Medium-Sized Cyclophanes.[1] Preparation and Valence Tautomerism of 8,16-Disubstituted [2.2]Metacyclophane-1,9-dienes

Takehiko Yamato,* Akira Miyazawa, and Masashi Tashiro[†]

Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan, and Research Institute of Advanced Material Study, Kyushu University, 6-1, Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

Received September 4, 1990 (Revised Manuscript Received June 27, 1991)

Introduction of functional groups other than hydrogen or alkyl groups into the internal positions of [2.2]metacyclophane-1,9-dienes was attempted. [2.2]Metacyclophane-1,9-dienes **6a–6g**, bearing variously halogen, methoxy, and methyl substituents in the 8 and 16 positions, were prepared from the corresponding bis(halomethyl)benzenes **1** and bis(mercaptomethyl)benzenes **2** involving use of Wittig rearrangement of 2,11-dithia[3.3]metacyclophanes followed by Hofmann elimination. Although **6a–6c**, **6f**, and **6g** were isolated as thermally stable crystals, isolation of **6d** failed since this compound was thermally labile and transformed spontaneously into 2,7-di-*tert*-butyl-1-chloropyrene (**7**). The photochemical and thermal valence tautomerizations of [2.2]metacyclophanes which were prepared in the present work are described. Attempts to convert 8,16-disubstituted [2.2]metacyclophane-1,9-dienes **6** to 4,5,9,10-tetrabromo-10b,10c-disubstituted 10b,10c-dihydropyrenes by treatment of these compounds with bromine in carbon tetrachloride failed but instead gave addition products **13** and transannular reaction products **14**. The reaction pathways of the bromination are also discussed.

Introduction

Boekelheide et al. indicated that one of the striking features of 10b,10c-dihydropyrenes where the substituents at 10b and 10c positions are hydrogen or alkyl groups is their valence tautomerization, both thermally and photochemically, to the corresponding [2.2]metacyclophane-1,9-dienes[2,3] and that when 8,16-difluoro[2.2]metacyclophane-1,9-diene is heated in a sealed tube at 120 °C, it is transformed into 1-fluoropyrene via 10b,10c-difluoro-10b,10c-dihydropyrene as a transient intermediate (Scheme I).[4]

Attempts at introducing functional groups other than alkyl or fluoro into the internal positions have not been successful and, therefore, their chemical natures are still not known. We undertook the present work in order to obtain more detailed information about the valence tautomerization of [2.2]metacyclophane-1,9-dienes. We previously reported that 5,13-di-*tert*-butyl-8,16-difluoro[2.2]metacyclophane-1,9-diene is stable and photochemically converted to 2,7-di-*tert*-butyl-*trans*-10b,10c-difluoro-10b,10c-dihydropyrene.[5]

In this paper, we wish to report the preparation of 8,16-disubstituted [2.2]metacyclopane-1,9-dienes and their chemical properties.

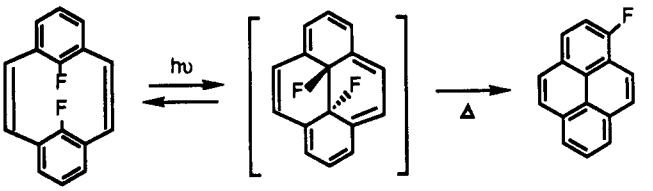
Results and Discussion

The preparation of [2.2]metacyclophane-1,9-dienes **6a–6g**, bearing variously halogen, methoxy, and methyl substituents in the 8 and 16 positions from the corresponding bis(halomethyl)benzenes **1** and bis(mercaptomethyl)benzenes **2** was attempted according to the method reported previously.[6-9]

The desired, 8,16-difluoro- **6a–6c** and 8,16-dichloro-[2.2]metacyclophane-1,9-dienes **6d** were obtained by Hofmann elimination from the corresponding bissulfonium salts **5a–5d** via the bis-sulfides **4a–4d**, which were prepared, in turn, by Wittig rearrangement of dithia[3.3]metacyclophanes **3a–3d**. But 5,13-di-*tert*-butyl-8,16-dibromo[2.2]metacyclophane-1,9-diene (**6e**) was not formed. Although **6a–6c** formed thermally stable crystals, isolation of **6d** failed since it was thermally labile and transformed spontaneously into 2,7-di-*tert*-butyl-1-chloropyrene (**7**). Compounds **6f** and **6g** were also prepared in good yields from 8,16-disubstituted dithia[3.3]-

[†] Research Institute of Advanced Material Study.

