83 °C; 1H NMR ($CDCl_3$, -50 °C) δ = 6.92 (1H, d, J = 8.1 Hz), 6.86 (1H, d, J = 5.2 Hz), 6.83 (1H, d, J = 8.1 Hz), 6.73 (1H, d, J = 5.2 Hz), 2.93 (1H, dd, J = 12.9, 5.9 Hz), 2.85 (1H, dd, J = 12.8, 5.8 Hz), 2.14 (1H, ddd, J = 11.8, 11.8, 5.9 Hz), 2.00 (3H, s), 1.96 (1H, m), 1.88 (3H, s), 1.54 (2H, m), 1.17 (1H, m), 0.82 (1H, m), 0.69 (1H, m), 0.27 (1H, m), 0.04 (1H, m), -0.92 (1H, m); ^{13}C NMR ($CDCl_3$, -40 °C) δ = 155.6 (s), 150.6 (s), 146.1 (d), 144.6 (d), 138.1 (s), 136.9 (s), 132.7 (d), 128.1 (d), 89.4 (s), 88.8 (s), 33.4 (t), 33.1 (t), 33.0 (t), 32.9 (t), 26.7 (t), 22.3 (t), 18.0 (q), 17.4 (q); UV λ_{max} ($CHCl_3$) 314 (log ϵ 2.32), 246 (3.80) nm; IR (KBr) 1280, 1130, 860, 770, 730 cm^{-1} ; MS m/z (rel intensity) 254 (M^+ ; 82), 211 (100), 155 (96). HRMS Calcd for $C_{18}H_{22}O$: M, 254.1671. Found: m/z 254.1691.

9,10-Dihydro-9,10-epoxy[6](1,4)anthracenophanes (7a) and (8a). To a suspension of the mixed base prepared from 835 mg (21.4 mmol) of sodium amide and 507 mg (6.84 mmol) of *t*-butyl alcohol in 3 mL of THF was added a solution of isobenzofuran¹² (ca. 4.8 mmol in ether–hexane), followed by a solution of 227 mg of bromocyclophane **4** in 0.9 mL of THF. The mixture was stirred at room temperature for 17 h and worked up as described for the preparation of **5a** and **5b** to give 55 mg (21%) of **7a** and 117 mg (45%) of **8a**.

syn-7a: Colorless solid, mp 142–145 °C; 1H NMR ($CDCl_3$, -50 °C) δ = 7.43 (2H, m), 7.10 (2H, m), 6.94 (1H, d, J = 8.6 Hz), 6.88 (1H, d, J = 8.2 Hz), 6.23 (1H, s), 6.15 (1H, s), 3.21 (1H, dd, J = 12.8, 5.2 Hz), 2.83 (1H, dd, J = 12.7, 5.7 Hz), 2.51 (1H, ddd, J = 12.4, 12.4, 5.5 Hz), 2.14 (1H, ddd, J = 12.5, 12.5, 5.6 Hz), 1.77 (2H, m), 1.32 (2H, m), 0.93 (1H, m), 0.73 (1H, m), -0.15 (2H, m); ^{13}C NMR ($CDCl_3$, -50 °C) δ = 152.8 (s), 148.4 (s), 147.6 (s), 147.4 (s), 136.2 (s), 135.9 (s), 133.5 (d), 128.8 (d), 125.9 (2C, d), 120.5 (d), 120.4 (d), 80.7 (d), 80.6 (d), 35.2 (t), 33.9 (t), 33.62 (t), 33.60 (t), 26.5 (t), 25.1 (t); UV λ_{max} ($CHCl_3$) 310 (log ϵ 2.53), 276 (3.77), 244 (4.30) nm; IR (KBr) 975, 830, 780, 760, 670 cm^{-1} ; MS m/z (rel intensity) 276 (M^+ ; 91), 69 (100). HRMS Calcd for $C_{20}H_{20}O$: M, 276.1514. Found: m/z 276.1537.

