Medium-Sized Cyclophanes.[1] Bromination of 8-Methoxy[2.2]metacyclophanes

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When 8-methoxy[2.2]metacyclophanes **5** are treated with benzyl trimethylammonium tribromide in dichloromethane, the transannular reaction products, tetrahydropyrene **6** and **7** are obtained along with 5-bromo-8-methoxy[2.2]metacyclophanes **8**. The bromination of 5-*tert*-butyl-8-methoxy[2.2]metacyclophanes **9a–9g** in dichloromethane is carried out under the same conditions to afford tetrahydropyrene derivatives exclusively. On the other hand, when the bromination reactions are performed in various alcohols, alkoxy-substituted tetrahydropyrenes **11** and **12** are obtained in good yields, which are easily dehydrogenated with DDQ to afford the corresponding pyrene derivatives. The reaction mechanisms of the above reactions are also discussed.

Introduction

Sato and his co-workers[2] have reported that reaction of 8,16-unsubstituted [2.2]metacyclophane (MCP = metacyclophane) with bromine in the presence of iron powder afforded the corresponding tetrahydropyrene via the addition–elimination mechanism.

Recently, we reported[3] that bromination of 8,16-dimethyl[2.2]MCP with bromine in the presence or absence of iron powder as a catalyst afforded different types of products and that similar reactions of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP also gave different types of products, 2,7-di-*tert*-butyl-4,5,9,10-tetrabromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene and 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene, respectively (Scheme I).

On the other hand, although some 8-monosubstituted [2.2]MCPs have been prepared,[4,5] there has not been any report concerning the bromination of these compounds.

We report here the bromination of 8-monosubstituted [2.2]MCPs in order to obtain information about their chemical natures for electrophilic substitution reactions.

Results and Discussion

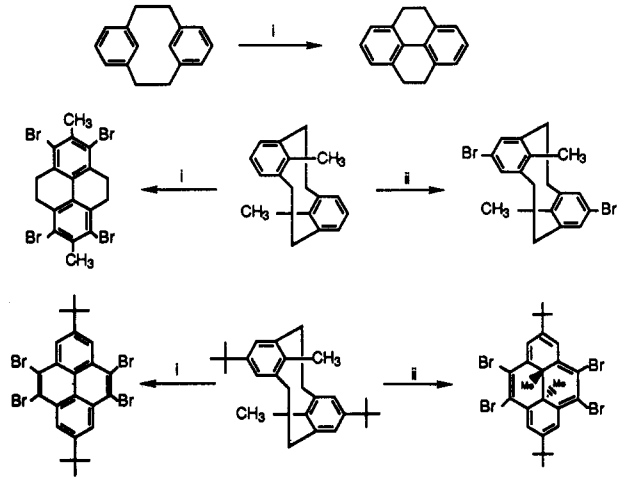
The preparative route to 8-methoxy[2.2]MCPs **5a–5c** is shown in Scheme II and the preparations of **1** and **2** are described in a previous paper.[5] Compounds **3** were prepared according to the reported methods,[5–7] respectively. The desired **5a–5c** were prepared from the corresponding **1** and **2** via the disulfides **3** and bissulfones **4**. The preparation of other 5-*tert*-butyl-8-methoxy[2.2]MCPs **9a–9g** was previously reported.[4,5]

Attempted bromination of 8-methoxy[2.2]MCP (**5a**) with 6 equiv of bromine in carbon tetrachloride carried out under the same reaction conditions as [2.2]MCP[2] and 8,16-dimethyl[2.2]MCPs[3] failed to produce readily identifiable products. In contrast, compound **5a** was treated with an equimolar amount of benzyltrimethylammonium tribromide (BTMA Br_3) in dichloromethane, which was recently found to be a convenient solid brominating agent,[8] to afford the corresponding tetrahydropyrene (**6a**) and 2-bromotetrahydropyrene (**7a**) along with 5-bromo-8-methoxy[2.2]MCP (**8a**).

Bromination of other 8-methoxy-13-substituted [2.2]-MCPs **5b–5c** was also carried out under the same conditions in order to obtain information about the effect of substituents at the 13 position of 8-methoxy[2.2]MCP. The results are summarized in Table I.

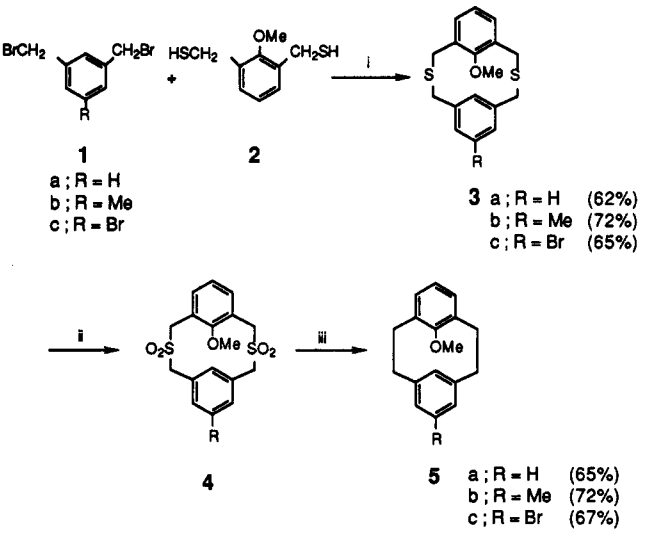
As shown in Table I, in the case of **5b**, having an electron-releasing group such as methyl, the yield of the transannular reaction products tetrahydropyrenes **6b** and **7b** increased. In contrast, the reaction of **5c**, having an electron-withdrawing group, with BTMA Br_3, did not af-

Scheme I[a]



[a] Key: (i) $Br_2/Fe/CCl_4$; (ii) Br_2/CCl_4.