Scheme I



metacyclophanes **3** as in Scheme II. It was found that [2.2]metacyclophane-1,9-dienes having fluoro or methoxy groups at the 8,16-positions are stable and do not spontaneously isomerize to the corresponding valence tautomers, *trans*-10b,10c-disubstituted 10b,10c-dihydropyrenes.

It has already been reported that the ^{1}H NMR spectra of the internal substituent protons of *anti*-[2.2]metacyclophanes show upfield shifts due to the ring current of the opposite aromatic ring.[10] The selected ^{1}H NMR data of 8,16-disubstituted metacyclophane-1,9-dienes **6** obtained in the present work show that the structure of the [2.2]metacyclophane-1,9-dienes **6** are exclusively anti conformers. However, the internal methyl and methoxy proton signals of [2.2]metacyclophane-1,9-dienes **6** appeared at much lower field than those of [2.2]metacyclophanes. This finding suggests that the internal methyl and methoxy protons are deshielded by the bridge double bonds.

When **6b** and **6c** were irradiated in the solid state by sun light or a tungsten lamp, the pale yellow color immediately changed to reddish brown. In the dark this latter color reverted to the original color (Scheme III). This phenomenon was attributed to the phototautomerization **6** ⇄ **8**, analogous to *trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes.[2,3,5]

(1) Metacyclophanes and Related Compounds. 22. For 21 in the series, see: Tashiro, M.; Mataka, S.; Takezaki, Y.; Takeshita, M.; Arimura, T.; Tsuge, A.; Yamato, T. *J. Org. Chem.* **1989**, *54*, 451.
(2) Boekelheide, V.; Miyasaka, T. *J. Am. Chem. Soc.* **1967**, *89*, 1709.
(3) Boekelheide, V.; Sturm, E. *J. Am. Chem. Soc.* **1969**, *91*, 902.
(4) Boekelheide, V.; Anderson, P. H. *J. Am. Chem. Soc.* **1973**, *38*, 3928.
(5) Tashiro, M.; Yamato, T.; Kobayashi, K.; Kobayashi, H. *Rep. Res. Inst. Ind. Sci., Kyushu Univ.* **1984**, *77*, 15.
(6) Tashiro, M.; Yamato, T. *Chem. Lett.* **1980**, 1127.
(7) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.
(8) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1982**, *47*, 2783.
(9) Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104*, 3701.
(10) (a) Sherrodd, S. A.; da Costa, R. L.; Barnes, R. A.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1565. (b) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 4556. (c) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1983**, *48*, 1461.

0022-3263/92/1957-0266$03.00/0

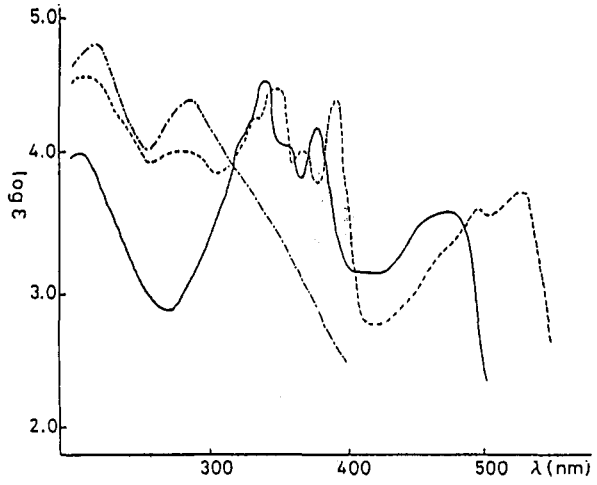
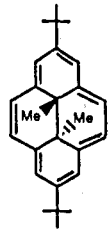


Figure 1. Spectrum change of 5,13-di-*tert*-butyl-8,16-dimethoxy[2.2]metacyclophane-1,9-diene (**6f**) in cyclohexane with sunlight irradiation: ---, before irradiation; - - -, after 20 min of irradiation; —, 2,7-di-*tert*-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene (**9**).[9]



9

Table I. Bromination of [2.2]Metacyclophane-1,9-dienes 6 with Bromine in Carbon Tetrachloride

substrate	time (min)	products yield[a] (%)	
6a	15	**13a** (95)	**14c** (0)
6b	15	**13b** (85)	**14b** (0)
6c	15	**13c** (90)	**14a** (0)
6f	1	**13f** (0)	**14a** (96)
6g	1	**13g** (47)[b]	**14a** (53)[b]

[a] Isolated yields are shown. [b] Relative yields are shown.

