Supplementary Material Available: Time course of changes observed in the reactions of compounds 10–12 with 3 by methods A and C (Figures 1–3) (the zero value is considered when compounds 13–15 are not detected by ^{1}H NMR), ^{1}H chemical shifts (δ) and coupling constants (Hz) of 5–8, 14–18, and 21–23 (Table II), and ^{13}C chemical shifts of compounds 5–8, 16–18, and 21–23 (Table III) (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Notes

Medium-Sized Cyclophanes. 19.[1] Preparation and Conformational Studies of [*m.n*]Metacyclophanes

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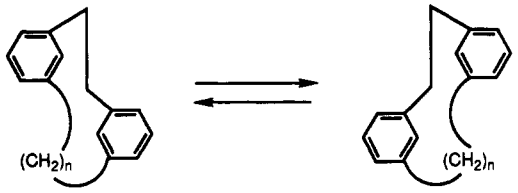
Introduction

The synthesis and stereochemical aspects of conformationally mobile [*m.n*]metacyclophanes (MCP = metacyclophane) have been of interest for the past decade,[2] with particular attention[3] paid to [2.2]MCPs, which possess an anti-stepped conformation. The pioneering work of the conformational investigation of 2,11-dithia[3.3]MCPs was reported by Vögtle et al.[4] Sato and his co-workers have also reported the conformational behavior in the 2-thia-[3.2]MCPs and their analogues.[5] While in [3.3]MCP the aromatic rings preferentially appear to adopt the syn arrangement, its lower and higher homologues, i.e., [3.2]-, [4.2]-, and [4.3]-MCPs, appear to have the mobile anti conformation.[6]

The ring inversion barriers for the higher [*m.n*]MCPs have been determined and increase with decreasing length of the bridges (eq 1).[6] Most of the reported [*m.n*]MCPs,

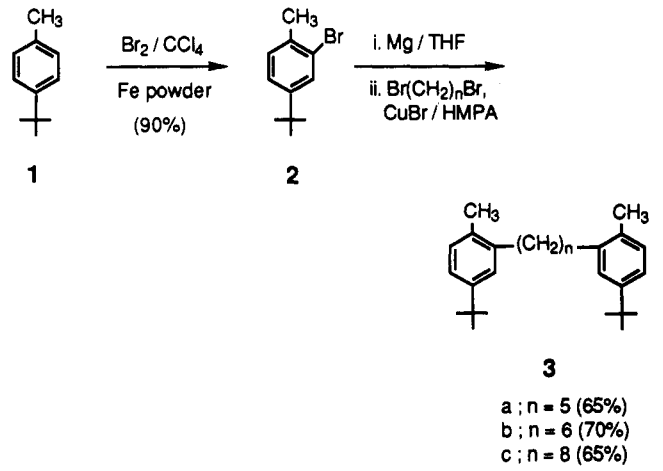


(eq. 1)

n	T_c (°C)	$\Delta G_c^{\ddagger}$ (kcal/mol)
2	>190	>27
3	90	17.5
4	35	14.3

however, are internally unsubstituted ones. Introduction of intraannular substituents such as $-CH_3$ increases the barrier to conformational flipping;[7] for example, both *syn*- and *anti*-9,18-dimethyl-2,11-dithia[3.3]MCP exist as discrete compounds, whereas 2,11-dithia[3.3]MCP itself is conformationally mobile.[8,9] Surprisingly, none of the higher MCPs containing internal methyl substituents appears to have been studied despite the fact that the chemical shift of the $-CH_3$ group provides a convenient probe by ^{1}H NMR of any possible conformation changes. Hence, introduction of substituents into internal positions of higher [*m.n*]MCPs may influence not only the ring inversion but also may give rise to a change of the equilibrium position of syn and anti conformers.

Scheme I



Recently, we have reported[10] the preparation of *anti*-8,16-dimethyl[2.2]MCP, *anti*-9,17-dimethyl[3.2]MCP, and *anti*-10,18-dimethyl[4.2]MCP from toluene by using the *tert*-butyl function as a positional protective group.

We report here the preparation of the [*m.n*]MCPs higher than [4.2]MCP and their conformational behaviors.