Scheme II[a]



[a] Key: (i) KOH/EtOH, high dilutions; (ii) *m*-chloroperbenzoic acid/$CHCl_3$; (iii) 500 °C (1 mmHg).

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(1) Medium-Sized Cyclophanes. 2. Part 1: Yamato, T.; Miyazawa, A.; Tashiro, M. Submitted to *J. Org. Chem.*

(2) Sato, T.; Wakabayashi, M.; Okamura, T.; Amada, T.; Hata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2363.

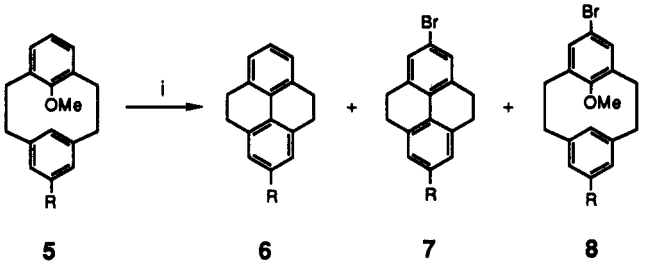
0022-3263/92/1957-0271$03.00/0

Table I. Bromination of 8-Methoxy[2.2]metacyclophanes 5 with BTMA Br_3 in CH_2Cl_2

substrate (5)	product yield[a] (%)		
R = H	**6a** (7.1)	**7a** (32.0)	**8a** (58.3)
R = CH_3	**6b** (9.5)	**7b** (61.4)	**8b** (25.6)
R = Br	**6c** (0)	**7c** (0)	**8c** (100)

[a] Yields were determined by GC analysis.

ford the transannular products **6c** and **7c**. Instead, only the corresponding 5,13-dibromo-8-methoxy[2.2]MCP (**8c**) is formed exclusively. These results suggested that the



5 **6** **7** **8**

a ; R = H
b ; R = Me
c ; R = Br

a ; R = H
b ; R = Me
c ; R = Br

[a] (i) BTMA Br_3 (1.1 eq.) in CH_2Cl_2, r.t. for 5 min.

transannular cyclization reaction to give **6** and **7** was affected by the π-electron density of the benzene ring of the other side.

It was also found that the bromination of **6b** and **8b** with BTMA Br_3 under the same reaction conditions did not afford any reaction product, and **6b** and **8b** were recovered in quantitative yield (Scheme III). These results suggest that compounds **6** and **8** should not be intermediates for the formation of **7** in the bromination of **5**.

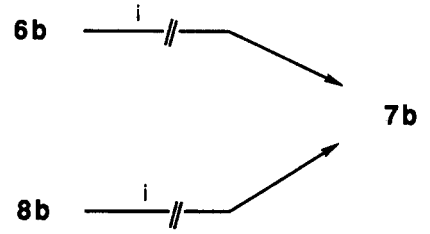
In order to study this bromination reaction in more detail, we have attempted to protect the 5-position of 8-methoxy[2.2]metacyclophanes by the bulky substituent, *tert*-butyl group. The bromination of 5-*tert*-butyl-8-methoxy[2.2]metacyclophanes **9a–9g** with BTMA Br_3 in dichloromethane was carried out under the same conditions as described above.

As shown in Scheme IV, the reaction of **9a–9d** with BTMA Br_3 gave exclusively the corresponding tetrahydropyrenes **10a–10d**, respectively. In contrast, the reaction of **9e–9g**, having electron-withdrawing groups such as bromo, cyano and nitro at the 13 position did not afford any reaction product, and **9e–9g** were recovered in quantitative yield.

Although the detailed mechanism of formation of **10** is not clear, one might assume the reaction pathway shown in Scheme V.

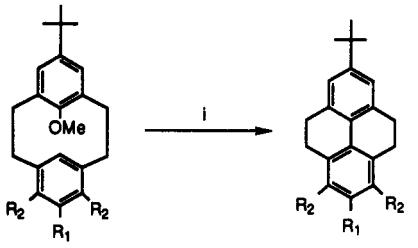
It seems reasonable to assume that when R (in **9**) is electron donating, interannular bond formation at the 8- and 16-positions is concerted with bromophilic attack at the ipso position of the *tert*-butyl group to form inter-

Scheme III[a]



[a] Key: (i) BTMA Br_3 (1.1 equiv) in CH_2Cl_2, rt for 5 min.

