Synthesis, Characterization, and Molecular Structure of [6](9,10)Anthracenophane and Its Peri-Substituted Derivatives: The Smallest 9,10-Bridged Anthracenes

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Abstract: [6](9,10)Anthracenophane (**1a**) was synthesized by the benzoannelation method starting from dibromo-[6]paracyclophane **6** via diepoxyanthracenophanes **3a** and **4a**. In a similar fashion, peri-substituted derivatives, tetramethyl (**1b**) and tetraphenyl (**1c**), were synthesized through the corresponding diepoxyanthracenes **3b**, **4b**, and **3c**. Molecular structures of tetramethyldiepoxyanthracenophanes **3b** and **5b** are discussed with regard to the Mills−Nixon effect on the basis of their X-ray structure analyses. The parent anthracenophane **1a** is extremely air- and acid-sensitive, so it is characterized spectroscopically as a mixture containing its dihydro derivative **8a**. The peri-substituted derivatives **1b** and **1c** are more stable than **1a**, and are fully characterized by spectroscopic methods and X-ray crystallographic analyses. X-ray structures reveal that the out-of-plane deformation angles of the bridged aromatic ring of **1b** and **1c** are the largest observed in any short-bridged [*n*]cyclophanes. Semiempirical AM1 calculations indicate that the out-of-plane deformation of the aromatic rings **1b** and **1c** is more severe than that of **1a** due to the steric repulsion between the benzylic methylenes and the peri substituents. That the kinetic stability observed for **1b** and **1c** was greater than that of **1a** is, therefore, ascribable to the steric protection of the reactive bridgehead carbons by the peri substituents. Acid-catalyzed rearrangement of **1a−c** gave the corresponding methylenedihydro isomers **2a−c**, which represent the first examples of bridged methylenedihydroanthracenes. Photochemical isomerization of **1b** and **1c** took place readily, giving the corresponding Dewar anthracenes **11b** and **11c**. Thermal cycloreversion of **11b** and **11c** gave the cyclophanes **1b** and **1c** with E_a values of 22.3 and 25.4 kcal/mol, respectively.

Introduction

The chemistry of short-bridged [*n*]cyclophanes has attracted much interest in recent years because the lower limit of their existence has been explored successfully and their extraordinary structures and properties have been unveiled.[1] The smallest isolable representative among the series of [*n*]paracyclophanes has been [6]paracyclophane,[2] whereas the lower homologues, [5]- and [4]paracyclophanes, were characterized by spectroscopic and chemical methods.[3] By contrast, little has been learned about condensed benzenoid cyclophanes, despite the fact that the aromatic character of such a system would be more sensitive to strain imposed by the short bridge.[1d,4] We synthesized the smallest isolable 1,4-bridged [6]naphthale-

nophane and [6]anthracenophane and investigated their structures and unusual reactivities.[5] Recently, the lower homologue in the naphthalene series, a [5](1,4)naphthalenophane derivative, was characterized below room temperature by Bickelhaupt.[6] It appears, therefore, that the kinetic stabilities of 1,4-bridged [*n*]-naphthaleno- and anthracenophanes are similar to those of the corresponding [*n*]paracyclophanes. However, in view of the enhanced reactivity of the 9,10-positions of the anthracene ring relative to that of the 1,4-positions, the kinetic stability of 9,10-bridged [*n*]anthracenophane must be substantially diminished. Indeed, the smallest known [8]anthracenophanes, the 2,7-diketo,[7] 3,6-diketo,[8] and 2,7-dithia[9] compounds, are sensitive to air oxidation, although the bridged aromatic ring of these com-

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(1) For recent reviews see: (a) Bickelhaupt, F.; de Wolf, W. H. *Recl. Trav. Chim. Pays-Bas* **1988,** *107,* 459. (b) Bickelhaupt, F.; de Wolf, W. H. In *Advances in Strain in Organic Chemistry;* Halton, B., Ed.; JAI Press: Greenwich, CT, 1993; Vol. 3, p 185. (c) Kane, de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1994,** *50,* 4575. (d) Tobe Y. In *Topics in Current Chemistry;* Weber, E., Ed.; Springer: Heidelberg, 1994; Vol. 172, p 1.

(2) (a) Kane V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974,** *96,* 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977,** *99,* 5815. (c) Tobe, Y.; Ueda, K. -I.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron* **1986,** *42,* 1851.

(3) For [5]paracyclophane see: (a) Jenneskens, L. W.; de Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; de Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985,** *107,* 3716. For [4]paracyclophane: (b) Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1987,** 1189; (c) *J. Am. Chem. Soc.* **1988,** *110,* 2157. (d) Kostermans, G. B. M.; Bobeldijk, M.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1987,** *109,* 2471.

(4) Reiss, J. A. In *Cyclophanes;* Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. 2, p 443.

(5) (a) Tobe, Y.; Takahashi, T.; Ishikawa, T.; Yoshimura, M.; Suwa, M.; Kobiro, K.; Kakiuchi, K.; Gleiter, R. *J. Am. Chem. Soc.* **1990,** *112,* 8889. (b) Tobe, Y.; Takahashi, T.; Kobiro, K.; Kakiuchi, K. *Ibid.* **1991,** *113,* 5804. (c) Tobe, Y.; Takemura, A.; Jimbo, M.; Takahashi, T.; Kobiro, K.; Kakiuchi, K. *Ibid.* **1992,** *114,* 3479.

(6) van Es, D. S.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 2553.

(7) Ohta, M.; Tamura, S.; Okajima, T.; Fukazawa Y. 63rd Annual Meeting of the Chemical Society of Japan, March 28−31, 1992; Abstract No. 3B234.

pounds is only slightly deformed from planarity.[9d] Moreover, there exists another threat to the stability of the 9,10-bridged anthracenes; the isomerization to methylenedihydro (isotoluene) type tautomers. Rosenfeld observed such isomerization of dithia[n](9,10)anthracenophanes with $n = 8-12$ under basic conditions,[9c] and predicted difficulties in synthesizing smaller [n](9,10)anthracenophanes with $n \leq 7$ on the basis of MMX and AM1 calculations.[10] Specifically, the methylenedihydroanthracene isomer becomes substantially more favorable in the thermodynamic sense than the anthracenophane structure as the bridge becomes smaller than $n = 7$. In light of these considerations, we focused our attention on the [6](9,10)-anthracenophane system as the next synthetic challenge. We report here the synthesis and characterization of the smallest known example of 9,10-bridged anthracene, extremely air- and acid-sensitive [6](9,10)anthracenophane (**1a**).[11a] Moreover, we describe the syntheses, structure determination, and isomerization reactions of its kinetically stabilized derivatives **1b** and **1c** bearing methyl or phenyl groups at the four peri positions, respectively.[11b] We also report the first isolation of bridged methylenedihydroanthracenes **2a−c**, isotoluene type tautomers of the respective anthracenophanes **1a−c**.

1a R=H
1b R=Me
1c R=Ph

2a R=H
2b R=Me
2c R=Ph
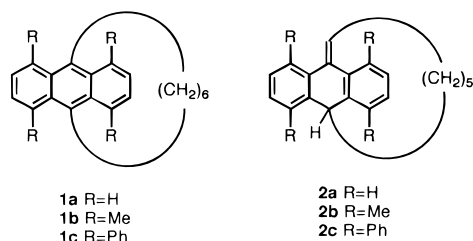
Results and Discussion

Syntheses. Because of the expected sensitivity of the central ring of the small (9,10)anthracenophanes, we thought it would be difficult to synthesize [6]anthracenophane **1a** by introducing the cyclophane structure of the central ring in the last stage of the synthesis. We planned instead to start from a molecule already having the [6]paracyclophane substructure and to construct thereon the anthracene ring using bis-benzoannelation.[12] For the same reason, we also planned to prepare the tetramethyl and tetraphenyl peri-substituted derivatives **1b** and **1c** in hope that the substituents would sterically protect the reactive central ring of the anthracene core. Retrosynthetic analysis revealed that 8,11-dibromo[6]paracyclophane (**6**)[13] serves as the benzyne source to which 2-fold addition of furan derivatives gives the diepoxyanthracenophanes **3a−5a** and their peri-substituted derivatives **3b−5b** and **3c−5c**, from which reductive deoxygenation furnishes the corresponding anthracenophanes **1a−c** without touching the sensitive central ring.

(8) (a) Helder, R. Ph.D. Thesis, Rijksuniversiteit te Groningen, 1974. (b) Rosenfeld, S. M.; Sanford, E. M. *Tetrahedron Lett.* **1987**, *28*, 4775.

(9) (a) Chung, J.; Rosenfeld, S. *J. Org. Chem.* **1983**, *48*, 387. (b) Rosenfeld, S.; Shedlow, A. M.; Kirwin, J. M.; Amaral, C. A. *Ibid.* **1990**, *55*, 1356. (c) Rosenfeld, S.; Sheldow, A. *Ibid.* **1991**, *56*, 2247. (d) Rosenfeld, S.; Cheer, C. L. *Acta Crystallogr.* **1992**, *C48*, 311.

(10) Rosenfeld, S. *J. Org. Chem.* **1993**, *58*, 7572.

(11) For preliminary reports of this work see: (a) Tobe, Y.; Ishii, H.; Saiki, S.; Kakiuchi, K.; Naemura, K. *J. Am. Chem. Soc.* **1993**, *115*, 11604. (b) Tobe, Y.; Utsumi, N.; Saiki, S.; Naemura, K. *J. Org. Chem.* **1994**, *59*, 5516.

(12) For bis-annelation of arenes using bis-aryne equivalents see: (a) Hart, H.; Lai, C.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6651. (b) Raymo, F.; Kohnke, F. H.; Cardullo, F.; Girreser, U.; Stoddart, J. F. *Tetrahedron* **1992**, *48*, 6827.

(13) Tobe, Y.; Jimbo, M.; Ishii, H.; Saiki, S.; Kakiuchi, K.; Naemura, K. *Tetrahedron Lett.* **1993**, *34*, 4969.