Results and Discussion

Preparation of 1,*n*-Bis(5-*tert*-butyl-2-methyl-

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phenyl)alkanes 3. Although it has been previously reported[11] that 1,3-bis(5-*tert*-butyl-2-methylphenyl)propane and 1,4-bis(5-*tert*-butyl-2-methylphenyl)butane could be prepared in six steps from 4-*tert*-butyltoluene, this synthetic route seems too long to be practical. Recently, we have found[12] a simpler and convenient route for the preparation of 1,3-bis(5-*tert*-butyl-2-substituted phenyl)propanes. The cross-coupling reaction of 5-*tert*-butyl-2-substituted phenylmagnesium bromide with 1,3-dibromopropane gave a good yield in refluxing tetrahydrofuran (THF)–hexamethylphosphoramide (HMPA) with cuprous bromide as a catalyst. In fact, the cross-coupling reactions of 5-*tert*-butyl-2-methylphenylmagnesium bromide with other 1,*n*-dibromoalkanes were carried out under the same conditions to give the desired 1,*n*-bis(5-*tert*-butyl-2-methylphenyl)alkanes (**3a–3c**) in good yield as shown in Scheme I.

Preparation of Di-*tert*-butyldimethyl[*n*.2]MCPs 7 and Dimethyl[*n*.2]MCPs 8. The title compounds **7** and **8** were prepared according to Scheme II.

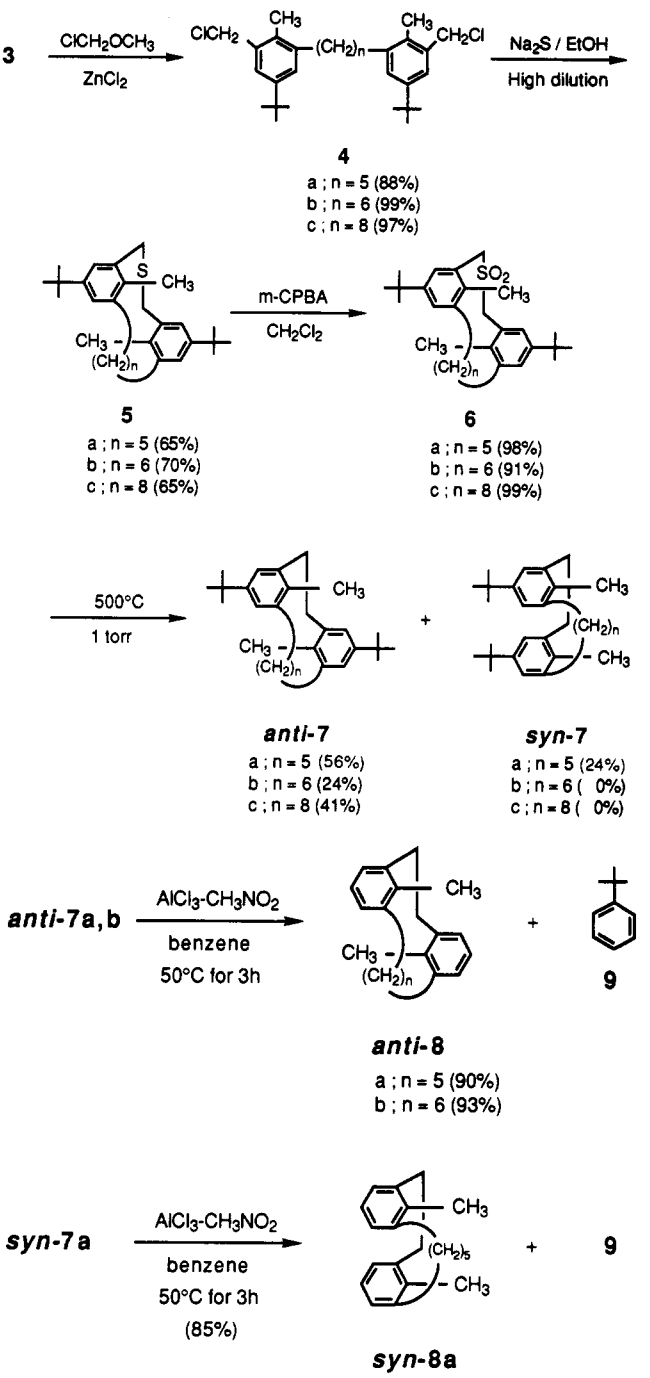
The chloromethylation of diarylalkanes **3a–3c** with chloromethyl methyl ether in the presence of $ZnCl_2$ afforded the corresponding bischloromethyl derivatives **4a–4c** in 88, 99, and 97% yield, respectively.