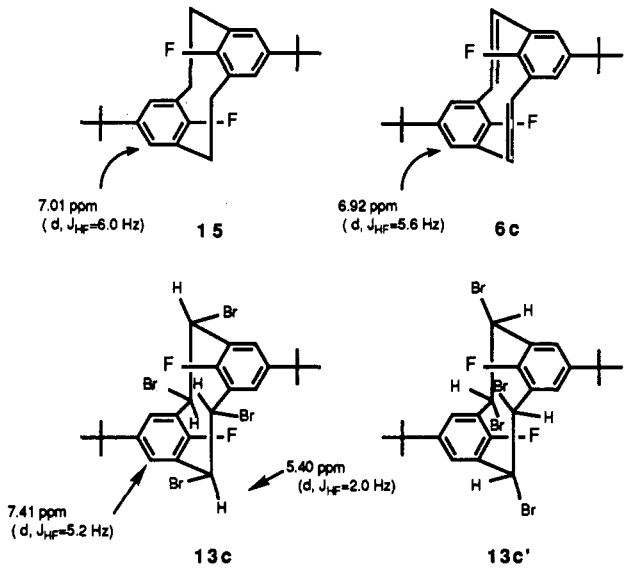
On the other hand, in the case of **6a**, **6f**, and **6g** this phenomenon was not observed. This result indicates that the *tert*-butyl group in **6b** and **6c** plays an important role in the phototautomerization reaction. Also, the internal substituents of [2.2]metacyclophane-1,9-dienes affect the transannular reaction.

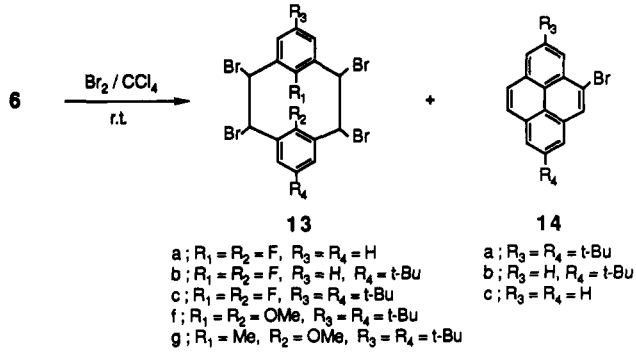
Although **6f** was pale yellow in the solid state, in cyclohexane solution the color gradually changed to pale purple within 20 min. after dissolution. When the solvent was evaporated, compound **6f** was obtained again as pale yellow crystals. As shown in Figure 1 in the electronic spectrum of **6f** in cyclohexane, the absorption band at 290 nm gradually decreases and new absorption bands are observed at 400 and 500 nm, probably characteristic of the *trans*-10b,10c-dialkyl-10b,10c-dihydropyrene structure. This result suggests that **6f** photochemically changes to its valence tautomer, *trans*-10b,10c-dimethoxy-10b,10c-dihydropyrene **8f**.

We previously reported that treatment of 8,16-dimethyl[2.2]metacyclophane **10** and 8,16-dimethyl[2.2]-metacyclophan-1-ene **11** with bromine in carbon tetrachloride affords tetrabrominated *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **12** in good yields (Scheme IV).[6,7,9]

Therefore, we attempted to prepare *trans*-10b,10c-disubstituted 10b,10c-dihydropyrenes via bromination of the corresponding 8,16-disubstituted [2.2]metacyclophane-1,9-dienes **6**. Compounds **6a–6c** with bromine in carbon tetrachloride at room temperature for 15 min led to the addition of bromine to the ethylene double bonds to give 1,2,9,10-tetrabromo[2.2]metacyclophanes (**13a–13c**) without formation of any desired *trans*-10b,10c-difluoro-10b,10c-dihydropyrenes (Table I). The structures of **13a–13c** were assigned on the basis of elemental analyses and spectral data.