Scheme 1

3a R=H (*syn,syn*)
3b R=Me (*syn,syn*)
3c R=Ph (*syn,syn*)

4a R=H (*syn,anti*)
4b R=Me (*syn,anti*)
4c R=Ph (*syn,anti*)

5a R=H (*anti,anti*)
5b R=Me (*anti,anti*)
5c R=Ph (*anti,anti*)
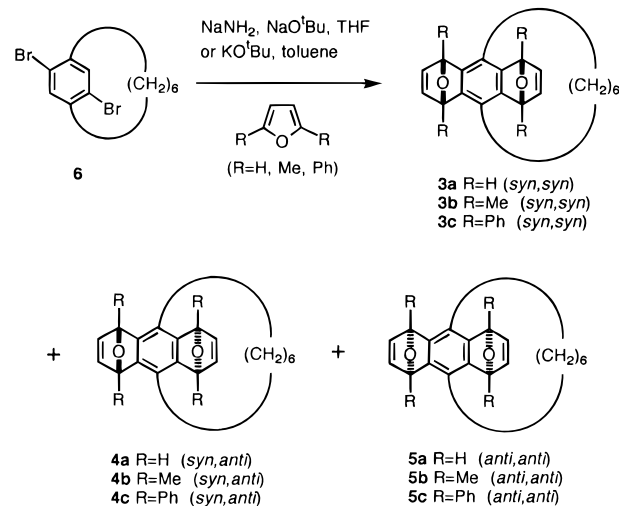
When dibromocyclophane **6** was treated with a large excess of the mixed base NaNH$_2$/NaO^{t}Bu[14] in the presence of excess furan at room temperature, three isomers of [4 + 2] cycloadducts **3a**, **4a**, and **5a** were obtained in 17, 10, and 5% yields, respectively (Scheme 1). Similarly, reaction of **6** in the presence of 2,5-dimethylfuran afforded the tetramethyl derivatives **3b**, **4b**, and **5b** in 12, 47, and 28% yields, respectively. However, similar reaction of **6** with 2,5-diphenylfuran did not give the corresponding [4+2] adducts, presumably because of the low reactivity of the furan toward cycloaddition with the benzyne intermediates. The reaction was therefore undertaken in refluxing toluene using KO^{t}Bu as the base to yield adducts **3c** and **4c** in 9 and 8% yields, respectively. The corresponding *anti,anti* adduct **5c** was not detected in this case. The stereochemical assignments for the less symmetrical *syn,anti* isomers **4a−c** were readily made on the basis of the NMR spectra. The structures of *syn,syn* and *anti,anti* tetramethyl derivatives **3b** and **5b** were unambiguously determined by the X-ray crystal structure analyses (Figure 1). The structural details are discussed in the next section. The stereochemistries of the other products were deduced on the basis of the ^{1}H NMR chemical shifts of the bridge methylene protons Hb, Hd, and Hf. In the case of *syn,syn* isomers **3a−c**, these protons are expected to suffer from steric compression by the fused oxanorbornadiene units. Table 1 shows the ^{1}H NMR chemical shifts of the methylene protons (Ha−Hf) of **3a−c**, **4a−c**, and **5a,b** and their reference compound **7**[2] measured at −50 °C. At this temperature, the flipping of the methylene bridge is frozen on the NMR time scale.[15] The protons Hf of *syn,syn* isomers **3a−c** are shifted downfield from that of [6]paracyclophane (**7**) by more

3a-5a R=H
3b-5b R=Me
3c-4c R=Ph

7
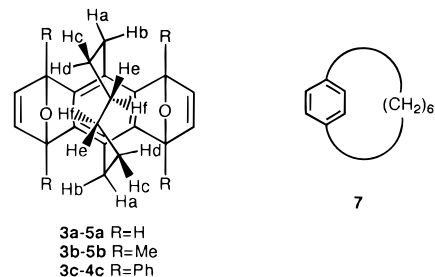
(14) (a) Bachelet, J. -P.; Caubere, P. *J. Org. Chem.* **1982**, *47*, 234. (b) Bachelet, J. -P.; Caubere, P. *Acc. Chem. Res.* **1974**, *7*, 301.

(15) The barriers for the flipping of the methylene bridge of **3a−c**, **4a−c**, and **5a,b** are listed in Table S17 of the supporting information.
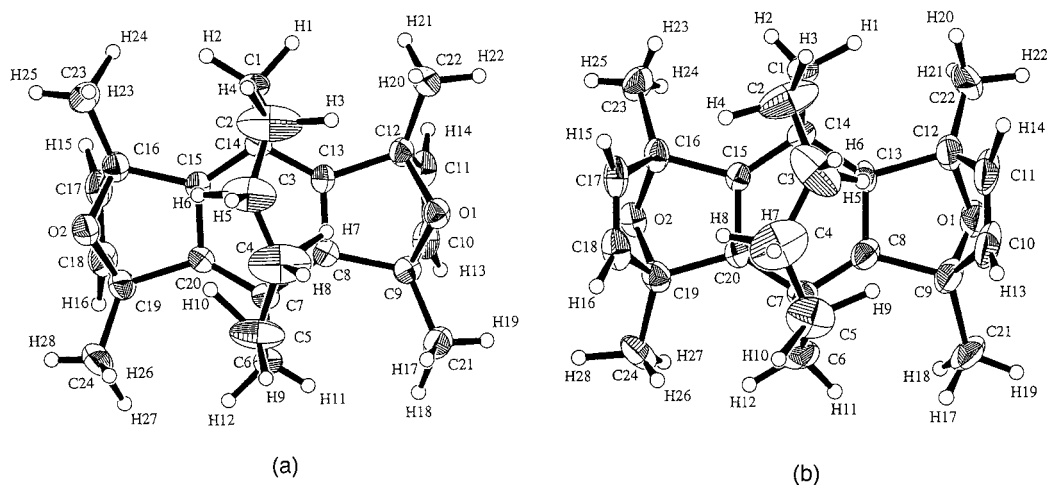
Figure 1. X-ray structures of (a) *syn,syn*-diepoxy[6](9,10)anthracenophane **3b** and (b) *anti,anti*-diepoxy[6](9,10)anthracenophane **5b**.

Table 1. ^{1}H NMR Chemical Shifts of Diepoxyanthracenophanes **3a−5a**, **3b−5b**, **3c**, and **4c**, and [6]Paracyclophane (**7**)[a]

compd	Ha	Hb	Hc	Hd	He	Hf
3a[b]	2.94	2.38	1.66	0.87	1.20	−0.01
4a	3.09, 2.76	2.56, 1.97	1.62 (2H)	0.96, 0.31	1.21, 0.96	0.31, −0.67
5a	2.87	2.08	1.43	0.22	0.85	−0.48
3b	2.98	2.62	1.75	0.88	1.35	−0.07
4b	3.09, 2.7	2.7, 1.9	1.59 (2H)	0.90, 0.21	1.23, 0.90	0.35, −0.63
5b[b,c]	2.83	1.98	1.32	0.15	0.82	−0.49
3c[d]	1.73	1.39	1.39	0.77	1.12	0.35
4c[d]	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]	0.35, −0.24
7[f]	2.79	1.97	1.58	0.51	1.06	−0.62

[a] Measured in CDCl$_3$ at −50 °C unless otherwise stated. [b] Measured in CD$_2$Cl$_2$. [c] Measured at −80 °C. [d] Measured in toluene-d_8. [e] Not determined because of ill separation of the signals. [f] Reference 5a.

than 0.5 ppm due to steric compression by the oxygen atoms.[16] Similarly, Hd protons of **3a** and **3b** are shifted downfield by about 0.35 ppm for the same reason. Moreover, the benzylic protons Hb of **3a** and **3b** are observed at a lower field than that of **7** by 0.41 and 0.65 ppm, respectively, because of the steric compression by the bridgehead hydrogen (for **3a**) and the methyl group (for **3b**). By contrast, such apparent shift is not observed for the methylene protons of *anti,anti* isomers **5a,b**; the chemical shifts of **5a,b** are similar to those of the corresponding protons of **7**. The small (0.2−0.3 ppm) upfield shifts of Hd and He can be ascribed to the shielding effect[16] exerted by the double bond of the oxanorbornadiene units. Half of the methylene protons of *syn,anti* isomers **4a** and **4b** are shifted downfield, while the chemical shifts of the other half are similar to those of *anti,anti* isomers **5a,b**, in accord with the above assignments. The relative yields of the furan adducts seem to be dependent on the steric effect of the peri substituents; the more sterically crowded the substituents are, the more *anti* isomers are formed. The reason for the absence of *anti,anti* isomer **5c** is not clear, however.

After screening several reagents for the reductive deoxygenation using tetramethyl derivatives **3b−5b**, we found that low-valent titanium reagents were most effective. Thus, treatment of a mixture of **3b−5b** with the titanium reagents prepared from TiCl$_4$, LiAlH$_4$, and triethylamine (TEA) (7:2.5:25)[17] furnished anthracenophane **1b** (yellow solid; mp 161−162 °C) in 68% yield. The use of a large excess of TEA was essential; otherwise variable amounts of methylenedihydro isomer **2b** and the dihydro derivative **8b** were formed (Scheme 2). Anthra-

(16) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,* 2nd ed.; Pergamon Press: Oxford, 1969.
(17) (a) Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140. (b) Wong, H. N. C. *Acc. Chem. Res.* **1989**, *22*, 145.

Scheme 2
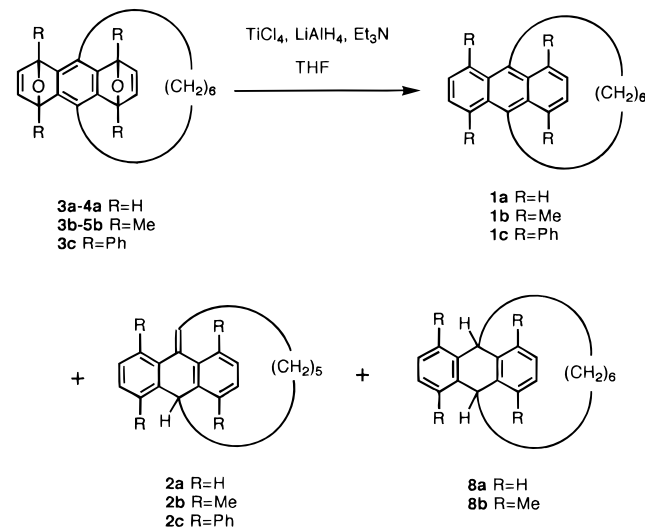
cenophane **1b** was stable to air but sensitive to acid; even trace amounts readily induced its isomerization to **2b**. For example, chromatography of the above deoxygenation products on untreated silica gel or alumina yielded only **2b**, and no **1b**.

Deoxygenation of **3c** as described above afforded tetraphenylanthracenophane **1c** (yellow-orange solid; mp 310−311 °C) in 58% yield. This anthracenophane is much more stable in the presence of acid than tetramethyl **1b**; treatment of a CDCl$_3$ solution of **1c** with a large excess of TFA induced slow isomerization of **1c** to **2c**.