The cyclization of bis(chloromethyl) derivatives **4a–4c** was carried out under high-dilution conditions in ethanolic Na_2S. Products 9,20-dimethyl-6,17-di-*tert*-butylthia[3.5]- (**5a**), 9,21-dimethyl-6,18-di-*tert*-butylthia[3.6]- (**5b**), and 9,23-dimethyl-6,23-di-*tert*-butylthia[3.8]metacyclophane (**5c**) were obtained in 65, 70, and 65% yield, respectively. The assignment of structure **5** was made from its ^1H NMR spectrum. The internal methyl protons should show an upfield shift due to the ring current of the opposite benzene ring.[13,14] The ^1H NMR spectra of the thia[3.*n*]MCPs **5a**, **5b**, and **5c** prepared in the present work showed the internal methyl protons at 1.47, 1.49, and 1.80 ppm. The conformation of **5b** was also confirmed by X-ray crystallographic analysis.

Oxidation of **5a–5c** with *m*-chloroperbenzoic acid (*m*-CPBA) afforded the corresponding sulfones **6a–6c** in almost quantitative yields. Pyrolysis of **6a–6c** under reduced pressure (1 Torr) was carried out according to the reported method[15–17] to afford *anti*-di-*tert*-butyldimethyl[*n*.2]MCPs *anti*-**7a–7c** and *syn*-di-*tert*-butyldimethyl[5.2]MCP (*syn*-**7a**).

The ^1H NMR spectrum of **7a** showed two kinds of methyl protons, each as a singlet. By careful column chromatography (silica gel, Wako C-300), two conformers, *anti*-**7a** and *syn*-**7a**, were separated. They are thermally stable and not interconvertible (at 180 °C in Me_2SO solution or at 400 °C in the solid state). The ^1H NMR spectra of conformers *anti*-**7a** and *syn*-**7a** showed the methyl protons at 1.19 and 2.25 ppm, respectively. The aromatic protons of the conformer *syn*-**7a** were observed at a much higher field position (6.60 and 6.67 ppm) than that of conformer *anti*-**7a** (6.88 and 7.15 ppm). It is well-known that the internal methyl protons of the *anti*-[2.2]MCPs should show an upfield shift due to the ring current of the opposite aromatic ring.

Scheme II



Although the parent *anti*-[2.2]MCP was first reported as early as 1899 by Pellegrin,[18] the synthesis of *syn*-[2.2]MCP was realized at long last 85 years later. Mitchel et al.[19] successfully prepared *syn*-[2.2]MCP at low temperature using (arene)chromium carbonyl complexation to control the stereochemistry. However, *syn*-[2.2]MCP isomerized readily to the *anti*-isomer above 0 °C. More recently, Itô et al. reported[20] the characterization and isolation of *syn*-[2.2]MCP without complexation. However, the pyrolysis of thia[3.*n*]MCP dioxides to give the corresponding *syn*-[*n*.2]MCPs have not yet been reported. In the present work, we have first prepared the syn conformer *syn*-**7a** by pyrolysis of the corresponding *anti*-sulfone **6a**.

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Table I. Chemical Shifts (δ) of Internal Methyl Protons of 2-Thia[3.*n*]MCPs 5, 2-Thia[3.*n*]MCP Dioxides 6, and [*n*.2]MCPs 7 in $CDCl_3$[a]

methylene no. *n*	2-thia[3.*n*]MCPs 5	2-thia[3.*n*]MCP dioxides 6	[*n*.2]MCPs 7
2	0.84		0.55
3	1.12	1.12	0.68
4	1.28	1.24	0.86
5	1.47	1.23	1.19
6	1.49	1.39	1.25
8	1.80	1.70	1.47

[a] The other signals are given in the Experimental Section.

However, the pyrolysis of *anti*-[3.6]- and -[3.8]sulfones gave exclusively the corresponding anti conformers identical to our previously reported pyrolysis of *anti*-[3.3]- and -[3.4]sulfones.[10]

The ^1H NMR spectra of the MCPs obtained in the present work and those previously reported[10] are summarized in Table I.

The $AlCl_3$–CH_3NO_2-catalyzed trans-*tert*-butylation of *anti*-**7a**, *anti*-**7b**, and *syn*-**7a** was carried out in benzene at 50 °C for 3 h. The corresponding *anti*-**8a**, *anti*-**8b**, and *syn*-**8a** were obtained in 90, 93, and 85% yield, respectively, along with *tert*-butylbenzene (**9**). No syn–anti isomerization with Lewis acid was observed under the reaction conditions used.