anti-8a: Colorless solid, mp 109–112 °C; 1H NMR ($CDCl_3$, -50 °C) δ = 7.3–7.5 (2H, m), 7.0–7.1 (2H, m), 6.99 (1H, d, J = 8.6 Hz), 6.89 (1H, d, J = 8.2 Hz), 6.31 (1H, s), 6.17 (1H, s), 2.88 (1H, dd, J = 12.8, 6.6 Hz), 2.83 (1H, dd, J = 12.5, 6.1 Hz), 2.25 (1H, ddd, J = 12.1, 12.1, 7.0 Hz), 2.07 (1H, ddd, J = 12.4, 12.4, 5.4 Hz), 1.43 (1H, m), 1.27 (1H, ddd, J = 14.6, 7.3, 7.3 Hz), 0.78 (1H, m), 0.53 (1H, m), 0.17 (1H, m), -0.14 (2H, m), -2.76 (1H, m); ^{13}C NMR ($CDCl_3$, -50 °C) δ = 150.1 (s), 147.7 (s), 146.4 (s), 145.2 (s), 139.3 (s), 137.1 (s), 132.8 (d), 128.1 (d), 125.5 (2C, d), 121.0 (d), 120.5 (d), 82.0 (d), 81.9 (d), 34.5 (t), 33.0 (t), 32.5 (t), 30.2 (t), 25.4 (t), 21.2 (t); UV λ_{max} ($CHCl_3$) 310 (log ϵ 2.56), 291 (2.94), 245 (4.32) nm; IR (KBr) 1195, 890, 845, 780, 750, 735, 680, 665 cm^{-1} ; MS m/z (rel intensity) 276 (M^+ ; 54), 119 (100). HRMS Calcd for $C_{20}H_{20}O$: M, 276.1514. Found: m/z 276.1523.

9, 10-Dihydro- 9, 10-diphenyl- 9, 10- epoxy[6](1, 4)anthracenophanes (7b) and (8b). The reaction of bromocyclophane **4** (231 mg, 0.967 mmol) and 392 mg (1.45 mmol) of 1,3-diphenylisobenzofuran was carried out as described for the reaction with isobenzofuran using 855 mg (21.8 mmol) of sodium amide and 516 mg (6.96 mmol) of *t*-butyl alcohol in 4.7 mL of THF. The products were separated by flash chromatography on silica gel to afford 124 mg (30%) of anti isomer **8b**. In another run, a small amount (3%) of syn isomer **7b** was obtained by careful chromatography of the recovered isobenzofuran fraction and subsequent preparative HPLC.

syn-7b: Colorless solid, mp 277–279 °C (sealed tube); 1H NMR (CD_2Cl_2 , -80 °C) δ = 8.11 (1H, d, J = 7.2 Hz), 7.97 (1H, d, J = 7.9 Hz), 7.92 (1H, d, J = 6.2 Hz), 7.79 (1H, d, J = 7.4 Hz), 7.59 (2H, m), 7.45 (6H, m), 7.00 (2H, m), 6.85 (1H, d, J = 8.2 Hz), 6.74 (1H, d, J = 8.2 Hz), 2.42 (1H, dd, J = 12.9, 4.9 Hz), 2.24 (1H, dd, J = 13.0, 5.1 Hz), 1.59 (2H, m), 1.08 (2H, m), 0.85 (2H, m), 0.34 (1H, m), 0.15 (1H, m), -0.55 (2H, m); ^{13}C NMR (CD_2Cl_2 , -80 °C) δ = 153.3 (s), 149.7 (s), 149.6 (s), 148.3 (s), 135.9 (s), 135.83 (s), 135.80 (s), 135.75 (s), 134.1 (d), 129.8 (d), 128.8 (d), 128.2 (d), 127.7 (d), 127.5 (d), 127.4 (d), 127.3 (2C, d), 127.0 (d), 125.4 (2C, d), 124.7 (d), 124.2 (d), 119.6 (d), 119.4 (d), 90.1 (s), 90.0 (s), 35.0 (t), 34.3 (t), 34.2 (t), 31.2 (t), 27.3 (t), 24.1 (t); UV λ_{max} ($CHCl_3$) 313 (log ϵ 2.66), 277 (3.95), 269 (4.01), 246 (4.32) nm; IR (KBr) 1310, 1000, 790, 745, 700, 680 cm^{-1} ; FAB MS m/z 429 (MH^+).