Scheme IV[a]

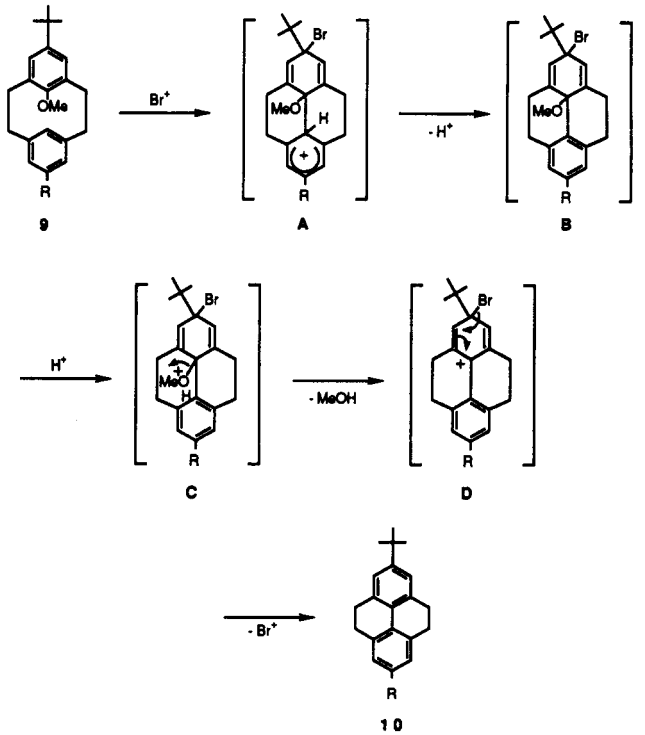


9 **10**

a ; $R_1 = R_2 = H$ — a ; $R_1 = R_2 = H$ (69 %)
b ; $R_1 = Me$, $R_2 = H$ — b ; $R_1 = Me$, $R_2 = H$ (81 %)
c ; $R_1 = t\text{-Bu}$, $R_2 = H$ — c ; $R_1 = t\text{-Bu}$, $R_2 = H$ (86 %)
d ; $R_1 = R_2 = Me$ — d ; $R_1 = R_2 = Me$ (95%)
e ; $R_1 = Br$, $R_2 = H$ — e ; $R_1 = Br$, $R_2 = H$ (no reaction)
f ; $R_1 = CN$, $R_2 = H$ — f ; $R_1 = CN$, $R_2 = H$ (no reaction)
g ; $R_1 = NO_2$, $R_2 = H$ — g ; $R_1 = NO_2$, $R_2 = H$ (no reaction)

[a] Key: (i) BTMA Br_3 (1.1 equiv) in CH_2Cl_2, rt for 5 min.

Scheme V



9 **A** **B** **C** **D** **10**

mediate A. When R is an electron-attracting group such as Br, CN, and NO_2 (e.g., in **9e–9g**), the intermediate A does not form because of deactivation of the second aromatic ring by these groups. The aromatization transforming A to B generates acid which can facilitate removal of the methoxy group from C, generating a cyclohexadienyl

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(4) Tashiro, M.; Yamato, T.; Kobayashi, K.; Arimura, T. *J. Org. Chem.* **1987**, *52*, 3196.
(5) Tashiro, M.; Mataka, S.; Takezaki, Y.; Takeshita, M.; Arimura, T.; Tsuge, A.; Yamato, T. *J. Org. Chem.* **1989**, *54*, 451.
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(8) Kajigaeshi, S.; Kakinami, T.; Tokiyama, H.; Hirakawa, T.; Okamoto, T. *Chem. Lett.* **1987**, 627.

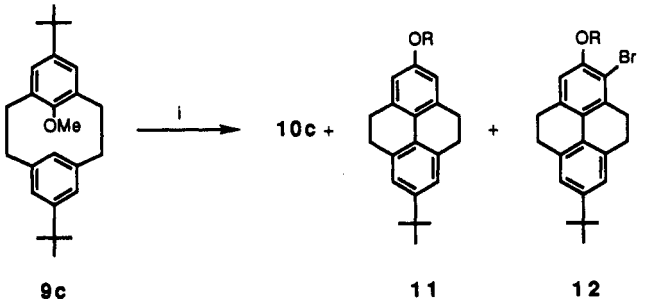
Table II. Bromination of 8-Methoxy[2.2]metacyclophane 9c with BTMA Br_3 in Alcohols and Acetic Acid

run	ROH	BTMA Br_3/9c (mol/mol)	products yield[a] (%)		
1	MeOH	1.1	10c (<1)	11a (43.7)	12a (27.2)
2	MeOH	2.1	10c (3.1)	11a (8.6)	12a (86.5)
3	EtOH	2.1	10c (19.5)	11b (2.9)	12b (65.5)
4	n-PrOH	2.1	10c (15.3)	11c (1.2)	12c (76.6)
5	AcOH	1.1	10c (96.8)	11d (0)	12d (0)

[a] Yields were determined by GC analysis.

cation D. Removal of Br^+ now restores aromaticity to that ring; Br^- can serve as a nucleophile in this process.