Conformational Behavior of [*m*.*n*]MCPs. The solution conformation of [*m*.*n*]MCPs is sensitive to the chain length of the bridges. The ring inversion barriers determined by variable-temperature ^1H NMR decrease with increasing length of the bridges. In the case of thia-[3.*n*]MCP **5** and thia[3.*n*]MCP dioxide **6**, [3.5] analogues **5a** and **6a** are both conformationally rigid below 150 °C on the NMR time scale. The ^1H NMR spectrum of the CH_2SCH_2 bridge of **5b** and **6b** showed a pair of doublets at room temperature. With increasing temperature, the doublets became fused, and finally a singlet peak was observed above 90 and 120 °C, respectively. This behavior strongly suggests that the rate of conformational ring flipping is faster than the NMR time scale above these temperatures. The rate constant (k_c) of the observed conformational interconversion at the coalescence (T_c) can be calculated by using eq 2.[21] The free energy of activation ($\Delta G_c^{\ddagger}$) at coalescence can then be estimated by using the Eyring equation (eq 3).[21]

$$k_c = \pi/2^{1/2}(\Delta\nu^2 + 6J^2)^{1/2} \quad (2)$$

$$\Delta G_c^{\ddagger} = 2.303RT_c(10.32 + \log T_c - \log k_c) \quad (3)$$

Estimated activation energy for ring flipping are 16.6 and 18.9 kcal/mol, respectively (Table II). The activation energy of sulfone **6b** for ring flipping is larger than that of sulfide **5b**. The difference could mainly be attributed to the bulkiness of the sulfone group compared with the sulfide group.

The X-ray crystallographic study of **5b** shows that **5b** adopts the thermodynamically most stable anti conformation and has sufficient space for the conformational flipping.

On the other hand, [3.8] analogues **5c** and **6c** exhibit much more flexible conformational behavior than [3.6] analogues **5b** and **6b**. The signals of the methylene bridge of [5.2]- (**7a**) and [6.2]MCP **7b** do not coalescence below 150 °C, and the energy barriers of flipping are both above 25 kcal/mol, but [8.2]MCP **7c** exhibits conformational flipping above 140 °C. The estimated activation energy for flipping is 20.5 kcal/mol.

In conclusion, we have been the first to demonstrate the preparation of intraannularly substituted [*m*.*n*]MCPs and their solution conformation.

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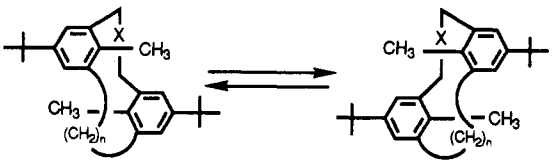
Table II. Coalescence Temperatures and Energy Barriers of 2-Thia[3.*n*]MCPs 5, 2-Thia[3.*n*]MCP Dioxides 6, and [*n*.2]MCPs 7[a]



5 ; X = S
6 ; X = SO_2
7 ; X = —

methylene no. *n*	2-thia[3.*n*]MCPs 5 $T_c(\Delta G_c^{\ddagger})$	2-thia[3.*n*]MCP dioxides 6 $T_c(\Delta G_c^{\ddagger})$	[*n*.2]MCPs 7 $T_c(\Delta G_c^{\ddagger})$
5	>150	>150	>150
6	90 (16.6)	120 (18.9)	>150
8	<–60[b]	–50 (10.3)[b]	140 (20.5)

[a] Key: T_c (°C); $\Delta G_c^{\ddagger}$ (kcal/mol). T_c and $\Delta G_c^{\ddagger}$ were determined in hexachloro-1,3-butadiene using $SiMe_4$ as reference unless otherwise indicated. [b] Solvent:$CDCl_3/CS_2$ = 1/3.

Experimental Section

All melting and boiling points are uncorrected. ^1H NMR spectra were recorded at 270 MHz with Me_4Si as an internal reference. IR spectra were measured as KBr pellets. Mass spectra were obtained at 75 eV using a direct inlet system.