anti-8b: Colorless solid, mp 254–256 °C (sealed tube); 1H NMR (CD_2Cl_2 , -50 °C) δ = 7.9–8.1 (4H, m), 7.0–7.6 (12H, m), 2.74 (1H, dd, J = 12.7, 5.7 Hz), 2.63 (1H, dd, J = 12.7, 6.6 Hz), 2.21 (1H, ddd, J = 11.8, 11.8, 7.2 Hz), 1.89 (1H, ddd, J = 12.4, 12.4, 5.4 Hz), 1.31 (1H, m), 1.13 (1H, m), 0.76 (1H, m), 0.56 (1H, m), 0.18 (1H, m), -0.11 (2H, m) -0.28 (1H, m); ^{13}C NMR (CD_2Cl_2 , -50 °C) δ = 152.1 (s), 151.8 (s), 150.0 (s), 147.5 (s), 141.4 (s), 138.7 (s), 134.0 (s), 133.4 (s), 133.3 (d), 129.8 (2C, d), 129.7 (2C, d), 129.4 (d), 129.3 (d), 128.6 (d), 128.5 (2C, d), 128.4 (2C, d), 125.5 (d), 125.4 (d), 122.6 (d), 121.8 (d), 93.3 (s), 92.7 (s), 34.2 (t), 33.4 (t), 32.6 (t), 29.9 (t), 25.8 (t), 21.2 (t); UV λ_{max} ($CHCl_3$) 317 (log ϵ 2.42), 251 (3.84) nm; IR (KBr) 1310, 1300, 990, 975, 770, 750, 700 cm^{-1} ; FAB MS m/z 429 (MH^+). HRMS Calcd for $C_{32}H_{29}O$: M, 429.2218. Found: m/z 429.2214.

9,10-Dihydro-9,10-bis(trimethylsilyl)-9,10-epoxy[6](1,4)anthracenophane (8c). To an ice-cooled solution of 545 mg (3.81 mmol) of 2-methoxyphthalan and 82 mg (0.61 mmol) of tetramethylpiperidine in 3 mL of ether was added 7.3 mL (12.4 mmol) of a hexane solution of butyllithium; the solution was stirred at 0 °C for 3 h. After the solution was cooled to -78 °C, 304 mg (8.50 mmol) of chlorotrimethylsilane was added dropwise. The solution was warmed to 0 °C, and 303 mg (1.27 mmol) of bromocyclophane **4** was added followed by a solution of lithium tetramethylpiperidide (3.8 mmol) in ether–hexane. The mixture was stirred at room temperature for 20 h and worked up as described above to give 268 mg (50%) of **8c**. Colorless solid, mp 85–87 °C; 1H NMR ($CDCl_3$, -50 °C) δ = 7.30 (2H, m), 6.90 (2H, m), 6.87 (1H, d, J = 8.9 Hz), 6.76 (1H, d, J = 8.2 Hz), 2.92 (1H, dd, J = 12.5, 6.1 Hz), 2.74 (1H, dd, J = 11.4, 5.1 Hz), 2.17 (1H, ddd, J = 12.1, 12.1, 6.6 Hz), 2.01 (1H, ddd, J = 12.2, 12.2, 4.9 Hz), 1.36 (1H, m), 1.23 (1H, m), 0.80 (1H, m), 0.41 (1H, m), 0.36 (9H, s), 0.27 (9H, s), 0.21 (1H, m), -0.17 (2H, m), -2.81 (1H, m); ^{13}C NMR ($CDCl_3$, -50 °C) δ = 155.6 (s), 153.2 (s), 152.2 (s), 150.2 (s), 138.7 (s), 136.1 (s), 131.9 (d), 127.3 (d), 124.4 (d), 124.2 (d), 121.1 (d), 120.3 (d), 85.4 (s), 85.1 (s), 34.8 (t), 33.9 (t), 33.6 (t), 30.5 (t), 25.9 (t), 21.0 (t), -1.7 (q), -2.2 (q); IR (KBr) 1240, 765, 750 cm^{-1} ; MS m/z (rel intensity) 420 (M^+ ; 37), 73 (100). HRMS Calcd for $C_{26}H_{36}OSi_2$: M, 420.2305. Found: m/z 420.2297.

To a solution of 68 mg (1.2 mmol) of potassium hydroxide in 1.7 mL of DMSO was added 200 mg (0.476 mmol) of **8c** in 1 mL of THF. The solution was stirred at room temperature for 10 min before saturated aqueous solution of sodium chloride was added. The mixture was extracted with dichloromethane and the extract was dried (K_2CO_3) and evaporated. The products were separated by flash chromatography on silica gel to afford 116 mg (88%) of **8a**.