Reduction of a mixture of **3a** and **4a** under similar conditions followed by aqueous workup furnished methylenedihydro isomer **2a** and dihydro derivative **8a** in a ratio of 1:2. However, when the reaction mixture was worked up by being directly

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Table 2. ^{1}H NMR Chemical Shifts of Anthracenophanes **1a**−**c** and the Corresponding Anthracene Derivatives **10a**−**c**

compd	Ha	Hb	Hc	Hd	He	Hf	Hg	Hh	Hi	Hj
1a^a	3.39	2.90	1.43	0.42	0.67	−1.84	7.95	8.05	7.23	7.16
1b^b	3.74	2.73	1.47	0.05	0.79	−1.83			7.03	7.03
1c^c	1.68	1.68	0.83	−0.21	0.51	−2.10			7.45	7.45
10a^d							8.51	8.51	7.51	7.51
10b^e									7.14	7.14
10c^f									7.42	7.42

^{a} Measured in toluene-d_8 at −50 °C. ^{b} Measured in CD$_2$Cl$_2$−CS$_2$ (1:1) at −110 °C. Methyl protons: δ 2.80 and 2.73 ppm. ^{c} Measured in CD$_2$Cl$_2$−CS$_2$ (1:1) at −110 °C. Phenyl protons: δ 7.70, 7.47, and 7.34 ppm. ^{d} Measured in CDCl$_3$ at 30 °C. Methyl protons: δ 3.10 ppm. ^{e} Measured in CDCl$_3$ at 30 °C. Methyl protons: δ 2.93 (6H) and 2.83 (12H) ppm. ^{f} Measured in C$_6$D$_6$−CD$_2$Cl$_2$ (9:1) at 0 °C. Phenyl protons: δ 7.46, 7.28, and 7.14 ppm. Methyl protons: 1.78 ppm.

passed through deactivated alumina in a nitrogen atmosphere, we obtained a hydrocarbon fraction revealed by the ^{1}H and ^{13}C NMR spectra (toluene-d_8, −50 °C) to be a 3:2 mixture of **1a** and dihydro **8a**. In the ^{1}H NMR spectra, the most-shielded methylene protons (Hf) appear at δ −1.84; the chemical shift is similar to that of the corresponding protons of [6](1,4)-anthracenophane (**9**; δ −1.81 in CD$_2$Cl$_2$).[5a] The ^{13}C NMR

1a R=H
1b R=Me
1c R=Ph

9

10a R^1=H, R^2=Me
10b R^1=R^2=Me
10c R^1=Ph, R^2=Me
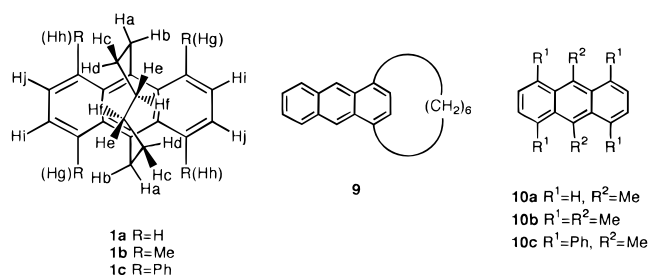
spectrum (−50 °C) exhibited nine signals for **1a** (135.6 (s), 133.2 (s), 125.6 (d), 125.0 (d), 124.9 (d), 124.5 (d), 34.2 (t), 33.7 (t), 25.8 (t) ppm)[18] along with seven signals for **8a**. The electronic spectrum of the product containing **1a** shows absorption maxima at 435, 415, and 392 (sh) nm in hexane (see also Table 4) which are characteristic of the anthracene chromophore, although the absorptions are long-wavelength-shifted and structureless. Treatment of a mixture of **1a** and **8a** (3:2) with silica gel in nitrogen immediately yielded a mixture of **2a** and **8a** (1:2). These results strongly indicate that the unstable species possesses the anthracenophane structure of **1a**. We were not able to purify the parent hydrocarbon **1a** because of its extremely high reactivity. By contrast, it appeared that tetramethyl derivative **1b** is fairly stable and tetraphenyl derivative **1c** even more stable; thus, the steric protection of the reactive central ring by the peri substituents effectively enhanced the kinetic stabilities as we expected.

The isomerization products **2a**−**c** represent the first examples of bridged methylenedihydroanthracenes observed under basic conditions.[9b,c] The parent hydrocarbon **2a** and the tetramethyl derivative **2b** are not very stable in air. By contrast, tetraphenyl **2c** is very stable again due to steric protection of the reactive bridgehead double bond by the phenyl groups. The vinyl proton of **2c** appears at δ 5.27, which, when compared to the corresponding proton of **2a**, is shifted upfield by 0.46 ppm due to the shielding effect of one of the phenyl groups at the peri positions.

Table 2 lists the ^{1}H NMR chemical shifts of anthracenophanes **1a**−**c** and the corresponding 9,10- and 1,4,5,8,9,10-substituted

(18) The signals for the secondary and tertiary carbons which overlapped with the solvent peaks were found by the DEPT experiments. One of the quaternary carbon signals of **1a**, however, has not been found yet.

Table 3. Barriers for the Flipping of the Methylene Bridge of Anthracenophanes **1a**−**c** and **9**

compd	peri substituent	$\Delta G^\ddagger$ (298 K) (kcal/mol)	compd	peri substituent	$\Delta G^\ddagger$ (298 K) (kcal/mol)
1a	H	13.7^a	**1c**	Ph	10.1 (233)^b
1b	Me	9.5 (217)^b	**9**		13.3^c

^{a} Determined by the line-shape analysis. ^{b} Determined from the coalescence temperauture (given in parentheses) and $\Delta\nu$ values for the most-shielded protons Hf. ^{c} The $\Delta G^\ddagger$ estimated from the coalescence temparature (268 K) was 13.4 kcal/mol (ref 5a).

Table 4. Absorption Maxima in the UV−vis Spectra of Anthracenophanes **1a**−**c** and the Corresponding Anthracene Derivatives **10a**−**c**^{a}

compd	λ_{max} (nm) (log ϵ)			
1a^{b,c}	435	415	392 (sh)	
1b	455 (3.63)	289 (4.70)		
1c	482 (3.71)	456 (3.67)	299 (4.44)	
10a^c	398 (3.67)	377 (3.67)	358 (3.44)	341 (3.12)
	260 (5.83)	252 (5.51)		
10b^d	426 (3.58)	415 (3.52)	404 (3.60)	276 (4.67)
10c^e	453 (3.62)	427 (3.60)	291 (4.35)	

^{a} Measured in cyclohexane unless otherwise stated. ^{b} Extinction coefficient was not determined. ^{c} Measured in hexane. ^{d} References 20 and 21a. ^{e} References 20 and 21b.

anthracenes **10a**−**c**. The measurements for **1a**−**c** were undertaken at low temperature where the flipping of the methylene bridge is frozen. The assignments for the protons of **1a**−**c** were done on the basis of 2D NMR spectra. Taking into account the difference of the solvent,[19] the chemical shifts of the aromatic protons of **1a**−**c** are similar to those of the corresponding model compounds **10a**, **10b**,[20] and **10c**,[20] indicating little effect from strain imposed by the short bridge on the ring current of **1a**−**c**. Similarly, given the difference of the solvent, the chemical shifts of the methylene protons of **1a** and **1b** are quite similar. By contrast, the methylene protons Ha, Hb, Hc, and Hd of **1c** are remarkably shifted upfield from the corresponding protons of **1a** and **1b**, owing to the anisotropic shielding effect of the phenyl groups at the peri positions. The proton Hf of **1b** (δ −1.83) and **1c** (δ −2.10), which suffer from the largest shielding effect of the anthracene ring, appear at the region similar to that of **1a**.
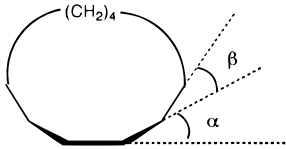
The barrier for the flipping of the methylene bridge of **1a**−**c** is summarized in Table 3. The barrier for **1a** (13.7 kcal/mol) is as large as that of 1,4-bridged anthracene **9** (13.3 kcal/mol),[5a] but is considerably larger than those of **1b** and **1c**. The flexibility of the methylene bridge might be related to the distance between the two benzylic positions; the shorter the distance, the more flexible the bridge must be. Therefore, the above observations indicate that the out-of-plane deformation of the bridged aromatic ring of **1b** and **1c** is larger than that of parent **1a** (i.e., a shorter distance between the benzylic carbons), despite that **1b** and **1c** are *kinetically more stable* than **1a**.

Absorption maxima of anthracenophanes **1a**−**c** and their corresponding reference compounds **10a**−**c** are listed in Table 4. The longest wavelength absorption of **1a** exhibits a remarkable bathochromic shift (0.26 eV) in comparison with that of **10a**, indicating a severe out-of-plane deformation of the anthracene ring of **1a**. The bathochromic shifts of the longest wavelength absorptions of **1b** (0.19 eV) and **1c** (0.17 eV)

(19) It is well known that an aromatic solvent causes an upfield shift by more than 0.5 ppm relative to chloroform; see p 104 of ref 16.

(20) The reference compounds **10b**[21a] and **10c**[21b] were prepared by the same bis-benzoannelation method as that used for the syntheses of anthracenophanes **1b** and **1c**.

(21) (a) Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251. (b) Dickerman, S. C.; Haase, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5458.

Table 5. Deformation Angles Determined by X-ray Crystal Structure Analyses of Anthracenophanes **1b** and **1c** and Diepoxyanthracenophanes **3b** and **5b**

compd	α (deg)[a]	β (deg)[b]	$\alpha + \beta$ (deg)	$\angle$(A/B) (deg)[c]	$\angle$(B/C) (deg)[d]
1b	24.7	18.5	43.2	9.3	11.4
1c	23.0	19.8	42.9	3.1	1.7
3b	19.8	20.9	40.7		
5b	20.5	20.4	40.9		

[a] Average out-of-plane bent angle of the para carbons. [b] Average out-of-plane bending angle of the benzylic carbons. [c] Bending angle of ring A relative to the base plane of ring B. [d] Bending angle of ring C relative to the base plane of ring B.

(a)

(b)
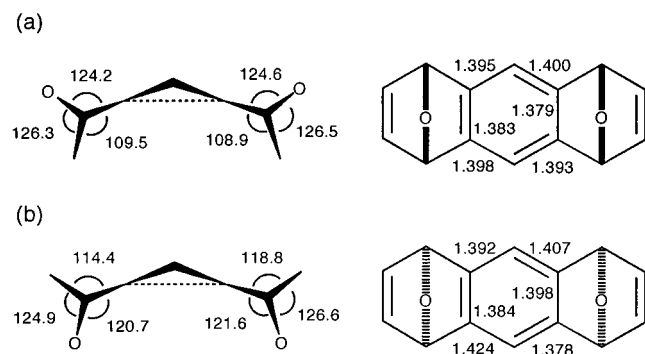
Figure 2. Representative dihedral angles (deg) and bond lengths (Å) of the aromatic ring of (a) *syn,syn*-diepoxy[6](9,10)anthracenophane **3b** and (b) *anti,anti*-diepoxy[6](9,10)anthracenophane **5b**.

relative to the corresponding reference compounds **10b** and **10c** are smaller than that of **1a**. This is ascribed to the distortion already present in the reference compounds **10b** and **10c** due to the peri interaction between the substituents.