In order to provide evidence of the intermediate B, we have attempted to trap this intermediate or the intermediate F (see Scheme VIII) by carrying out the reaction in alcohol and acetic acid solution. The reaction of **9c** with BTMA Br_3 in alcohol solution was carried out under the same reaction conditions as dichloromethane solution, but the intermediate F was in fact not trapped. Only 2-alkoxytetrahydropyrene **11** and 1-bromo-2-alkoxytetrahydropyrene **12** were obtained along with 2,7-di-*tert*-butyl-4,5,9,10-tetrahydropyrene (**10c**) (Table II).



a ; R = Me
b ; R = Et
c ; R = n-Pr
d ; R = $COCH_3$

[a] (i) BTMA Br_3 in ROH, r.t. for 5 min.

It was also found that the reaction of **10c** with 1.1 equiv of BTMA Br_3 under the same conditions resulted in the recovery of the starting compounds in almost quantitative yield. However, the reaction of **11a** with 1.1 equiv of BTMA Br_3 afforded compound **12a** in 95% yield (Scheme VI).

Scheme VI[a]

$$\mathbf{10c} \xrightarrow{i} \text{no reaction}$$

$$\mathbf{11a} \xrightarrow[(95\%)]{i} \mathbf{12a}$$

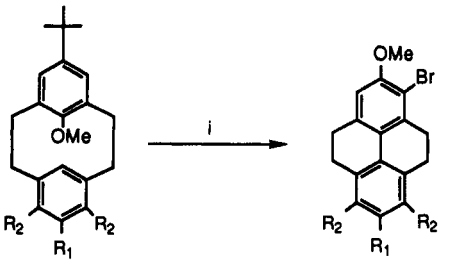
[a] Key: (i) BTMA Br_3 (1.1 equiv) in ROH, rt for 5 min.

This result strongly suggests that compound **11** was the intermediate for the formation of **12**.

On the other hand, when the reaction was carried out in acetic acid, only 2,7-di-*tert*-butyl-4,5,9,10-tetrahydropyrene (**10c**) was obtained in 97% yield. This result is explained in that acetic acid behaves as acid to remove the methoxy group from the intermediate B by protonation as shown in Scheme V.

Furthermore, it was also found that the reaction of **9c** with BTMA Br_3 in alcohol to afford 1-bromo-2-alkoxytetrahydropyrene **12** can be applied other 8-methoxy[2.2]MCPs (**9a**, **9b**, and **9d**) (Scheme VII). In fact, 8-methoxy[2.2]MCPs **9a**, **9b**, and **9d** were treated with

Scheme VII[a]

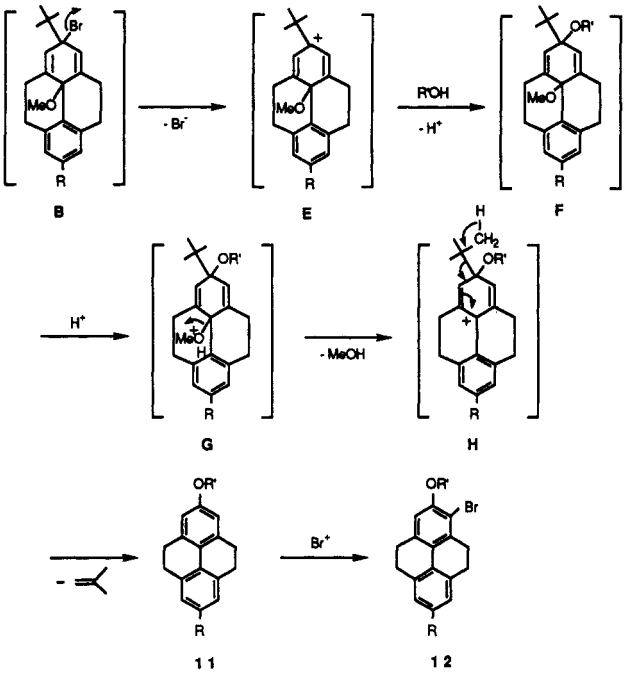


9 **12**

a ; $R_1 = R_2 = H$
b ; R_1 = Me, $R_2 = H$
d ; $R_1 = R_2$ = Me
e ; $R_1 = R_2 = H$ (92%)
f ; R_1 = Me, $R_2 = H$ (85%)
g ; $R_1 = R_2$ = Me (94%)

[a] Key: (i) BTMA Br_3 (2.1 equiv) in MeOH, rt for 5 min.

Scheme VIII



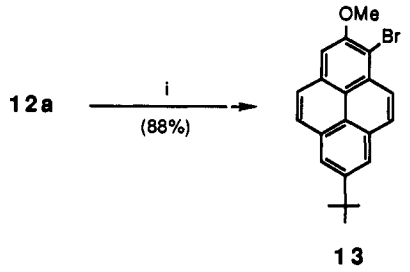
BTMA Br_3 in methanol to give the corresponding 1-bromo-2-methoxy-4,5,9,10-tetrahydropyrenes **12e**, **12f**, and **12g** in good yield, respectively (Scheme VII). Therefore, this method appears to be practical for removal of *tert*-butyl group as well as introduction of alkoxy groups into 2-position of 4,5,9,10-tetrahydropyrenes.

From the above results, one might assume the reaction pathway of formation of **11** and **12** as shown in Scheme VIII.