Reductive Deoxygenation of Dihydroepoxynaphthalenophanes 5a and 5b. Titanium(IV) chloride (556 mg, 2.98

mmol) was added to 4.5 mL of THF cooled in an ice bath followed by addition of 43 mg (1.1 mmol) of lithium aluminum hydride in two portions. To the resulting black suspension 46 mg (0.46 mmol) of triethylamine was added dropwise and the mixture was heated at 65 °C for 5 min. After the mixture was allowed to cool to room temperature, a solution of 83 mg (0.367 mmol) of a mixture of **5a** and **5b** in 2.3 mL of THF was added dropwise. After 2 h, the reaction was quenched by the addition of 30 mL of a 20% potassium carbonate solution. The mixture was filtered and the filtrate was extracted with ether. The extract was washed with saturated sodium chloride solution and dried (MgSO₄). Removal of the solvent followed by flash chromatography furnished 40 mg (52%) of **1a**.

9,10-Dimethyl[6](1,4)naphthalenophane (1c). Deoxygenation of 100 mg (0.394 mmol) of a mixture of **5c** and **6c** was carried out as described above using 1.06 g (5.56 mmol) of titanium(IV) chloride, 83 mg (2.2 mmol) of lithium aluminum hydride, and 2.19 g (21.7 mmol) of triethylamine in 11 mL of THF to give 56 mg (60%) of **1c**. Colorless solid, mp 69–72 °C; ¹H NMR (CD₂Cl₂, –85 °C) δ = 7.40 (1H, d, *J* = 7.4 Hz), 7.27 (1H, d, *J* = 7.4 Hz), 7.13 (1H, d, *J* = 7.5 Hz), 7.09 (1H, d, *J* = 7.4 Hz), 3.50 (1H, dd, *J* = 12.1, 4.0 Hz), 2.97 (1H, dd, *J* = 12.9, 6.2 Hz), 2.63 (3H, s), 2.57 (3H, s), 2.54 (1H, m), 2.19 (1H, ddd, *J* = 12.8, 12.8, 4.9 Hz), 1.56 (2H, m), 1.16 (1H, m), 0.66 (2H, m), 0.10 (1H, m), –0.36 (1H, m), –1.87 (1H, m); ¹³C NMR (CD₂Cl₂, –85 °C) δ = 142.4 (s), 139.7 (s), 139.2 (s), 133.5 (s), 132.8 (d), 130.5 (s), 129.6 (s), 128.7 (d), 127.4 (d), 127.2 (d), 38.0 (t), 36.7 (t), 34.9 (t), 32.0 (t), 27.8 (t), 23.8 (t), 23.8 (q), 23.7 (q); UV λ_{max} (cyclohexane) 324 (log ε 3.82), 252 (4.60) nm; IR (KBr) 930, 815, 795 cm^{–1}; MS *m/z* (rel intensity) 238 (M⁺; 93), 223 (100). HRMS Calcd for C₁₈H₂₂: M, 238.1721. Found: *m/z* 238.1708.

9,10-Diphenyl[6](1,4)naphthalenophane (1b). Deoxygenation of 77 mg (0.20 mmol) of **5b** was carried out as described above using 547 mg (2.88 mmol) of titanium(IV) chloride, 43 mg (1.1 mmol) of lithium aluminum hydride, and 1.14 g (11.3 mmol) of triethylamine in 5.6 mL of THF to give 64 mg (87%) of **1b**. Colorless solid, mp 176–177 °C; ¹H NMR (CD₂Cl₂, –80 °C) δ = 7.2–7.8 (14H, m), 2.50 (1H, dd, *J* = 12.4, 4.7 Hz), 2.11 (1H, br d, *J* = 9.6 Hz), 1.84 (1H, m), 1.71 (1H, m), 1.34 (1H, m), 1.20 (1H, m), 1.06 (1H, m), 0.63 (2H, m), –0.02 (1H, m), –0.51 (1H, m), –1.89 (1H, m); ¹³C NMR (CD₂Cl₂, –80 °C) δ = 143.4 (s), 143.2 (s), 142.9 (s), 139.6 (s), 139.3 (s), 138.1 (s), 137.0 (s), 134.2 (s), 133.8 (d), 129.8 (d), 128.8 (d, 2C), 128.7 (d, 2C), 127.79 (d), 127.76 (d), 127.64 (d), 127.62 (d), 127.3 (d), 127.2 (d), 126.6 (d, 2C), 38.0 (t), 36.4 (t, 2C), 31.9 (t), 27.4 (t), 24.0 (t); UV λ_{max} (cyclohexane) 342 (log ε 3.65), 256 (4.06), 220 (4.15), 210 (4.15) nm; IR (KBr) 845, 760, 710 cm^{–1}; MS *m/z* (rel intensity) 362 (M⁺; 0.1), 220 (100). Found: C, 92.51; H, 7.23%. Calcd for C₂₈H₂₆: C, 92.77; H, 7.23%.