Molecular Structures. X-ray crystallographic structure analyses of tetramethyldiepoxyanthracenophanes **3b** and **5b** (Figure 1) were undertaken not only to determine their stereochemistry, but also to observe the effects of the fusion of the strained oxanorbornadiene units on the structure of the [6]-paracyclophane core.[22] Out-of-plane deformation angles of the benzene ring (α and β) are listed in Table 5. The deformation angles of **3b** and **5b** are nearly 20°, which are within the range of those observed for the other [6]paracyclophane derivatives.[1d] There are many short nonbonded contacts between the bridge methylene and the oxanorbornadiene units, both in **3b** and **5b**, and particularly between the benzyl methylene and methyl groups. Thus, in **3b**, the following are less than or close to the sum of van der Waals radii (2.26−2.48 Å): H1···H20, H1···H21, H2···H23, H2···H24, H11···H17, H11···H18, H12···H26, and H12···H27. Since the methyl groups of **3b** are inclined upward from the base plane of the benzene ring (C8−C13−C15−C20), each benzylic hydrogen is affixed by the two methyl hydrogens. As a result of the nonbonded repulsion, the oxanorbornadiene units are considerably deformed, as shown in Figure 2. The dihedral angles between the oxygen bridge and the benzeno bridge (124.6° and 124.2°) are larger than those

(22) For the effect of the fusion of oxanorbornadiene units on the structure of a benzene ring with regard to the Mills−Nixon effects see: Cardullo, F.; Giuffrida, D.; Kohnke, F. H.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 339.

of the reported examples,[22,23] while the angles between the benzeno and etheno bridges (108.9° and 109.5°) are smaller than those reported. In the case of **5b**, by contrast, short nonbonded contacts are observed between the benzylic hydrogens and only one of the methyl hydrogens, because the methyl groups are directed downward from the base plane of the benzene ring; the distances H1···H20, H2···H23, H11···H17, and H12···H26 are less than or close to the sum of the van der Waals radii (2.19−2.55 Å). As a result, the oxanorbornadiene units of **5b** are not deformed from their normal structure (Figure 2). The bond distances for the benzene ring of **3b** and **5b** are also shown in Figure 2. The average lengths of the bridged aromatic bonds (C7−C8, C7−C20, C13−C14, and C14−C15) of **3b** (1.400 Å) and **5b** (1.397 Å) are longer than those of the edge bonds C8−C13 and C15−C20 (**3b**, 1.388 Å; **5b**, 1.381 Å). The observed bond lengths are typical of the [6]paracyclophane structures, in which the bridged aromatic bonds are longer than those of the edge bonds due to an unfavorable overlap of p orbitals.[24] On the other hand, the edge bonds would grow longer than the bridged bonds if the contribution of the bond fixation due to the Mills−Nixon effect were important.[22,23] It is thus deduced that the deformation of the aromatic bond lengths is mainly due to the out-of-plane bending, and that the Mills−Nixon effect is not important in these systems.

Molecular structures of **1b** and **1c**, determined by X-ray crystallographic analyses, are shown in Figures 3 and 4, respectively. The lengths of the bridged aromatic bonds (C7−C8, C7−C20, C13−C14, and C14−C15; average distances: **1b**, 1.422 Å; **1c**, 1.418 Å) are longer than those of anthracene itself[25] because of the poor overlap of the p orbitals due in turn to the short bridge. However, the other bond distances are similar to those of anthracene, indicating little perturbation of the electronic structure of the condensed aromatic ring by the hexamethylene bridge. Table 5 lists the deformation angles of the bridged aromatic ring of **1b** and **1c**. The internal torsion angles of the central rings of **1b** are −25.8°, −3.8°, −30.6°, 27.8°, 1.8°, and 28.6°, and those for **1c** are −25.9°, −1.0°, −26.8°, 26.0°, 0.7°, and 26.8°. The out-of-plane deformation angles (α and β) of **1b** and **1c** are similar, when the experimental error is taken into account; the sum of the deformation angles ($\alpha + \beta$) of **1b** (43.2°) and **1c** (42.9°) represents the largest deformation angle observed in any small-bridged [n]cyclophane.[1d] Just as in the *anti,anti* isomer of diepoxyanthracenophane **3b**, there are short nonbonded contacts between the benzylic hydrogens and one of the hydrogens of the methyl groups of tetramethylanthracenophane **1b**; the distances H1···H7, H2···H23, H11···H17, and H12···H26 are less than or close to the sum of the van der Waals radii (2.19−2.44 Å). Likewise, short nonbonded distances are observed in **1c** between the benzylic hydrogens and the phenyl carbons (H1···C27 = 2.48 Å, H2···C33 = 2.48 Å, H11···C21 = 2.37 Å, and H12···C39 = 2.46 Å). The aromatic rings A and C are slightly deformed from planarity (deviations from the respective mean planes are 0.012 and 0.009 Å for **1b** and 0.024 and 0.023 Å for **1c**) to reduce the nonbonded repulsion. In tetraphenyl derivative **1c**, the twist angles between ring A and the peri-attached phenyl rings D and E are 47.7° and 55.3°, respectively, and those between ring C and rings F and G are 62.9° and 45.7°, respectively. A notable difference

(23) (a) Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357. (b) Kohnke, F. H.; Stoddart, J. F.; Slawin, A. M. Z.; Williams, D. J. *Acta Crystallogr.* **1988**, *C44*, 738. (c) *Ibid.* **1988**, *C44*, 742.

(24) (a) Lee, T. J.; Rice, J. E.; Allen, W. D.; Remington, R. B.; Schaefer, H. F., III. *Chem. Phys.* **1988**, *123*, 1. (b) Gready, J. E.; Hambley, T. W.; Kakiuchi, K.; Kobiro, K.; Sternhell, S.; Tansey, C. W.; Tobe, Y. *J. Am. Chem. Soc.* **1990**, *112*, 7357. (c) Tobe, Y.; Sorori, T.; Kobiro, K.; Kakiuchi, K.; Odaira, Y. *J. Phys. Org. Chem.* **1996**, *9*, 1.

(25) Mason, R. *Acta Crystallogr.* **1964**, *17*, 547.
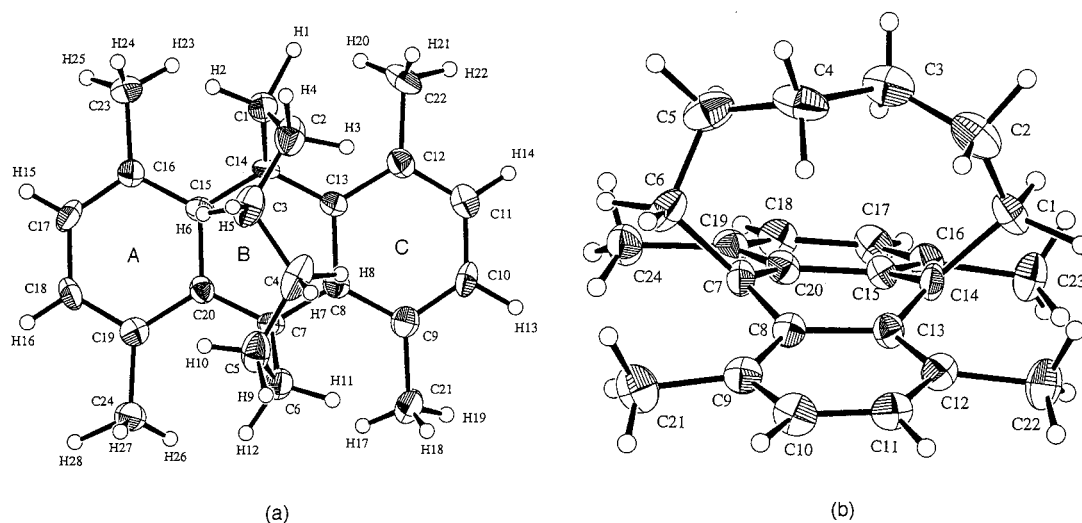
Figure 3. (a) Top view and (b) side view of the X-ray structure of tetramethyl[6](9,10)anthracenophane **1b**.
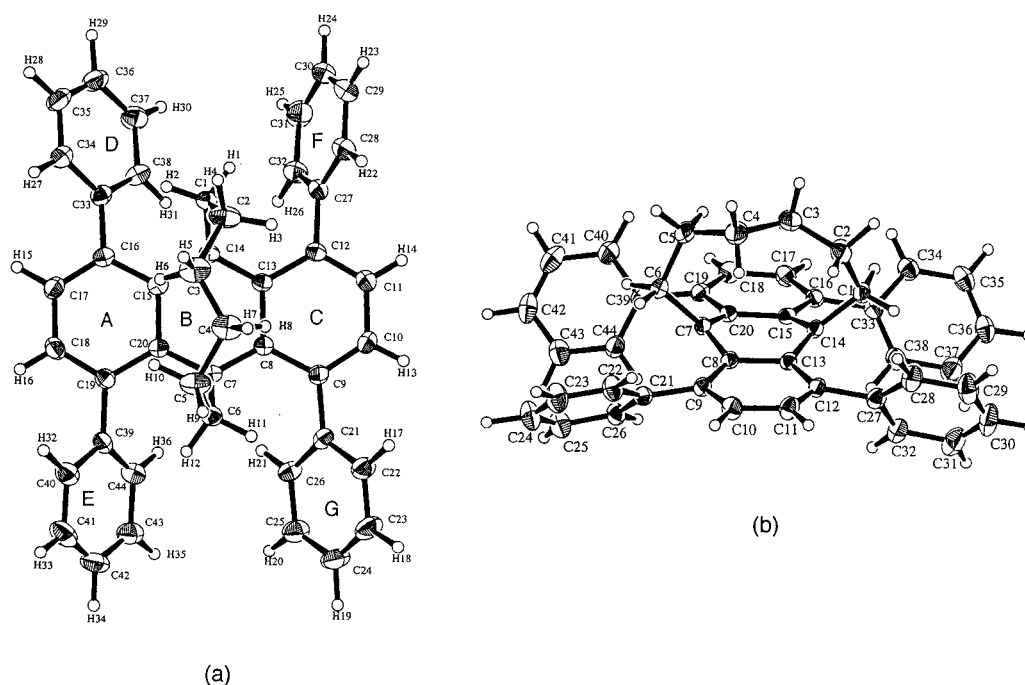
Figure 4. (a) Top view and (b) side view of the X-ray structure of tetraphenyl[6](9,10)anthracenophane **1c**.

between the structures of the anthracene rings of **1b** and **1c** is the set of dihedral angles between the base plane of the bridged ring B (C8−C13−C15−C20) and the mean planes of rings A and C. That is, the tilt angles of rings A and C with respect to the base plane of ring B of **1b** are 9.3° and 11.4°, respectively, while those of **1c** are 3.1° and 1.7°; the bending of the anthracene ring of **1b** along its long axis is substantially larger than that of **1c**.