From the intermediate *B* as shown in Scheme VIII, Br^- can be eliminated by assistance of both Br_2 and quaternary ammonium cation, generating cyclohexadienyl cation intermediate E. The resultant cyclohexadienyl cation then might be trapped by reaction with alcohol to form F, and previously generated acid again could assist in removal of methoxy group. From the intermediate G the *tert*-butyl group might be removed as isobutene via basic attack on one of the nine methyl protons and the whole aromatization process could be concerted to give **11**, which is further brominated by BTMA Br_3 to afford **12**.

Dehydrogenation of **12a** with DDQ in benzene afforded the corresponding pyrene **13** in good yield (Scheme IX). The above results suggest that the reaction route **9** → **12**

Scheme IX[a]



[a] Key: (i) DDQ in benzene, reflux for 4 h.

→ **13** might be useful for the preparation of pyrene derivatives having alkoxy group.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were recorded at 270 MHz on a Nippon Denshi JEOL FT-270 NMR spectrometer with Me_4Si as an internal reference. IR spectra were measured on KBr pellets or a liquid film on NaCl plates on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct inlet system.

Materials. Preparation of [2.2]MCPs **9a–9g** were previously described.[4,5] The other [2.2]MCPs **5a–5c** were prepared according to the route shown in Scheme II.

Preparation of 9-Methoxydithia[3.3]metacyclophanes 3. Typical Procedure. A solution of 3.61 g (18 mmol) of α,α'-dibromo-*m*-xylene (**1a**) and 3.02 g (18 mmol) of 2,6-bis(mercaptomethyl)anisole (**2**) in 200 mL of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 3.29 g (58 mmol) of potassium hydroxide and 0.78 g (27 mmol) of sodium borohydride in 4.0 L of absolute ethanol. When addition was complete (12 h), the reaction mixture was concentrated and the residue was extracted with 500 mL of dichloromethane. The dichloromethane extract was concentrated and the residue was chromatographed over silica gel using a mixture of hexane–benzene 1:1 as an eluent to give a colorless solid, which was recrystallized from hexane to afford 3.37 g (62%) of 9-methoxy-2,11-dithia[3.3]metacyclophane (**3a**): colorless prisms (hexane); mp 162 °C; ^1H NMR ($CDCl_3$) δ 3.49 (2 H, d, J = 14.6 Hz), 3.69 (2 H, d, J = 14.6 Hz), 3.73 (3 H, s), 3.78 (2 H, d, J = 14.6 Hz), 4.26 (2 H, d, J = 14.6 Hz), 6.65 (1 H, br s), 6.8–7.0 (5 H, m), 7.09 (1 H, s); MS m/e 302 (M^+). Anal. Calcd for $C_{17}H_{18}OS_2$: C, 67.51; H, 6.00. Found: C, 67.34; H, 6.05.

Similarly, compounds **3b** and **3c** were synthesized in the same manner as described above.

9-Methoxy-15-methyl-2,11-dithia[3.3]metacyclophane (3b): yield 72%; colorless prisms (hexane); mp 184–185 °C; ^1H NMR ($CDCl_3$) δ 2.11 (3 H, s), 3.72 (3 H, s), 3.47, 4.25 (8 H, AB pattern, J = 14 Hz), 6.57–6.96 (6 H, m); MS m/e 316 (M^+). Anal. Calcd for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37. Found: C, 68.48; H, 6.32.

9-Methoxy-15-bromo-2,11-dithia[3.3]metacyclophane (3c): yield 65%; colorless prisms (hexane); mp 180–182 °C; ^1H NMR ($CDCl_3$) δ 3.49 (2 H, d, J = 14.5 Hz), 3.64 (2 H, d, J = 14.5 Hz), 3.69 (3 H, s), 3.75 (2 H, d, J = 14.5 Hz), 4.24 (2 H, d, J = 14.5 Hz), 6.76 (1 H, t, J = 7.5 Hz), 6.96–7.02 (5 H, m); MS m/e 380, 382 (M^+). Anal. Calcd for $C_{17}H_{17}OS_2Br$: C, 53.54; H, 4.49. Found: C, 53.34; H, 4.57.

Preparation of 9-Methoxy-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetraoxide (4). Typical Procedure. To a solution of 2.0 g (6.6 mmol) of **3a** in 150 mL of chloroform was added 5.10 g (29.5 mmol, 85% purity) of *m*-chloroperbenzoic acid at 0 °C while stirring with a magnetic stirrer. After the solution was stirred for 48 h at room temperature, the solvent was evaporated in vacuo to leave the residue which was washed with 10% sodium bicarbonate solution, water, and ethanol to afford 2.40 g (99%) of 9-methoxy-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (**4a**): colorless prisms; mp >300 °C; ^1H NMR ($CDCl_3$) δ 3.78 (3 H, s), 3.93, 3.99 (2 H, dd, J = 3.2, 14.4 Hz), 4.14, 4.20 (2 H, dd, J = 3.2, 14.4 Hz), 4.40, 4.83 (each 2 H, d, J = 14.4 Hz), 6.82 (1 H, t, J = 8.0 Hz), 7.29–7.36 (6 H, m); MS m/e 366 (M^+). Anal. Calcd for $C_{17}H_{18}O_5S_2$: C, 54.24; H, 4.82. Found: C, 54.40; H, 5.02.