Reductive Deoxygenation of Dihydroepoxyanthracenophanes 7a and 8a. Deoxygenation of 50 mg (0.18 mmol) of a mixture of **7a** and **8a** was carried out as described above using 247 mg (1.30 mmol) of titanium(IV) chloride, 19 mg (0.50 mmol) of lithium aluminum hydride, and 20 mg (0.20 mmol) of triethylamine in 3 mL of THF to give 64 mg (87%) of **2a**.

9,10-Diphenyl[6](1,4)anthracenophane (2b). Deoxygenation of 100 mg (0.234 mmol) of **8b** was carried out as described above using 623 mg (3.28 mmol) of titanium(IV) chloride, 50 mg (1.3 mmol) of lithium aluminum hydride, and 1.31 g (12.9 mmol) of triethylamine in 6.6 mL of THF to give 57 mg (59%) of **2b**. Yellow solid, mp 194–196 °C; ¹H NMR (CD₂Cl₂, –80 °C) δ = 7.93 (1H, d, *J* = 6.5 Hz), 7.77 (1H, br d, *J* = 8.2 Hz), 7.0–7.7 (12H, m), 7.23 (1H, d, *J* = 7.3 Hz), 7.10 (1H, d, *J* = 7.3 Hz), 2.25 (1H, dd, *J* = 12.6,

7.8 Hz), 1.68 (3H, m), 1.36 (1H, m), 1.17 (2H, m), 0.61 (2H, m), 0.17 (1H, m), –0.29 (1H, m), –1.60 (1H, m); ¹³C NMR (CD₂Cl₂, –80 °C) δ = 143.5 (s), 141.3 (s), 141.0 (s), 139.4 (s), 139.0 (s), 134.4 (s), 133.4 (s), 133.5 (s), 132.8 (d), 131.2 (d), 131.0 (d), 130.1 (d), 129.8 (d), 129.4 (d), 129.0 (s), 128.85 (d), 128.83 (s), 128.7 (d), 127.6 (d), 127.2 (d), 126.8 (d), 126.6 (d), 126.1 (d), 125.6 (d), 124.8 (d), 124.6 (d), 37.8 (t), 36.7 (t), 34.8 (t), 31.4 (t), 28.0 (t), 23.7 (t); UV-vis λ_{max} (cyclohexane) 403 (log ε 4.05), 273 (4.93) 219 (4.76) nm; IR (KBr) 765, 750, 700 cm^{–1}; MS *m/z* (rel intensity) 412 (M⁺; 14), 109 (100). HRMS Calcd for C₃₂H₂₈: M, 412.2191. Found: *m/z* 412.2198.

Photochemical Valence Isomerization of Naphthalenophane 1b and Anthracenophane 2b. A solution of 5 mg of **1b** or 10 mg of **2b** in benzene-*d*₆ and CD₂Cl₂ (9 : 1) in an NMR tube was irradiated through a uranium glass filter (λ > 350 nm) with a 300 W high-pressure mercury lamp at 0 °C until the NMR measurement indicated the disappearance of the starting material.