Since the parent hydrocarbon **1a** is too unstable for X-ray structure determination, we carried out AM1 calculations[26] for **1a−c** to evaluate the effect of the peri substituents on the geometries and energies of these anthracenophanes. The calculated out-of-plane bending angles (α and β) and heats of formation of **1a−c** and 1,4-bridged anthracene **9** are listed in Table 6. The calculated deformation angles (α and β) for **1b** and **1c** are qualitatively in good agreement with the observed values, though this semiempirical method tends to overestimate the angle α. While the angles α and β of **1a** are similar to

(26) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

Table 6. AM1-Calculated Geometries of Anthracenophanes **1a−c** and **9** and Heats of Formation of **1a−c**, **9**, and Their Methylenedihydro Isomers **2a−c**

compd	α (deg)[a]	β (deg)[b]	$\alpha + \beta$ (deg)	ΔH_f° (kcal/mol)
1a	25.6	16.1	41.7	68.4
1b	28.8	14.8	43.6	50.0
1c	27.9	15.0	42.9	187.9
9	25.4	16.0	41.4	66.0
2a				49.4
2b				24.2
2c				164.0

[a] Average out-of-plane flip angle of the para carbons. [b] Average out-of-plane bending angle of the benzyl carbons.

those of 1,4-bridged anthracenophane **9**, the calculated as well as observed values for **1b** and **1c** are considerably larger than those for **1a** and **9**, indicating that the greater deformation in **1b** and **1c** is due to the additional steric interaction between the benzylic methylene of the bridge and the peri substituents. Similarly, the thermodynamic stability of **1a−c**, estimated from comparison of their calculated heats of formation with those of their corresponding methylenedihydro isomers **2a−c**, reveals

that **1b** and **1c** are less stable than **1a**, as will be described. On the other hand, in spite of the greater deformations of the aromatic ring due to the peri interactions, the observed kinetic stabilities of **1b** and **1c** are remarkably larger than that of the parent **1a**. The side views of the molecular structures of **1b** and **1c** (Figures 3b and 4b) clearly show how the substituents attached to the peri positions protect the reactive bridgehead carbons (C7 and C14) from attack of electrophilic reagents, particularly in the case of **1c**.

Reactions. Parent hydrocarbon **1a** is highly sensitive to air; exposure of a solution of **1a** immediately yielded an uncharacterized polymeric material. By contrast, the peri-substituted derivatives **1b** and **1c** are stable in the presence of air. Acid-catalyzed isomerization of **1a** was affected by silica gel to give the isotoluene type isomer **2a**. Tetramethyl **1b** is also sensitive to acid; isomerization to **2b** took place upon treatment with untreated silica gel or a catalytic amount of TFA. On the other hand, tetraphenyl **1c** is much more stable with acid; isomerization to **2c** took place slowly in the presence of excess TFA. The increasing kinetic stability in the sequence of **1a** < **1b** < **1c** is ascribed to the steric protection of the reactive bridgehead carbons (C7 and C14) by the peri substituents. It has been documented that isomerization of highly peri-substituted 9,10-dimethylanthracene derivatives readily took place to give the corresponding methylenedihydroanthracenes.[21,27] The reaction, which is inherently endothermic for 9-methylanthracene itself,[28] is driven by release of nonbonded interactions between the peri substituents at the expense of aromatic stabilization. Table 6 lists the AM1-calculated heats of formation of **2a**−**c** and the energies relative to the corresponding anthracenophanes **1a**−**c**. As shown in Table 6, isomerization of **1a** to **2a** is *highly exothermic* by 19 kcal/mol. Moreover, isomerization of **1b** and **1c** to the corresponding isomers **2b** and **2c** is *energetically more favorable,* despite **1b** and **1c** being less reactive experimentally than **1a** toward isomerization.

It has been well documented that [6]paracyclophane (**7**) and its derivatives undergo photochemical valence isomerization to their corresponding Dewar isomers.[1d,29] Cycloreversion of the Dewar isomers to the cyclophanes takes place both thermally and photochemically. It is equally well known that sterically crowded anthracene derivatives undergo thermally reversible photochemical isomerization to give Dewar 9,10-anthracenes.[27a,30] It may well be anticipated, therefore, that 9,10-bridged anthracenophanes **1b** and **1c** would undergo photochemical isomerization to the corresponding Dewar anthracenes **11b** and **11c**.
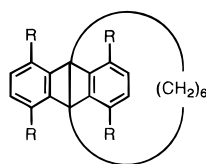
11a R=H
11b R=Me
11c R=Ph

Indeed, irradiation of a solution of **1b** in a mixed benzene-d_6/

THF-d_8 solvent resulted in the quantitative formation of the Dewar isomer **11b**. Similarly, irradiation (λ > 360 nm) of a benzene solution of **1c** gave the Dewar isomer **11c** (quantitative by NMR). The structures of **11b** and **11c** were readily assigned on the basis of the NMR spectra, in particular by the presence of the signals due to the quaternary carbon in the ^{13}C NMR spectra (δ 66.2 for **11b** and δ 67.8 for **11c**).

Thermal cycloreversion of **11b** and **11c** took place quantitatively to afford the corresponding anthracenophanes **1b** and **1c**. The rates of cycloreversion **11b** (in cyclohexane) and **11c** (in toluene) were measured to give the following activation parameters: **11b**, $\Delta H^{\ddagger}$ = 21.7 kcal/mol, $\Delta S^{\ddagger}$ = −1.5 cal/(deg mol), E_a = 22.3 kcal/mol; **11c**, $\Delta H^{\ddagger}$ = 24.9 kcal/mol, $\Delta S^{\ddagger}$ = 3.4 cal/(deg mol), E_a = 25.4 kcal/mol. Whereas the activation enthalpies for the cycloreversion of **11b** and **11c** are within the range of those reported for the Dewar 9,10-anthracenes,[31] the value for the reaction of **11c** is larger than that of **11b**. This might be because a larger geometrical change is required for the isomerization of **11c** compared for that of **11b**.

Conclusion

The smallest 9,10-bridged anthracenophanes **1a**−**c** were synthesized. Although the parent hydrocarbon **1a** was too unstable for isolation, its peri-substituted derivatives **1b** and **1c** were fully characterized. X-ray crystallographic structure analyses of **1b** and **1c** reveal that the out-of-plane deformation angles of the bridged aromatic ring are the largest observed in any small-bridged [*n*]cyclophanes. Conformational behavior, semiempirical AM1 calculations, and X-ray analyses indicate that **1b** and **1c** are more strained than **1a** due to the steric interaction between the benzylic methylenes and the peri substituents. On the other hand, the peri-substituted derivatives **1b** and **1c** are kinetically more stable than the parent **1a**, due to the steric protection of the reactive bridgehead carbons of the central ring. As a result of the severe deformation of the aromatic ring, the anthracenophanes **1a**−**c** undergo unusual reactions, such as acid-catalyzed rearrangement to the corresponding methylenedihydro isomers **2a**−**c**, which represent the first examples of bridged methylenedihydroanthracenes, and thermally reversible photochemical isomerization to the corresponding Dewar anthracenes **11b** and **11c**.

Experimental Section

Analytical HPLC was carried out with a Shimadzu LC-10AS chromatograph equipped with a Inertsil ODS column, and preparative HPLC separation was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H. NMR, 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 Mo Kα radiation.

Diepoxy[6](9,10)anthracenophanes 3a, 4a, and 5a. To a suspension of 1.68 g (43.1 mmol) of sodium amide in 5.0 mL of THF was added dropwise 1.02 g (13.8 mmol) of *tert*-butyl alcohol under a nitrogen atmosphere, and the mixture was heated at 40 °C for 2 h. The mixture was cooled in an ice bath, and a solution of dibromocyclophane **6**[13] (305 mg, 0.954 mmol) in 6.7 mL (95 mmol) of furan was added dropwise. The mixture was allowed to warm to room temperature and stirred for 15 h before it was poured into ice−water. The mixture was

(27) (a) Hart, H.; Ruge, R. *Tetrahedron Lett.* **1977**, 3143. (b) Bowden, B. F.; Cameron, D. W. *J. Chem. Soc., Chem. Commun.* **1977**, 78.

(28) Bartmas, J. E.; Griffith, S. S. *J. Am. Chem. Soc.* **1990**, *112,* 2931.

(29) For more recent reports on the valence isomerization of [6]-paracyclophanes see: (a) Miki, S.; Shimizu, R.; Nakatsuji, H. *Tetrahedron Lett.* **1992**, *33,* 953. (b) Gleiter R.; Treptow, B. *J. Org. Chem.* **1993**, *58,* 7740. (c) Frank, I.; Grimme, S.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1994**, *116,* 5949. (d) Dreeskamp, H.; Sarge, S. M.; Tochtermann, W. *Tetrahedron Lett.* **1995**, *51,* 3137.

(30) (a) Güsten H.; Mintas, M.; Klasinc, L. *J. Am. Chem. Soc.* **1980**, *102,* 7936. (b) Dreeskamp, H.; Jahn, B.; Pabst, J. *Z. Naturforsch.* **1981**, *36a,* 665. (c) Jahn, B.; Dreeskamp, H. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88,* 42. (d) Kraljic, I.; Mintas, M.; Klasinc, L.; Ranogajec, F.; Güsten, H. *Nouv. J. Chim.* **1983**, *7,* 239. (e) Meador, M. A.; Hart, H. *J. Org. Chem.* **1989**, *54,* 2336. For a review see: (f) Becker, H.-D. *Chem. Rev.* **1993**, *93,* 145.