Compounds **4b** and **4c** were prepared according to the method described above.

9-Methoxy-15-methyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (4b): yield 95%; colorless prisms; mp >300 °C; ^1H NMR ($CDCl_3$) δ 2.06 (3 H, s), 3.71 (3 H, s), 4.04–5.00 (8 H, m), 6.65 (1 H, s), 7.29–7.36 (5 H, m); MS m/e 380 (M^+). Anal. Calcd for $C_{18}H_{20}O_5S_2$: C, 56.82; H, 5.30. Found: C, 56.95; H, 5.46.

9-Methoxy-15-bromo-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (4c): yield 96%; colorless prisms; mp >300 °C; ^1H NMR ($CDCl_3$) δ 3.78 (3 H, s), 3.97 (2 H, d, J = 15.0 Hz), 3.97–4.20 (2 H, m), 4.31–4.42 (2 H, m), 4.82 (2 H, dd, J = 15.0, 4.4 Hz), 6.89 (1 H, t, J = 8.0 Hz), 7.29–7.46 (5 H, m); MS m/e 446, 448 (M^+). Anal. Calcd for $C_{17}H_{17}O_5BrS_2$: C, 45.85; H, 3.85. Found: C, 46.11; H, 3.89.

Pyrolysis of Disulfone 4 To Give 8-Methoxy[2.2]metacyclophane (5a). Pyrolysis of disulfones of [2.2]metacyclophane **4** was carried out in an apparatus consisting of a horizontal tube (15 mm in diameter) passing through two adjacent tube furnace, each of which 20 cm long. The first furnace provided a temperature that would induce sublimation of the sulfone; the second was used at a higher temperature (500 °C) that would assure pyrolysis. A vacuum pump was connected at the exit from the second furnace. Disulfone **4a** (1 g) was pyrolyzed at 500 °C under reduced pressure (2–3 mmHg) in the above apparatus as follows. The sample of disulfone was placed in the first furnace, and small glass beads were collected and chromatographed on silica gel with hexane to yield the desired [2.2]metacyclophane. Recrystallization from methanol afforded 442.3 mg (65%) of 8-methoxy[2.2]-metacyclophane (**5a**): colorless prisms (hexane); mp 107–108 °C; ^1H NMR ($CDCl_3$) δ 2.07–2.16 (2 H, m), 2.54–2.63 (2 H, m), 2.73–2.81 (2 H, m), 2.96–3.07 (2 H, m), 3.01 (3 H, s), 4.03 (1 H, s), 7.02–7.13 (6 H, m); MS m/e 238 (M^+). Anal. Calcd for $C_{17}H_{18}O$: C, 85.68; H, 7.61. Found: C, 85.67; H, 7.65.

Compounds **5b** and **5c** were prepared according to the method described above.

13-Methyl-8-methoxy[2.2]metacyclophane (5b): yield 72%; colorless prisms (hexane); mp 72–73 °C; ^1H NMR ($CDCl_3$) δ 2.29 (3 H, s), 1.95–2.96 (8 H, m), 3.01 (3 H, s), 3.85 (1 H, br s), 6.83 (2 H, s), 7.02 (3 H, s); MS m/e 252 (M^+). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.97; H, 8.21.

13-Bromo-8-methoxy[2.2]metacyclophane (5c): yield 67%; colorless prisms (hexane); mp 99–103 °C; ^1H NMR ($CDCl_3$) δ 2.02–2.99 (8 H, m), 3.06 (3 H, s), 3.98 (1 H, s), 7.07 (3 H, m), 7.19 (2 H, d, J = 1.47 Hz); MS m/e 316, 318 (M^+). Anal. Calcd for $C_{17}H_{17}OBr$: C, 64.36; H, 5.40. Found: C, 64.10; H, 5.37.

Bromination of 8-Methoxy[2.2]metacyclophane (5) with BTMA Br_3 in Dichloromethane. Typical Procedure. To a solution of 100 mg (0.41 mmol) of **5a** in 10 mL of dichloromethane was added 177 mg (0.45 mmol) of benzyltrimethylammonium tribromide at room temperature. After the reaction mixture was stirred for 5 min, it was poured into a large amount of water. The organic layer was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to leave a residue which was analyzed by GLC. The structures were determined by ^1H NMR and by the comparison of the retention time of GLC with the authentic samples.

4,5,9,10-Tetrahydropyrene (6a): colorless prisms (methanol); mp 136–138 °C (lit.[9] mp 137–138 °C).

2-Bromo-4,5,9,10-tetrahydropyrene (7a): colorless prisms (methanol); mp 96.5–98 °C (lit.[10] mp 96–98 °C).

2-Methyl-4,5,9,10-tetrahydropyrene (6b): colorless prisms (methanol); mp 97–98 °C (lit.[5] mp 97–98 °C).

2-Bromo-7-methyl-4,5,9,10-tetrahydropyrene (7b): colorless prisms (methanol); mp 157–159 °C (lit.[5] mp 157–159 °C).