10b: ¹H NMR (C₆D₆ : CD₂Cl₂ = 9 : 1, –80 °C) δ = 7.60 (4H, dt, *J* = 6.9, 1.2 Hz), 7.40 (2H, s), 7.31 (4H, tt, *J* = 7.4, 1.2 Hz), 7.2 (m, concealed in the solvent peak), 6.78 (2H, s), 2.34 (2H, ddd, *J* = 15.3, 4.7, 3.5 Hz), 1.99 (2H, ddd, *J* = 11.9, 11.9, 3.7 Hz), 1.25 (2H, m), 1.10 (4H, m), 0.92 (2H, m); ¹³C NMR (C₆D₆ : CD₂Cl₂ = 9 : 1, 0 °C) δ = 148.8 (s), 146.1 (d), 139.1 (s), 135.8 (s), 129.0 (d), 128.3 (d), 127.5 (d), 125.9 (d), 65.1 (s), 26.9 (t), 25.8 (t), 25.4 (t).

11b: ¹H NMR (C₆D₆ : CD₂Cl₂ = 9 : 1, 0 °C) δ = 8.17 (2H, m), 7.53 (2H, br d, *J* = 7.0 Hz), 7.2–7.4 (10H, m), 6.69 (2H, s), 1.9–2.1 (4H, m), 1.1–1.6 (8H, br m); ¹³C NMR (C₆D₆ : CD₂Cl₂ = 9 : 1, 0 °C) δ = 146.4 (s), 145.9 (d), 138.2 (s), 133.5 (s), 132.7 (s), 130.4 (d), 128.6 (d), 127.5 (d), 126.4 (d), 125.4 (d), 65.2 (s), 26.5 (t), 26.0 (t), 25.5 (t).

Thermal Cycloreversion of Dewar Naphthalenophane 10b and Dewar Anthracenophane 11b. A solution of **10b** and 9,10-dibromoanthracene (internal standard) in toluene was placed in a thermocontrolled bath in the dark. Aliquots of the solution were taken and analyzed by HPLC to determine the rate of cycloreversion. A solution of **11b** in cyclohexane was placed in a thermocontrolled cell holder. The progress of the cycloreversion was followed by measuring the increase of absorption at 403 nm by a spectrometer. The kinetic results are summarized in Table 4.

Crystal Data for X-Ray Crystallography of 1b. C₂₈H₂₆, MW = 362.51, monoclinic, space group *P*2₁/*a*, *a* = 11.991(1), *b* = 12.062(2), *c* = 14.638(1) Å, β = 106.012(7)°, *V* = 2035.0(4) Å³, *Z* = 4, *d*_{calcd} = 1.183 g cm^{–3}, *R* = 0.051 (*R*_w = 0.035) and GOF = 3.52 for 2619 observed reflection (*I* > 3.00σ(*I*)).²⁰⁾

References

- For recent reviews see: a) F. Bickelhaupt and W. H. de Wolf, *Recl. Trav. Chim. Pays-Bas*, **107**, 459 (1988); b) F. Bickelhaupt, *Pure Appl. Chem.*, **62**, 373 (1990); c) W. H. de Wolf and F. Bickelhaupt, in "Advances in Strain in Organic Chemistry," ed by B. Halton, JAI Press, Greenwich (1993), Vol. 3, p. 185; d) V. V. Kane, W. H. de Wolf, and F. Bickelhaupt, *Tetrahedron*, **50**, 4575 (1994); e) Y. Tobe, in "Topics in Current Chemistry," ed by E. Weber, Springer, Heidelberg (1994), Vol. 172, p. 1.
- J. A. Reiss, in "Cyclophanes," ed by P. M. Kheen and S. M. Rosenfeld, Academic Press, New York (1983), Vol. 2, p. 443.
- [7](1,4)Naphthalenophane derivatives were the smallest-bridged naphthalenophanes reported: J. Hunger, C. Wolff, W. Tochtermann, E.-M. Peters, K. Peters, and H. G. von Schnering, *Chem. Ber.*, **119**, 2698 (1986).
- a) Y. Tobe, T. Takahashi, T. Ishikawa, Y. Yoshimura, M.