(31) (a) Pritschins, W.; Grimme, W. *Tetrahedron Lett.* **1979**, 4545. (b) *Ibid.* **1982**, *23,* 1151.

extracted with ether−dichloromethane (2:1). The extract was washed with 10% HCl, dried (MgSO$_4$), and evaporated. The products were separated by flash chromatography on silica gel to afford 63 mg (22%) of **3a**, 68 mg (24%) of **4a**, and 10 mg (3.6%) of **5a**, which were recrystallized from hexane−ether.

syn,syn-**3a**: white solid; mp 203−205 °C; ^{1}H NMR (CD$_2$Cl$_2$, −50 °C) δ 7.06 (dd, *J* = 5.5, 1.5 Hz, 2H), 7.05 (dd, *J* = 5.4, 1.8 Hz, 2H), 5.72 (s, 2H), 5.67 (s, 2H), 2.94 (dd, *J* = 13.2, 4.8 Hz, 2H), 2.38 (ddd, *J* = 12.7, 12.7, 5.6 Hz, 2H), 1.6−1.7 (m, 2H), 1.1−1.3 (m, 2H), 0.87 (tt, *J* = 13.0, 6.0 Hz, 2H), −0.1 to +0.1 (m, 2H); ^{13}C NMR (CDCl$_3$, −40 °C) δ 154.0 (s), 149.8 (s), 143.8 (d), 143.6 (d), 132.0 (s), 81.4 (d), 81.2 (d), 33.2 (t), 31.3 (t), 25.0 (t); IR (KBr) 1290, 1030, 1010, 870, 850, 760, 745 cm^{-1}; UV λ_{max} (CHCl$_3$) 250 (log ϵ 4.36) nm; MS *m/z* (relative intensity) 292 (M$^+$, 100). Anal. Calcd for C$_{20}$H$_{20}$O$_2$: C, 82.15; H, 6.89. Found: C, 82.15; H, 7.05.

syn,anti-**4a**: white solid; mp 195 °C dec; ^{1}H NMR (CDCl$_3$, −50 °C) δ 7.18 (dd, *J* = 5.4, 1.9 Hz, 1H), 7.14 (d, *J* = 1.2 Hz, 2H), 7.04 (dd, *J* = 5.2, 1.7 Hz, 1H), 5.85 (s, 2H), 5.80 (s, 1H), 5.69 (s, 1H), 3.09 (dd, *J* = 12.9, 5.0 Hz, 1H), 2.76 (br d, *J* = 8.2 Hz, 1H), 2.5−2.7 (m, 1H), 1.97 (ddd, *J* = 12.9, 12.4, 4.9 Hz, 1H), 1.5−1.7 (m, 2H), 1.1−1.3 (m, 1H), 0.9−1.1 (m, 2H), 0.2−0.4 (m, 2H), −0.8 to -0.6 (m, 1H); ^{13}C NMR (CDCl$_3$, −40 °C) δ 152.9 (s), 151.4 (s), 149.1 (s), 146.3 (s), 143.6 (d), 143.5 (d), 142.1 (d), 140.2 (d), 132.8 (s), 132.3 (s), 81.5 (d), 81.3 (d), 81.2 (d), 81.1 (d), 32.8 (t), 32.7 (s), 31.7 (t), 31.1 (t), 25.0 (t), 22.4 (t); IR (KBr) 1280, 1030, 1000, 860, 740 cm^{-1}; UV λ_{max} (CHCl$_3$) 323 (log ϵ 2.63), 252 (4.33) nm; MS *m/z* (relative intensity) 292 (M$^+$, 100); HRMS calcd for C$_{20}$H$_{20}$O$_2$ 292.1463, found 292.1449.

anti,anti-**5a**: white solid; mp 192−194 °C dec; ^{1}H NMR (CDCl$_3$, −50 °C) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.03 (d, *J* = 4.5 Hz, 2H), 5.90 (s, 2H), 5.72 (s, 2H), 2.87 (dd, *J* = 12.9, 5.7 Hz, 2H), 2.08 (ddd, *J* = 12.5, 12.5, 5.7 Hz, 2H), 1.4−1.45 (m, 2H), 0.75−0.95 (m, 2H), 0.15−0.3 (m, 2H), −0.5 to −0.4 (m, 2H); ^{13}C NMR (CDCl$_3$, −40 °C) δ 150.2 (s), 145.5 (s), 142.0 (d), 139.9 (d), 133.1 (s), 81.6 (d), 81.3 (d), 32.1 (t), 31.9 (t), 22.5 (t); IR (KBr) 1270, 1020, 870, 850, 740 cm^{-1}; UV λ_{max} (CHCl$_3$) 321 (log ϵ 2.69), 252 (4.34) nm; MS *m/z* (relative intensity) 292 (M$^+$, 100); HRMS calcd for C$_{20}$H$_{20}$O$_2$ 292.1463, found 292.1448.

Tetramethyldiepoxy[6](9,10)anthracenophanes 3b, 4b, and 5b. The reaction of dibromocyclophane **6** (155 mg, 0.487 mmol) and 3.4 mL (32 mmol) of 2,5-dimethylfuran was carried out as described above using 569 mg (14.6 mmol) of sodium amide and 360 mg (4.87 mmol) of *tert*-butyl alcohol in 3.1 mL of THF. The products were separated by flash chromatography on silica gel to afford 21 mg (12%) of **3b**, 80 mg (47%) of **4b**, and 48 mg (28%) of **5b**, which were recrystallized from hexane−ether.

syn,syn-**3b**: white solid; mp 195 °C dec; ^{1}H NMR (CDCl$_3$, −50 °C) δ 6.84 (d, *J* = 5.4 Hz, 2H), 6.81 (d, *J* = 5.4 Hz, 2H), 2.98 (dd, *J* = 13.5, 5.6 Hz, 2H), 2.62 (ddd, *J* = 12.8, 12.8, 5.3 Hz, 2H), 2.02 (s, 6H), 1.93 (s, 6H), 1.6−1.9 (m, 2H), 1.3−1.5 (m, 2H), 0.8−1.0 (m, 2H), −0.2−0.0 (m, 2H); ^{13}C NMR (CDCl$_3$, −40 °C) δ 155.0 (s), 150.6 (s), 149.3 (d), 148.3 (d), 129.5 (s), 90.8 (s), 90.0 (s), 34.8 (t), 28.9 (t), 26.2 (t), 18.8 (q), 17.4 (q); IR (KBr) 1375, 1300, 1240, 1155, 1110, 890, 860, 820, 800, 750, 730 cm^{-1}; UV λ_{max} (CHCl$_3$) 338 (log ϵ 2.57), 258 (4.34) nm; MS *m/z* (relative intensity) 348 (M$^+$, 100). Anal. Calcd for C$_{24}$H$_{28}$O$_2$: C, 82.71; H, 8.09. Found: C, 82.46; H, 8.12.

syn,anti-**4b**: white solid; mp 186−188 °C; ^{1}H NMR (CDCl$_3$, −50 °C) δ 6.88 (d, *J* = 5.2 Hz, 1H), 6.84 (d, *J* = 5.7 Hz, 1H), 6.81 (d, *J* = 5.4 Hz, 1H), 6.77 (d, *J* = 5.0 Hz, 1H), 3.09 (br dd, 1H), 2.6−2.8 (m, 2H), 2.03 (s, 3H), 1.93 (s, overlapping with a multiplet, 7H), 1.81 (s, 3H), 1.5−1.7 (m, 2H), 1.1−1.3 (m, 1H), 0.8−1.0 (m, 2H), 0.3−0.4 (m, 1H), 0.1−0.3 (m, 1H), −0.7 to −0.5 (m, 1H); ^{13}C NMR (CDCl$_3$, −40 °C) δ 155.9 (s), 154.2 (s), 151.2 (s), 150.2 (s), 149.2 (d), 148.4 (d), 146.0 (d), 144.5 (d), 131.5 (s), 130.4 (s), 91.0 (s), 89.7 (s), 89.4 (s), 88.8 (s), 34.5 (t), 32.7 (t), 31.2 (t), 28.1 (t), 25.5 (t), 23.5 (t), 18.6 (q), 18.0 (q), 17.6 (q), 17.0 (q); IR (KBr) 1380, 1300, 1150, 1130, 1120, 860, 750 cm^{-1}; UV λ_{max} (CHCl$_3$) 331 (log ϵ 2.45), 259 (4.33) nm; MS *m/z* (relative intensity) 348 (M$^+$, 100). Anal. Calcd for C$_{24}$H$_{28}$O$_2$: C, 82.71; H, 8.09. Found: C, 82.70; H, 8.20.

anti,anti-**5b**: white solid; mp 180−182 °C; ^{1}H NMR (CD$_2$Cl$_2$, −80 °C) δ 6.86 (d, *J* = 5.5 Hz, 2H), 6.76 (d, *J* = 5.5 Hz, 2H), 2.83 (dd, *J* = 12.8, 4.7 Hz, 2H), 1.98 (ddd, *J* = 12.6, 12.6, 4.9 Hz, 2H), 1.84 (s, 6H), 1.71 (s, 6H), 1.2−1.4 (m, 2H), 0.7−0.9 (m, 2H), 0.0−0.2 (m,

2H), −0.6 to −0.4 (m, 2H); ^{13}C NMR (CDCl$_3$, −40 °C) δ 154.8 (br s), 150.7 (br s), 145.8 (br d), 144.3 (br d), 132.0 (s), 89.3 (br s), 88.9 (br s), 32.4 (t), 30.6 (t), 23.0 (t), 18.1 (br q), 17.6 (br q); IR (KBr) 1375, 1295, 1150, 1130, 1110, 870, 860, 750 cm^{-1}; UV λ_{max} (CHCl$_3$) 327 (log ϵ 2.46), 257 (4.30) nm; MS *m/z* (relative intensity) 348 (M$^+$, 100). Anal. Calcd for C$_{24}$H$_{28}$O$_2$: C, 82.71; H, 8.09. Found: C, 82.54; H, 8.19.

Tetraphenyldiepoxy[6](9,10)anthracenophanes 3c and 4c. To a suspension of 1.56 g (16.8 mmol) of potassium *tert*-butoxide in 4.0 mL of toluene was added a solution of 1.95 g (8.88 mmol) of 2,5-diphenylfuran^{32} in 14 mL of toluene followed by 533 mg (1.68 mmol) of dibromocyclophane **6** in 6 mL of the same solvent. The mixture was heated at 120 °C for 3 days. The mixture was worked up as described above except that most of excess diphenylfuran was removed by sublimation prior to chromatography on silica gel. Final purification of the products was done by preparative HPLC to afford 89 mg (9%) of **3c** and 75 mg (8%) of **4c**, which were recrystallized from hexane−ether.

syn,syn-**3c**: white solid; mp 261−262 °C; ^{1}H NMR (toluene-*d$_8$*, −50 °C) δ 8.06 (m, 4H), 7.46 (m, 4H), 6.0−7.2 (m, 16H), 1.73 (dd, *J* = 12.7, 5.5 Hz, 2H), 1.39 (m, 4H), 1.12 (m, 2H), 0.77 (m, 2H), 0.35 (m, 2H); ^{13}C NMR (toluene-*d$_8$*, 90 °C) δ 154.7 (br s, hardly discernible at this temperature but splits into two peaks at 157.1 and 152.3 ppm at −50 °C), 148.7 (d), 139.0 (s), 131.6 (s), 128.6 (d), 127.9 (d), 126.6 (d), 95.0 (s), 35.6 (t), 28.6 (t), 27.1 (t); IR (KBr) 1305, 1010, 900, 740, 700 cm^{-1}; UV λ_{max} (CHCl$_3$) 333 (log ϵ 2.75), 264 (4.36) nm; FAB MS *m/z* (relative intensity) 597 (M$^+$ + 1, 100); HRMS calcd for C$_{44}$H$_{36}$O$_2$ 596.2715, found 596.2735.

syn,anti-**4c**: white solid; mp 218−220 °C; ^{1}H NMR (toluene-*d$_8$*, 90 °C) δ 7.7−7.8 (m, 8H), 6.9−7.3 (m, 16H), 1.82 (m, 4H), 0.95 (m, 2H), 0.80 (m, 4H), 0.50 (m, 2H); ^{13}C NMR (toluene-*d$_8$*, 90 °C) δ 156.0 (br s, hardly discernible at this temperature but splits into two peaks at 157.1 and 153.6 ppm at −50 °C), 154.2 (br s, hardly discernible at this temperature but splits into two peaks at 156.2 and 151.3 ppm at −50 °C), 148.8 (d), 144.6 (d), 138.9 (s), 138.2 (s), 133.7 (s), 129.2 (d), 128.9 (d), 128.7 (d), 128.6 (d), 127.9 (d), 126.5 (d), 95.6 (s), 95.0 (s), 34.2 (t), 30.2 (t), 25.6 (t); IR (KBr) 1020, 1010, 970, 740, 695 cm^{-1}; UV λ_{max} (CHCl$_3$) 265 (log ϵ 4.27) nm; FAB MS *m/z* (relative intensity) 597 (M$^+$ + 1, 100); HRMS calcd for C$_{44}$H$_{37}$O$_2$ 597.2794, found 597.2753.