13-Bromo-8-methoxy[2.2]metacyclophane (8a): colorless prisms (hexane); mp 140–142 °C; ^1H NMR ($CDCl_3$) δ 2.15–3.01 (8 H, m), 2.99 (3 H, s), 4.22 (1 H, s), 7.06–7.18 (5 H, br s); MS m/e 316, 318 (M^+). Anal. Calcd for $C_{17}H_{17}OBr$: C, 64.36; H, 5.40. Found: C, 64.57; H, 5.47.

5-Bromo-8-methoxy-13-methyl[2.2]metacyclophane (8b): colorless prisms (hexane); mp 122–123 °C; ^1H NMR ($CDCl_3$) δ

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2.09–2.20 (2 H, m), 2.29 (3 H, s), 2.48–2.60 (2 H, m), 2.68–2.72 (2 H, m), 2.94–3.00 (2 H, m), 3.00 (3 H, s), 4.05 (1 H, br s), 6.85 (2 H, br s), 7.17 (2 H, s); MS *m/e* 330, 332 (M^+). Anal. Calcd for $C_{18}H_{19}OBr$: C, 65.26; H, 5.78. Found: C, 64.99; H, 5.88.

5,13-Dibromo-8-methoxy[2.2]metacyclophane (8c): colorless prisms (methanol); mp 136–138 °C; ^1H NMR ($CDCl_3$) δ 2.06–3.01 (8 H, m), 3.04 (3 H, s), 4.16 (1 H, s), 7.19 (4 H, m); MS *m/e* 394, 396, 398 (M^+). Anal. Calcd for $C_{17}H_{16}Br_2O$: C, 51.54; H, 4.07. Found: C, 51.45; H, 4.06.

Bromination of 8-Methoxy-5-*tert*-butyl[2.2]metacyclophanes 9a–9g with BTMA Br_3 in Dichloromethane. Typical Procedure. To a solution of 100 mg (0.34 mmol) of **9a** in 10 mL of dichloromethane was added 141.4 mg (0.374 mmol) of benzyltrimethylammonium tribromide at room temperature. After the reaction mixture was stirred for 5 min, it was poured into a large amount of water. The organic layer was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to leave a residue, which was recrystallized from hexane to give 61.5 mg (69%) of 2-*tert*-butyl-4,5,9,10-tetrahydropyrene (**10a**) as colorless prisms, mp 108–109 °C (lit.[5] mp 108–109.5 °C).

2-Methyl-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (10b): yield 81%; colorless prisms (methanol); mp 116–117 °C (lit.[5] mp 116–117 °C).

2,7-Di-*tert*-butyl-4,5,9,10-tetrahydropyrene (10c): yield 86%; colorless prisms (methanol); mp 234–235 °C (lit.[11] mp 223–234 °C).

1,2,3-Trimethyl-7-*tert*-butyltetrahydropyrene (10d): yield 95%; colorless prisms (methanol); mp 190–191 °C (lit.[5] mp 190–191 °C).

Bromination of 8-Methoxy-5-*tert*-butyl[2.2]metacyclophane (9c) with BTMA Br_3 in Alcohols. Typical Procedure. To a solution of 100 mg (0.286 mmol) of **9c** in 10 mL of methanol was added 119.1 mg (0.315 mmol) of benzyltrimethylammonium tribromide at room temperature. After the reaction mixture was stirred for 5 min, it was poured into a large amount of water and extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to leave a residue, which was analyzed by GLC. The structures were determined by ^1H NMR and by the comparison of the retention time of GLC with the authentic samples. Compounds **12a–12c** were isolated by recrystallization from methanol the reaction residues, which were obtained in runs 2–4.

2-Methoxy-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (11a): colorless prisms (methanol); mp 130–133 °C; ^1H NMR ($CDCl_3$) δ 1.34 (9 H, s), 2.86 (8 H, s), 3.82 (3 H, s), 6.62 (2 H, s), 7.08 (2 H, s); MS *m/e* 292 (M^+). Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.01; H, 8.29.

1-Bromo-2-methoxy-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (12a): colorless prisms (methanol); mp 176–177 °C; ^1H NMR ($CDCl_3$) δ 1.34 (9 H, s), 2.83–3.10 (4 H, m), 2.86 (4 H, s), 3.92 (3 H, s), 6.66 (1 H, s), 7.10 (2 H, s); MS *m/e* 370, 372 (M^+). Anal. Calcd for $C_{21}H_{23}BrO$: C, 69.13; H, 6.63. Found: C, 69.10; H, 6.60.

1-Bromo-2-ethoxy-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (12b): colorless prisms (methanol); mp 174–176 °C; ^1H NMR ($CDCl_3$) δ 1.34 (9 H, s), 1.49 (3 H, t, J = 6.7 Hz), 2.80–3.10 (4 H, m), 2.85 (4 H, s), 4.13 (2 H, q, J = 6.7 Hz), 6.64 (1 H, s), 7.08 (2 H, s); MS *m/e* 384, 386 (M^+). Anal. Calcd for $C_{22}H_{25}BrO$: C, 68.57; H, 6.54. Found: C, 68.35; H, 6.58.