Preparation of 1,5-Bis(5-*tert*-butyl-2-methylphenyl)pentane (3a). To a solution of 3.4 g (143 mmol) of magnesium and a small amount of iodine in 5 mL of THF was added a solution of 17.01 g (70 mmol) of 2-bromo-4-*tert*-butyltoluene (**2**)[11] in 50 mL of THF. The mixture was refluxed for 12 h. To a solution of 6.9 g (30 mmol) of 1,5-dibromopentane and 750 mg (5.25 mmol) of CuBr in 8 mL of HMPA was added gradually a solution of 5-*tert*-butyl-2-methylphenylmagnesium bromide dropwise under the conditions of gentle refluxing. After the reaction mixture had been refluxed for additional 17 h, it was quenched with 10% ammonium chloride aqueous solution and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated in vacuo to leave a residue, which was distilled under reduced pressure to give 5.78 g (65%) of **3a** as a pale yellow liquid: bp 207–208 °C (3 mmHg); ^1H NMR ($CDCl_3$) δ 1.28 (18 H, s), 1.35–1.77 (6 H, m), 2.31 (6 H, s), 2.58 (4 H, t, J = 7.0 Hz), 6.85–7.20 (6 H, m); mass (*m*/*e*) 364 (M^+). Anal. Calcd for $C_{27}H_{40}$: C, 88.94; H, 11.06. Found: C, 88.57; H, 11.21.

Similarly, compounds **3b** and **3c** were prepared in the same manner as described above in 70% and 65% yield.

1,6-Bis(5-*tert*-butyl-2-methylphenyl)hexane (3b): pale yellow liquid; bp > 220 °C (3 mmHg); ^1H NMR ($CDCl_3$) δ 1.29 (18 H, s), 1.30–1.79 (8 H, m), 2.31 (6 H, s), 2.55 (4 H, t, J = 7.0 Hz), 6.85–7.20 (6 H, m); mass (*m*/*e*) 378 (M^+). Anal. Calcd for $C_{28}H_{42}$: C, 88.82; H, 11.17. Found: C, 88.90; H, 11.07.

1,8-Bis(5-*tert*-butyl-2-methylphenyl)octane (3c): colorless prisms (methanol); mp 65–66.5 °C; ^1H NMR ($CDCl_3$) δ 1.31 (18 H, s), 1.36 (8 H, broad s), 1.57 (4 H, broad s), 2.26 (6 H, s), 2.54–2.60 (4 H, m), 7.02–7.18 (6 H, m); mass (*m*/*e*) 406 (M^+). Anal. Calcd for $C_{30}H_{46}$: C, 88.60; H, 11.40. Found: C, 88.15; H, 11.01.

Preparation of 1,5-Bis[5-*tert*-butyl-3-(chloromethyl)-2-methylphenyl]pentane (4a). After a mixture of **3a** (10 g, 27.5 mmol), chloromethyl methyl ether (10 mL, 124 mmol), and zinc chloride (2.7 g, 19.8 mmol) had been refluxed for 4 h, the reaction mixture was poured into a large amount of ice/water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with water, dried over Na_2SO_4, and evaporated in vacuo to afford the crude product, which on recrystallization from hexane gave 11.13 g (88%) of **4a**: colorless prisms (hexane); mp 65–67 °C; ^1H NMR ($CDCl_3$) δ 1.30 (18 H, s), 1.40–1.80 (6 H, m), 2.33 (6 H, s), 2.64 (4 H, t, J = 7.0

Hz), 4.63 (4 H, s), 7.17 (4 H, broad s); mass (*m/e*) 460, 462, 464 (M^+). Anal. Calcd for $C_{29}H_{42}Cl_2$: C, 75.46; H, 9.17. Found: C, 75.07; H, 9.23.

Similarly, compounds **4b** and **4c** were prepared in the same manner as described above in 99% and 97% yield, respectively.

1,6-Bis[5-*tert*-butyl-3-(chloromethyl)-2-methylphenyl]-hexane (4b): colorless prisms (hexane); mp 96–97 °C; ^1H NMR ($CDCl_3$) δ 1.29 (18 H, s), 1.40–1.65 (8 H, m), 2.31 (6 H, s), 2.62 (4 H, t, J = 7.5 Hz), 4.61 (4 H, s), 7.16 (4 H, broad s); mass (*m/e*) 474, 476, 478 (M^+). Anal. Calcd for $C_{30}H_{44}Cl_2$: 75.77; H, 9.32. Found: C, 76.54; H, 9.95.