Reductive Deoxygenation of Diepoxyanthracenophanes 3a and 4a. All the operations were undertaken under a nitrogen atmosphere. TiCl$_4$ (740 mg, 3.90 mmol) was added to 5.0 mL of THF cooled in an ice bath followed by addition of 58 mg (1.51 mmol) of LiAlH$_4$ in two portions. To the resulting black suspension was added dropwise 1.52 g (15.1 mmol) of triethylamine (TEA), and the mixture was heated at 65 °C for 20 min. After the mixture was allowed to cool to room temperature, a solution of 100 mg (0.342 mmol) of a mixture of **3a** and **4a** in 2.6 mL of THF was added dropwise. After 2 h, the mixture was filtered through a column of alumina (activity III) under nitrogen using deaerated ether as an eluent. Removal of the solvent under nitrogen gave a yellow solid, which was chromatographed again on alumina (activity V) with deaerated hexane as an eluent to furnish 27 mg (31%) of a yellow solid containing anthracenophane **1a** and the dihydro derivative **8a** in a ratio of 3:2 (by ^{1}H NMR in toluene-*d$_8$*). Irrespective of the reaction conditions, extractive workup resulted in the formation of only **8a** and **2a** due to rapid decomposition of **1a** in air. Further separation of **8a** and **2a** was done by preparative HPLC. While **8a** was recrystallized from hexane, attempts to recrystallize bridgehead olefin **2a** failed due to rapid oxidation to the corresponding epoxide.

1a: ^{1}H NMR (toluene-*d$_8$*, −50 °C) δ 8.03−8.06 (m, 2H), 7.93−7.97 (m, 2H), 7.22−7.25 (m, 2H), 7.15−7.17 (m, 2H), 3.39 (dd, *J* = 12.5, 5.6 Hz, 2H), 2.90 (ddd, *J* = 18.1, 6.0, 6.0 Hz, 2H), 1.4−1.5 (m, 2H), 0.56−0.76 (m, 2H), 0.35−0.48 (m, 2H), −1.86 to −1.77 (m, 2H); ^{13}C NMR (toluene-*d$_8$*, −50 °C) δ 135.6 (s), 133.2 (s), 125.6 (d), 125.0 (d), 124.9 (d), 124.5 (d), 34.2 (t), 33.7 (t), 25.8 (t); UV−vis λ_{max} (hexane) 435, 415 nm.

8a: white solid; mp 128−129 °C; ^{1}H NMR (CDCl$_3$, 30 °C) δ 7.25 (d, *J* = 9.2 Hz, 1H), 7.21 (d, *J* =9.2 Hz, 1H), 4.42 (dd, *J* = 4.4, 4.2

(32) Nowlin, G. *J. Am. Chem. Soc.* **1950**, *72*, 5754.

Hz, 2H), 2.22 (ddd, J = 6.2, 5.0, 5.0 Hz, 4H), 1.1−1.2 (m, 4H), 0.8−0.9 (m, 4H); ^{13}C NMR (CDCl$_3$, 30 °C) δ 139.4 (s), 128.1 (d), 126.1 (d), 42.5 (d), 37.9 (d), 25.7 (t), 20.3 (t); IR (KBr) 770, 700 cm^{-1}; MS m/z (relative intensity) 262 (M$^+$, 100); HRMS calcd for C$_{20}$H$_{22}$ 262.1721, found 262.1707.

2a: white solid; this compound did not show a sharp melting point probably due to partial oxidation during the measurement; ^{1}H NMR (CDCl$_3$, 30 °C) δ 7.17−7.48 (m, 8H), 5.73 (dd, J = 11.6, 5.2 Hz, 1H), 4.06 (t, J = 11.6, 5.2 Hz, 1H), 2.79 (ddd, J = 24.5, 12.1, 4.0 Hz, 1H), 1.9−2.2 (m, 3H), 1.5−1.6 (m, 2H), 0.9−1.4 (m, 3H), 0.3−0.4 (m, 1H); ^{13}C NMR (CDCl$_3$, 30 °C) δ 143.9 (s), 142.5 (s), 141.2 (s), 138.9 (s), 138.7 (s), 132.9 (d), 127.0 (d), 126.74 (d), 126.67 (d), 126.62 (d), 126.54 (d), 126.0 (d), 125.6 (d), 122.4 (d), 47.4 (d), 40.8 (t), 30.2 (t), 29.3 (t), 26.5 (t), 26.4 (t); IR (KBr) 890, 770, 760, 750, 720 cm^{-1}; MS m/z (relative intensity) 260 (M$^+$, 100); HRMS calcd for C$_{20}$H$_{20}$ 260.1565, found 260.1564.

Reductive Deoxygenation of Tetramethyldiepoxyanthracenophanes 3b−5b. Reduction of 71 mg (0.20 mmol) of a mixture of **3b−5b** with the reducing agent prepared from 552 mg (2.9 mmol) of TiCl$_4$, 43 mg (1.1 mmol) of LiAlH$_4$, and 1.13 g (11.2 mmol) of TEA in 6 mL of THF was carried out at room temperature as described above for 18 h. The reaction was quenched by dropwise addition of the mixture to a solution of 20% potassium carbonate (40 mL) solution under nitrogen. Reverse addition of the carbonate solution to the reaction mixture resulted in the formation of the isomerization product **2b**. The mixture was extracted with ether, and the extract was washed with saturated sodium chloride solution and dried over MgSO$_4$. After removal of the solvent, the residue was chromatographed on alumina (activity III) to afford 44 mg (68%) of tetramethylanthracenophane **1b** as a yellow solid. Reduction of 117 mg (0.336 mmol) of a mixture of **3b−5b** with 912 mg (4.81 mmol) of TiCl$_4$, 70 mg (1.9 mmol) of LiAlH$_4$, and 75 mg (0.74 mmol) of TEA in 10 mL of THF gave 46 mg of a mixture of **1b**, dihydro derivative **8b**, and **2b** in a ratio of 11:2:1 (by ^{1}H NMR), which were separated by preparative HPLC.

1b: yellow solid from hexane−ether; mp 161−162 °C; ^{1}H NMR (CD$_2$Cl$_2$:CS$_2$ = 1:1, −110 °C) δ 7.03 (br s, 4H), 3.74 (br m, 2H), 2.80 (br s, 6H), 2.73 (br s, 6H), 2.73 (br m, 2H), 1.47 (br m, 2H), 0.79 (br m, 2H), 0.05 (br m, 2H), −1.83 (br m, 2H); ^{1}H NMR (CD$_2$Cl$_2$, 30 °C) δ 7.11 (s, 4H), 3.31 (t, J = 5.9 Hz, 4H), 2.80 (s, 12H), 0.87 (m, 4H), −0.38 (m, 4H); ^{13}C NMR (THF-d_8, 30 °C) δ 139.1 (s), 138.2 (s), 131.0 (s), 127.3 (d), 40.2 (t), 34.8 (t), 27.6 (t), 24.9 (q); IR (KBr) 820 cm^{-1}; UV−vis λ_{max} (cyclohexane) 455 (log ϵ 3.63), 289 (4.70) nm; MS m/z (relative intensity) 316 (M$^+$, 100); HRMS calcd for C$_{24}$H$_{28}$ 316.2191, found 316.2186.

8b: white solid from hexane−ether; mp 154−156 °C; ^{1}H NMR (CDCl$_3$, 30 °C) δ 6.99 (s, 4H), 4.55 (t, J = 5.8 Hz, 2H), 2.39 (s, 12H), 2.14 (q, J = 6.0 Hz, 4H), 1.2−1.3 (br m, 4H), 0.9−1.0 (br m, 4H); ^{13}C NMR (CDCl$_3$, 30 °C) δ 139.1(s), 132.9 (s), 128.2 (d), 38.1 (d), 32.1 (t), 26.6 (t), 22.2 (t), 19.9 (q); MS m/z (relative intensity) 318 (M$^+$, 58), 234 (100); HRMS calcd for C$_{24}$H$_{30}$ 318.2347, found 318.2336.

2b: white solid from hexane−ether; mp 156−157 °C; ^{1}H NMR (CDCl$_3$, 30 °C) δ 7.03 (d, J = 7.7 Hz, 1H), 6.95 (s, 1H), 6.93 (d, J = 7.7 Hz 1H), 5.64 (dd, J = 11.5, 5.1 Hz, 1H), 4.40 (dd, J = 4.5, 3.7 Hz, 1H) 2.49 (s, 3H), 2.38 (s, 9H), 2.2−2.3 (m, 1H), 2.1−2.2 (m, 2H), 1.9−2.0 (m, 1H), 1.5−1.6 (m, 1H), 1.2−1.4 (m, 3H), 1.0−1.1 (m, 1H), 0.3−0.5 (m, 1H); ^{13}C NMR (CDCl$_3$, 30 °C) δ 143.3 (s), 141.1 (s), 139.4 (s), 137.9 (s), 136.8 (s), 133.6 (d), 132.0 (s), 131.4 (s), 130.5 (s), 129.3 (s), 128.4 (d), 128.3 (d), 127.6 (d), 40.2 (d), 34.0 (t), 31.2 (t), 29.2 (t), 27.5 (t), 27.2 (t), 19.7 (q), 19.2 (q), 19.0 (q), 18.5 (q); IR (KBr) 810, 800 cm^{-1}; MS m/z (relative intensity) 316 (M$^+$, 45), 234 (100); HRMS calcd for C$_{24}$H$_{28}$ 316.2191, found 316.2209.