1-Bromo-2-*n*-propoxy-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (12c): colorless prisms (hexane); mp 160 °C; ^1H NMR ($CDCl_3$) δ 1.10 (3 H, t, J = 7.3 Hz), 1.34 (9 H, s), 1.80–1.95 (2 H, m), 2.80–3.10 (4 H, m), 2.84 (4 H, s), 4.01 (2 H, q, J = 6.7 Hz), 6.64 (1 H, s), 7.09 (2 H, br s); MS *m/e* 398, 400 (M^+). Anal. Calcd for $C_{23}H_{27}BrO$: C, 69.17; H, 6.81. Found: C, 69.15; H, 6.77.

1-Bromo-2-methoxy-4,5,9,10-tetrahydropyrene (12e): colorless prisms (methanol); mp 107–108 °C; ^1H NMR ($CDCl_3$) δ 2.86 (4 H, s), 2.80–3.10 (4 H, m), 3.93 (3 H, s), 6.68 (1 H, s), 7.05–7.15 (3 H, m); MS *m/e* 314, 316 (M^+). Anal. Calcd for $C_{17}H_{15}BrO$: C, 64.77; H, 4.80. Found: C, 65.32; H, 4.97.

1-Bromo-2-methoxy-7-methyl-4,5,9,10-tetrahydropyrene (12f): colorless prisms (methanol); mp 145–148 °C; ^1H NMR ($CDCl_3$) δ 2.33 (3 H, s), 2.83 (4 H, s), 2.81–3.05 (4 H, m), 3.92 (3 H, s), 6.67 (1 H, s), 6.90 (2 H, s); MS *m/e* 328, 330 (M^+). Anal. Calcd for $C_{18}H_{17}BrO$: C, 65.66; H, 5.17. Found: C, 65.63; H, 5.15.

1-Bromo-2-methoxy-6,7,8-trimethyl-4,5,9,10-tetrahydropyrene (12g): colorless prisms (methanol); mp 182–184 °C; ^1H NMR ($CDCl_3$) δ 2.27 (3 H, s), 2.28 (3 H, s), 2.29 (3 H, s), 2.80–3.05 (8 H, m), 3.93 (3 H, s), 6.67 (1 H, s); MS *m/e* 356, 358 (M^+). Anal. Calcd for $C_{20}H_{21}BrO$: C, 67.23; H, 5.92. Found: C, 67.74; H, 6.13.

Bromination of 2-Methoxy-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (11a) with BTMA Br_3 in Dichloromethane. To a solution of 100 mg (0.342 mmol) of **11a** in 10 mL of dichloromethane was added 142.1 mg (0.376 mmol) of benzyltrimethylammonium tribromide at room temperature. After the reaction mixture was stirred for 5 min, it was poured into a large amount of water. The organic layer was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to leave a residue, which was recrystallized from methanol to give 120.5 mg (95%) of **12a**.

Reaction of 12a with DDQ. A solution of 50 mg (0.135 mmol) of **12a** and 90 mg of DDQ (90% purity) in 5 mL of benzene was refluxed for 4 h. After the reaction mixture was cooled and concentrated, the residue was extracted and chromatographed on silica gel with a mixture of hexane and benzene (1:1) as an eluant to give 43.6 mg (88%) of **13**: colorless prisms (methanol); mp 232–234 °C; ^1H NMR ($CDCl_3$) δ 1.57 (9 H, s), 4.18 (3 H, s), 7.70 (1 H, s), 7.98 (1 H, d, J = 9.3 Hz), 8.08 (1 H, d, J = 9.3 Hz), 8.14 (1 H, d, J = 9.3 Hz), 8.23 (2 H, s), 8.43 (1 H, d, 9.3 Hz); MS *m/e* 366, 368 (M^+). Anal. Calcd for $C_{21}H_{19}BrO$: C, 68.67; H, 5.22. Found: C, 68.40; H, 5.18.

Registry No. **1a**, 626-15-3; **1b**, 19294-04-3; **1c**, 51760-23-7; **2**, 78007-12-2; **3a**, 30691-11-3; **3b**, 137594-30-0; **3c**, 137594-31-1; **4a**, 137594-32-2; **4b**, 137594-33-3; **4c**, 137594-34-4; **5a**, 137594-35-5; **5b**, 118249-36-8; **5c**, 137594-36-6; **6a**, 781-17-9; **6b**, 102251-75-2; **7a**, 10549-27-6; **7b**, 74163-62-5; **8a**, 137594-37-7; **8b**, 118249-22-2; **8c**, 137594-38-8; **9a**, 108835-14-9; **9b**, 108835-15-0; **9c**, 108835-16-1; **9d**, 108835-17-2; **9e**, 108835-18-3; **9f**, 108835-19-4; **9g**, 118249-23-3; **10a**, 108545-98-8; **10b**, 108545-97-7; **10c**, 69080-03-1; **10d**, 108835-20-7; **10e**, 108835-21-8; **10f**, 108835-22-9; **10g**, 118249-39-1; **11a**, 137594-39-9; **11b**, 137594-40-2; **11c**, 137594-41-3; **11d**, 137594-42-4; **12a**, 137594-43-5; **12b**, 137594-44-6; **12c**, 137594-45-7; **12d**, 137594-46-8; **12e**, 137594-47-9; **12f**, 137594-48-0; **12g**, 137594-49-1; **13**, 137594-50-4.

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