1,8-Bis[5-*tert*-butyl-3-(chloromethyl)-2-methylphenyl]-octane (4c): colorless prisms (hexane); mp 68–69 °C; ^1H NMR ($CDCl_3$) δ 1.30 (18 H, s), 1.24–1.60 (12 H, m), 2.32 (6 H, s), 2.58–2.68 (4 H, m), 4.63 (4 H, s), 7.16 (4 H, broad s); mass (*m/e*) 502, 504, 506 (M^+). Anal. Calcd for $C_{32}H_{48}Cl_2$: C, 76.31; H, 9.60. Found: C, 76.89; H, 9.59.

Preparation of 6,17-Di-*tert*-butyl-9,20-dimethyl-2-thia-[3.5]metacyclophane (5a). A solution of 6.34 g (13.6 mmol) of **4a** in 400 mL of ethanol and 40 mL of benzene and a solution of 6.72 g (28 mmol) of $Na_2S{\cdot}9H_2O$ in 400 mL of ethanol and 75 mL of water were added separately, but simultaneously, from two Hershberg funnels to boiling ethanol (4 L). When addition was completed (21 h), the mixture was refluxed for 16 h with stirring. Then the reaction was concentrated and the residue extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with water, dried over Na_2SO_4, and concentrated. The residue was column chromatographed over silica gel with a 5:1 benzene–hexane mixture as an eluent to give 3.73 (65%) of **5a**: colorless oil; ^1H NMR ($CDCl_3$) δ 1.19–1.45 (6 H, m), 1.32 (18 H, s), 1.47 (6 H, s), 2.25–2.33 (2 H, m), 2.59–2.69 (2 H, m), 3.63 (2 H, d, J = 14.6 Hz), 3.73 (2 H, d, J = 14.6 Hz), 6.91 (2 H, d, J = 1.8 Hz), 7.38 (2 H, d, J = 1.8 Hz); mass (*m/e*) 422 (M^+). Anal. Calcd for $C_{29}H_{42}S$: C, 82.40; H, 10.02. Found: C, 82.29; H, 10.00.

Similarly, compounds **5b** and **5c** were prepared in the same manner as described above in 70% and 65% yield, respectively.

6,18-Di-*tert*-butyl-9,21-dimethyl-2-thia[3.6]metacyclophane (5b): colorless prisms (hexane); mp 109–112 °C; ^1H NMR ($CDCl_3$) δ 1.33 (18 H, s), 1.40–1.65 (8 H, m), 1.49 (6 H, s), 2.40–2.63 (4 H, broad s), 3.50 (2 H, d, J = 18.0 Hz), 3.80 (2 H, d, J = 18.0 Hz), 6.96 (2 H, broad s), 7.52 (2 H, broad s); mass (*m/e*) 436 (M^+). Anal. Calcd for $C_{30}H_{44}S$: C, 82.51; H, 10.15. Found: C, 82.50; H, 10.52.

6,20-Di-*tert*-butyl-9,23-dimethyl-2-thia[3.8]metacyclophane (5c): colorless oil; ^1H NMR ($CDCl_3$) δ 1.29 (18 H, s), 1.20–1.61 (12 H, m), 1.70 (6 H, s), 2.59 (4 H, broad s), 3.69 (4 H, s), 7.06 (2 H, s), and 7.09 (2 H, s); mass (*m/e*) 464 (M^+). Anal. Calcd for $C_{32}H_{48}S$: C, 82.69; H, 10.41. Found: C, 82.40; H, 10.28.

Preparation of 6,17-Di-*tert*-butyl-9,20-dimethyl-2-thia-[3.5]metacyclophane 2,2-Dioxide (6a). To a solution of 2.92 g (6.92 mmol) of **5a** in 300 mL of CH_2Cl_2 was added 3.58 g (17.65 mmol) of *m*-chloroperbenzoic acid. After the reaction mixture had been stirred at room temperature for 17 h, it was washed with 10% $NaHCO_3$ aqueous solution and brine and dried over Na_2SO_4. The solvent was evaporated in vacuo to leave a residue which was recrystallized from hexane–benzene (1:1) to give 3.10 g (98%) of **6a**: colorless prisms (hexane–benzene (1:1)); mp 114–116 °C; ^1H NMR ($CDCl_3$) δ 1.23 (6 H, s), 1.33 (18 H, s), 1.20–1.77 (6 H, m), 2.15–2.30 (2 H, m), 2.80–2.90 (2 H, m), 4.12 (2 H, d, J = 15.2 Hz), 4.41 (2 H, d, J = 15.2 Hz), 6.99 (2 H, d, J = 1.8 Hz), 7.76 (2 H, d, J = 1.8 Hz); mass (*m/e*) 454 (M^+). Anal. Calcd for $C_{29}H_{42}O_2S$: C, 76.60; H, 9.31. Found: C, 75.98; H, 9.70.