Reductive Deoxygenation of Tetraphenyldiepoxyanthracenophane 3c. Reduction of 141 mg (0.237 mmol) of **3c** with 896 mg (6.16 mmol) of TiCl$_4$, 90.8 mg (2.37 mmol) of LiAlH$_4$, and 4.78 g (4.73 mmol) of TEA in 8 mL of THF was carried out under reflux for 6 h. The mixture was worked up as described above to give 78 mg (58%) of tetraphenylanthracenophane **1c**, which was recrystallized from hexane−ether.

1c: yellow-orange solid; mp 310−311 °C (sealed tube); ^{1}H NMR (CD$_2$Cl$_2$:CS$_2$ = 1:1, −110 °C) δ 7.2−7.7 (br m, 24H), 1.68 (br m, 4H), 0.83 (br m, 2H), 0.51 (br m, 2H), −0.21 (br m, 2H), −2.10 (br

m, 2H); ^{1}H NMR (CD$_2$Cl$_2$, 30 °C) δ 7.70 (dt, J = 6.9, 1.5 Hz, 8H), 7.47 (dt, J = 1.2, 6.9 Hz, 8H), 7.45 (s, 4H), 7.34 (tt, J = 7.1, 1.2 Hz, 4H), 1.89 (t, J = 6.1 Hz, 4H), 0.45 (br m, 4H), −0.61 (br m, 4H); ^{13}C NMR (CD$_2$Cl$_2$, 30 °C) δ 145.2 (s), 140.6 (s), 139.7 (s), 138.6 (s), 129.1 (d), 128.9 (d), 128.8 (d), 127.1 (d), 40.4 (t), 34.4 (t), 26.6 (t); IR (KBr) 1080, 855, 850, 760, 705, 695 cm^{-1}; UV−vis λ_{max} (cyclohexane) 482 (log ϵ 3.71), 456 (3.67), 299 (4.44), 248 (4.20) nm; FAB MS m/z (relative intensity) 565 (M$^+$ + 1, 100); HRMS calcd for C$_{44}$H$_{36}$ 564.2817, found 564.2807.

Acid-Catalyzed Isomerization of Anthracenophanes 1a−c. To a solution of a mixture of **1a**, **8a**, and **2a** (approximately 1:0.7:1.4) in benzene-d_6/acetone-d_6 mixture (1:4) was added one drop of trifluoroacetic acid via a syringe. The yellow color of the solution disappeared immediately, and white insoluble material appeared. The ^{1}H NMR spectrum of the solution indicated the disappearance of the peaks due to **1a** while the peaks of **8a** and **2a** remained unchanged, indicating that **1a** had polymerized. Alternatively, a solution of a mixture of **1a** and **8a** (3:2) in toluene-d_8 was added under nitrogen to a degassed slurry of silica gel in hexane. After the yellow color disappeared, the mixture was filtered and the solvent was evaporated. The ^{1}H NMR spectrum of the residue exhibited peaks due to **8a** and **2a** in a ratio of 2:1. This indicates that about 30% of **1a** had isomerized to **2a** by treatment with silica gel, while the remainder had presumably polymerized during these operations.

To a solution of **1b** in CDCl$_3$ was added one drop of TFA via a microsyringe. The yellow color disappeared immediately. ^{1}H NMR spectra of the solution indicated the formation of the isomer **2b** as a sole product.

To a solution of 35 mg (0.044 mmol) of **1c** in 1.5 mL of chloroform was added 60 μL (0.78 mmol) of TFA, and the solution was stirred at room temperature for 47 h. The solution was diluted with ether and washed with aqueous NaHCO$_3$. After removal of the solvent, the residue was chromatographed on silica gel to give 25 mg (71%) of the isomer **2c** as a yellow solid which was recrystallized from hexane−ether: mp 224−225 °C; ^{1}H NMR (CDCl$_3$, 30 °C) δ 7.1−7.5 (m, 24H), 5.27 (dd, J = 6.9, 4.9 Hz, 1H), 4.61 (t, J = 4.5 Hz, 1H), 1.7−1.9 (m,1H), 1.1−1.4 (m, 7H), 0.7−0.9 (m, 1H), 0.2−0.3 (m, 1H); ^{13}C NMR (CDCl$_3$, 30 °C) δ 142.0 (s), 141.7 (s), 141.5 (s), 141.1 (s), 141.0 (s), 140.2 (br s), 139.7 (s), 138.7 (s), 138.1 (br s), 137.9 (br d), 137.7 (br s), 137.4 (s), 135.1 (s), 130.2 (d), 129.6 (d), 129.2 (d), 129.1 (d), 129.0 (d), 128.5 (d), 127.91 (d), 129.87 (d), 127.51 (d), 127.48 (d), 127.2 (d), 126.73 (d), 127.70 (d), 126.6 (d), 126.3 (d), 39.7 (d), 36.6 (br t), 30.7 (t), 28.9 (br t), 27.2 (t), 26.7 (t); IR (KBr) 755, 695 cm^{-1}; MS m/z (relative intensity) 564 (M$^+$, 13), 69 (100); HRMS calcd for C$_{44}$H$_{36}$ 564.2817, found 564.2849.

Photochemical Valence Isomerization of Anthracenophanes 1b and 1c. A solution of 20 mg of **1b** in benzene-d_6 and THF-d_8 (3:1) in an NMR tube was irradiated through a Pyrex filter with a 300 W high-pressure mercury lamp at room temperature until the yellow color disappeared. NMR measurement indicated the quantitative formation of the Dewar isomer **11b**: ^{1}H NMR (benzene-d_6:THF-d_8 = 3:1, 0 °C) δ 6.78 (s, 4H), 2.48 (t, J = 6.0 Hz, 4H), 2.19 (s, 12H), 1.61 (br m, 4H), 1.26 (br m, 4H); ^{13}C NMR (benzene-d_6:THF-d_8 = 3:1, 0 °C) δ 149.1 (s), 130.0 (s), 128.3 (d), 66.2 (s), 27.4 (t), 26.3 (t), 25.5 (t), 17.0 (q).

A solution of 40 mg of **1c** in 3 mL of benzene was irradiated through a solution filter of 1,4-diphenyl-1,3-butadiene (0.12 M in THF) with a 300 W high-pressure mercury lamp at room temperature for 3 h. The white precipitate formed was filtered and washed with a small portion of hexane to give 20 mg (50%) of the Dewar isomer **11c**. Preliminary experiments by ^{1}H NMR for photoisomerization of **1c** as described for the reaction of **1b** indicated quantitative formation **11c**: white solid; ^{1}H NMR (CD$_2$Cl$_2$, 0 °C) δ 7.27−7.36 (m, 12H), 7.26 (s, 4H), 7.15 (m, 8H), 2.60 (t, J = 5.8 Hz, 4H), 1.12 (br m, 4H), 0.99 (br m, 4H); ^{13}C NMR (CD$_2$Cl$_2$, 0 °C) δ 148.4 (s), 139.2 (s), 137.4 (s), 128.8 (d), 128.5 (d), 128.3 (d), 127.5 (d), 67.8 (s), 28.4 (t), 26.3 (t), 25.3 (t); IR (KBr) 1010, 760, 700 cm^{-1}; UV λ_{max} (CHCl$_3$) 260 (log ϵ 4.65) nm.

Thermal Cycloreversion of Dewar Anthracenophanes 11b and 11c. A solution of **1b** (1.4×10^{-4} M) in cyclohexane was irradiated in a quartz cell with a high-pressure mercury lamp to give a solution

of **11b**, which was then placed in a thermocontrolled cell holder. The progress of the cycloreversion was followed by measuring the appearance of absorption at 455 nm by a spectrometer. For the measurement of the cycloreversion of **11c**, a solution of **11c** 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 at $\lambda = 350$ nm. The kinetic results are given in Table S18 of the supporting information.

X-ray Crystallographic Analyses of Diepoxyanthracenophanes 3b and 5b and Anthracenophanes 1b and 1c. The structures were solved by direct methods and refined using the program package TEXSAN.[33] Bond distances, bond angles, fractional atomic coordinates, and anisotropic thermal parameters are given in the supporting information.

syn,syn-**3b**: $C_{24}H_{28}O_2$, MW = 348.48, monoclinic $P2_1/c$, $a = 14.017(4)$ Å, $b = 8.559(2)$ Å, $c = 17.595(3)$ Å, $\beta = 112.59(2)°$, $V = 1948.8(8)$ Å^3, $Z = 4$, $d_{calcd} = 1.188$ g/cm^3, $R = 0.074$ ($R_w = 0.049$), and GOF = 4.29 for 4768 reflections.

anti,anti-**5b**: $C_{24}H_{28}O_2$, MW = 348.48, orthorhombic $Pca2_1$, $a = 13.045(3)$ Å, $b = 14.439(3)$ Å, $c = 10.555(6)$ Å, $V = 1988(1)$ Å^3, $Z =$

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(33) TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

4, $d_{calcd} = 1.164$ g/cm^3, $R = 0.064$ ($R_w = 0.038$), and GOF = 5.91 for 2611 reflections.

1b: $C_{24}H_{28}$, MW = 316.49, monoclinic $P2_1/c$, $a = 13.620(4)$ Å, $b = 9.286(2)$ Å, $c = 15.645(2)$ Å, $\beta = 115.10(1)°$, $V = 1792.1(6)$ Å^3, $Z = 4$, $d_{calcd} = 1.173$ g/cm^3, $R = 0.066$ ($R_w = 0.034$), and GOF = 1.64 for 4392 reflections.

1c: $C_{44}H_{36}$, MW = 564.77, triclinic $P\bar{1}$, $a = 11.439(2)$ Å, $b = 14.498(2)$ Å, $c = 9.668(2)$Å, $\alpha = 97.37(2)°$, $\beta = 101.40(2)°$, $\gamma = 92.56(1)°$, $V = 1554.7(5)$ Å^3, $Z = 2$, $d_{calcd} = 1.206$ g/cm^3, $R = 0.039$ ($R_w = 0.029$), and GOF = 3.34 for 3150 reflections.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR data for **1a−c**, **2a−c**, **3a−c**, **4a−c**, **5a,b**, **8a,b**, and **11b,c**, data for the crystallographic structure analyses of **3b**, **5b**, **1b**, and **1c**, tables of barriers for flipping of the methylene bridge of diepoxyanthracenophanes **3a−c**, **4a−c**, and **5a,b**, and the kinetic data for thermal cycloreversion of Dewar anthracenophanes **11b** and **11c** (90 pages). See any current masthead page for ordering and Internet access instructions.

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