- Suwa, K. Kobiro, K. Kakiuchi, and R. Gleiter, *J. Am. Chem. Soc.*, **112**, 8889 (1990); b) Y. Tobe, T. Takahashi, K. Kobiro, and K. Kakiuchi, *Chem. Lett.*, **1990**, 1587; c) Y. Tobe, T. Takahashi, K. Kobiro, and K. Kakiuchi, *J. Am. Chem. Soc.*, **113**, 5804 (1991); d) Y. Tobe, A. Takemura, M. Jimbo, T. Takahashi, K. Kobiro, and K. Kakiuchi, *J. Am. Chem. Soc.*, **114**, 3479 (1992).
- 5) D. S. van Es, F. J. J. de Kanter, W. H. de Wolf, and F. Bickelhaupt, *Angew. Chem., Int. Ed. Engl.*, **34**, 2553 (1995).
- 6) a) Y. Tobe, H. Ishii, S. Saiki, K. Kakiuchi, and K. Naemura, *J. Am. Chem. Soc.*, **115**, 11604 (1993); b) Y. Tobe, N. Utsumi, S. Saiki, and K. Naemura, *J. Org. Chem.*, **59**, 5516 (1994); c) Y. Tobe, S. Saiki, N. Utsumi, T. Kusumoto, H. Ishii, K. Kakiuchi, K. Kobiro, and K. Naemura, *J. Am. Chem. Soc.*, **118**, 9488 (1996).
- 7) Y. Tobe, M. Jimbo, H. Ishii, S. Saiki, K. Kakiuchi, and K. Naemura, *Tetrahedron Lett.*, **34**, 4969 (1993).
- 8) a) H. Hart, C. Lai, G. Nwokogu, S. Shamouilian, A. Teuerstein, and C. Zlotogorski, *J. Am. Chem. Soc.*, **102**, 6651 (1980); b) F. Raymo, F. H. Kohnke, F. Cardullo, U. Girreser, and J. F. Stoddart, *Tetrahedron*, **48**, 6827 (1992).
- 9) For preliminary report of this work see: Y. Tobe, S. Saiki, and K. Naemura, *Tetrahedron Lett.*, **36**, 939 (1995).
- 10) a) J.-P. Bachelet and P. Caubere, *J. Org. Chem.*, **47**, 234 (1982); b) J.-P. Bachelet and P. Caubere, *Acc. Chem. Res.*, **7**, 301 (1974).
- 11) G. Nowlin, *J. Am. Chem. Soc.*, **72**, 5754 (1950).
- 12) K. Naito and B. Rickborn, *J. Org. Chem.*, **45**, 4061 (1980).
- 13) S. L. Crump, J. Netka, and B. Rickborn, *J. Org. Chem.*, **50**, 2746 (1985).
- 14) a) V. V. Kane, A. D. Wolf, and M. Jones, Jr., *J. Am. Chem. Soc.*, **96**, 2643 (1974); b) S. L. Kammula, L. D. Iroff, M. Jones, Jr., J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, *J. Am. Chem. Soc.*, **99**, 5815 (1977); c) Y. Tobe, K.-I. Ueda, K. Kakiuchi, Y. Odaira, Y. Kai, and N. Kasai, *Tetrahedron*, **42**, 1851 (1986).
- 15) a) Y. D. Xing and N. Z. Huang, *J. Org. Chem.*, **47**, 140 (1982); b) H. N. C. Wong, *Acc. Chem. Res.*, **22**, 145 (1989).
- 16) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985). "MOPAC Ver. 6.00 (QCPE No. 445)," J. J. P. Stewart, *QCPE Bull.*, **10**, 86 (1990); T. Hirano, *JCPE Newsletter*, **2**, 39 (1991); revised as Ver. 6.02 by J. Toyoda for Apple Macintosh personal computers.
- 17) For more recent reports on the valence isomerization of [6]-paracyclophanes see: a) S. Miki, R. Shimizu, and H. Nakatsuji, *Tetrahedron Lett.*, **33**, 953 (1992); b) R. Gleiter and B. Treptow, *J. Org. Chem.*, **58**, 7740 (1993); c) I. Frank, S. Grimme, and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, **116**, 5949 (1994); d) H. Dreeskamp, S. M. Sarge, and W. Tochtermann, *Tetrahedron Lett.*, **51**, 3137 (1995).
- 18) a) E. J. Bowen, in "Advances in Photochemistry," ed by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Wiley Interscience, New York (1963), Vol. 1, p. 32; b) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).
- 19) Y. Tobe, A. Nakayama, K. Kakiuchi, Y. Odaira, Y. Kai, and N. Kasai, *J. Org. Chem.*, **52**, 2639 (1987).
- 20) Tables of fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and interatomic bond distances and angles for **1b** are deposited as Document No. 70025 at the Office of Editor of Bull. Chem. Soc. Jpn.