Similarly, compounds **6b** and **6c** were prepared in the same manner as described above in 91% and 99% yield, respectively.

6,18-Di-*tert*-butyl-9,21-dimethyl-2-thia[3.6]metacyclophane 2,2-dioxide (6b): colorless prisms (hexane–benzene (1:1)); mp 198–200 °C; ^1H NMR ($CDCl_3$) δ 0.90–1.15 (4 H, m), 1.34 (18 H, s), 1.39 (6 H, s), 1.50–1.82 (4 H, m), 2.50–2.58 (4 H, m), 4.08 (2 H, d, J = 15.0 Hz), 4.48 (2 H, d, J = 15.0 Hz), 7.11 (2 H, d, J = 2.0 Hz), 7.91 (2 H, d, J = 2.0 Hz); mass (*m/e*) 468 (M^+). Anal. Calcd for $C_{30}H_{44}O_2S$: C, 76.87; H, 9.46. Found: C, 76.17; H, 9.69.

6,20-Di-*tert*-butyl-9,23-dimethyl-2-thia[3.8]metacyclophane 2,2-dioxide (6c): colorless prisms (hexane–benzene (1:1)); mp 169–170 °C; ^1H NMR ($CDCl_3$) δ 1.31 (18 H, s), 1.04–1.60 (12 H, m), 1.70 (6 H, s), 2.58–2.64 (4 H, m), 4.40 (4 H, s), 7.13 (2 H, d, J = 2 Hz), 7.09 (2 H, d, J = 2 Hz); mass (*m/e*) 496 (M^+). Anal. Calcd for $C_{32}H_{48}O_2S$: C, 77.13; H, 9.60. Found: C, 76.95; H, 9.73.

Pyrolysis of Sulfone 6 To Give 7. Typical Procedure. The sulfone **6a** (500 mg, 1.15 mmol) was pyrolyzed at 500 °C under reduced pressure at 1 mmHg using the same procedure reported previously.[15-17] The sublimed product was collected and chromatographed on silica gel with hexane and 1:1 hexane–benzene mixture as eluents to give 251.2 mg (56%) of ***anti*-8,16-di-*tert*-butyl-11,19-dimethyl[5.2]metacyclophane** (*anti*-**7a**) and 107.6 mg (24%) of ***syn*-8,16-di-*tert*-butyl-11,19-dimethyl[5.2]metacyclophane** (*syn*-**7a**), respectively.

***anti*-7a**: colorless prisms (hexane); mp 135–136 °C; ^1H NMR ($CDCl_3$) δ 1.19 (6 H, s), 1.30 (18 H, s), 1.10–1.40 (2 H, m), 2.22–2.38 (4 H, m), 2.58–2.70 (4 H, m), 2.96 (4 H, s), 6.88 (2 H, d, J = 1.83 Hz), 7.15 (2 H, d, J = 1.83 Hz); mass (*m/e*) 390 (M^+). Anal. Calcd for $C_{29}H_{42}$: C, 89.16; H, 10.84. Found: C, 88.56; H, 11.28.

***syn*-7a**: colorless oil; ^1H NMR ($CDCl_3$) δ 1.16 (18 H, s), 1.10–1.40 (2 H, m), 2.25 (6 H, s), 2.22–2.40 (4 H, m), 2.55–2.70 (4 H, m), 2.98–3.06 (2 H, m), 3.38–3.45 (2 H, m), 6.60 (2 H, d, J = 2 Hz), 6.67 (2 H, d, J = 2 Hz); mass (*m/e*) 390 (M^+). Anal. Calcd for $C_{29}H_{42}$: C, 89.16; H, 10.84. Found: C, 88.90; H, 10.97.

Similarly, compounds *anti*-**7b** and *anti*-**7c** were prepared in the same manner as described above. The yields are summarized in Scheme II.

***anti*-9,17-Di-*tert*-butyl-12,20-dimethyl[6.2]metacyclophane (*anti*-7b)**: colorless prisms (hexane); mp 133–134 °C; ^1H NMR ($CDCl_3$) δ 0.88–1.02 (4 H, m), 1.25 (6 H, s), 1.31 (18 H, s), 1.35–1.70 (4 H, m), 2.46 (4 H, t, J = 7.0 Hz), 2.99 (4 H, s), 6.95 (2 H, d, J = 2.2 Hz), 7.16 (2 H, d, J = 2.2 Hz); mass (*m/e*) 404 (M^+). Anal. Calcd for $C_{30}H_{44}$: C, 89.16; H, 10.84. Found: C, 88.30; H, 11.16.

***anti*-11,19-Di-*tert*-butyl-14,22-dimethyl[8.2]metacyclophane (*anti*-7c)**: colorless oil; ^1H NMR ($CDCl_3$) δ 0.90–1.51 (12 H, m), 1.31 (18 H, s), 1.47 (6 H, s), 2.25–2.40 (2 H, m), 2.60–2.75 (2 H, m), 2.95–3.15 (8 H, m), 6.87 (2 H, d, J = 2.0 Hz), 7.20 (2 H, d, J = 2.0 Hz); mass (*m/e*) 432 (M^+). Anal. Calcd for $C_{32}H_{48}$: C, 88.82; H, 11.18. Found: C, 88.26; H, 11.42.

Trans-*tert*-butylation of *anti*-7 To Give *anti*-8. Typical Procedure. To a solution of 407 mg (1.04 mmol) of *anti*-**7a** in 50 mL of benzene was added a solution of 81 mg (0.61 mmol) of anhydrous aluminum chloride in 0.16 mL of nitromethane. After the reaction mixture was stirred for 6 h at 50 °C, the reaction was quenched by the addition of 10% hydrochloric acid, and the solution was washed with water, dried over Na_2SO_4, and concentrated in vacuo to leave a residue that upon recrystallization from hexane gave 261.2 mg (90%) of ***anti*-11,19-dimethyl-[5.2]metacyclophane** (*anti*-**8a**): colorless prisms (hexane); mp 118–119 °C; ^1H NMR ($CDCl_3$) δ 0.80–0.92 (2 H, m), 1.23 (6 H, s), 1.20–1.50 (4 H, m), 2.27–2.40 (2 H, m), 2.58–2.70 (2 H, m), 2.97 (4 H, s), 6.88 (2 H, dd, J = 1.0, 7.3 Hz), 7.01 (2 H, dd, J = 7.3, 7.3 Hz), 7.14 (2 H, dd, J = 1.0, 7.3 Hz); mass (*m/e*) 278 (M^+). Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.45; H, 9.50.

Similarly, compound *anti*-**8b** was prepared in the same manner as described above in 93% yield.

***anti*-12,20-Dimethyl[6.2]metacyclophane (*anti*-8b)**: colorless prisms (hexane); mp 133–134 °C; ^1H NMR ($CDCl_3$) δ 0.90–1.20 (4 H, m), 1.43 (6 H, s), 1.50–1.90 (4 H, m), 2.58–2.62 (4 H, m), 3.11 (4 H, s), 7.07 (2 H, dd, J = 1.0, 7.3 Hz), 7.18 (2 H, dd, J = 7.3, 7.3 Hz), 7.24 (2 H, dd, J = 1.0, 7.3 Hz); mass (*m/e*) 292 (M^+). Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.41; H, 9.73.

Trans-*tert*-butylation of *syn*-7a To Give *syn*-8a. To a solution of 407 mg (1.04 mmol) of *syn*-**7a** in 50 mL of benzene was added a solution of 81 mg (0.61 mmol) of anhydrous aluminum chloride in 0.16 mL of nitromethane. After the reaction mixture was stirred for 6 h at 50 °C, it was treated as described above to give 246.7 mg (85%) of ***syn*-11,19-dimethyl[5.2]metacyclophane** (*syn*-**8a**): colorless oil; ^1H NMR ($CDCl_3$) δ 1.22–1.50 (2 H, m), 2.00–2.30 (4 H, m), 2.15 (6 H, s), 2.40–2.60 (4 H, m), 2.80–3.00 (2 H, m), 3.25–3.40 (2 H, m), 6.45–6.60 (6 H, m); mass (*m/e*) 278 (M^+). Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.36; H, 9.39.

Supplementary Material Available: X-ray data for **5b** and ^1H NMR spectra showing the dynamic behavior of **6c** and **7c** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.