Chart I



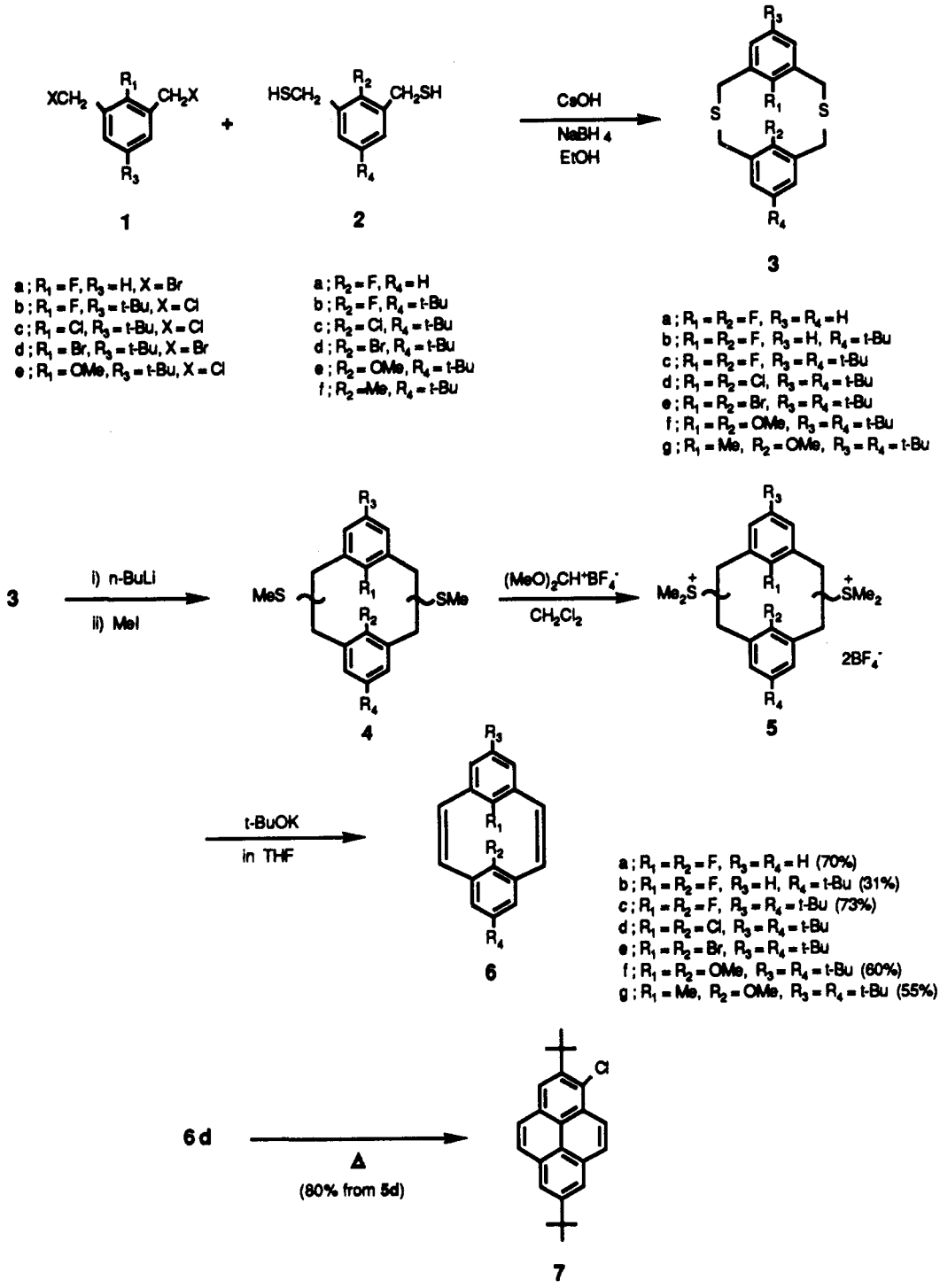


Theoretically, there could be many possible isomers for the compound **13c**. However, the ^{1}H NMR spectrum of **13c** appears to be quite simple and due to a single isomer. It was also found that compound **13c** has C_2 symmetry in consideration of the ^{1}H NMR spectrum of **13c** which shows *tert*-butyl protons at 1.38 ppm as a singlet, methine protons at 5.40 ppm as a doublet (J_{H-F} = 2.0 Hz), and aromatic protons at 7.41 as a doublet (J_{H-F} = 5.2 Hz). On the basis of these data, one might assume the two possible structures for **13c** (or **13c'**) as indicated in Chart I.

We previously assigned[11] the ^{1}H NMR signals of 1-*exo*-5,13-trichloro-8,16-dimethyl[2.2]metacyclophane, and we have assigned the ^{1}H NMR signals of **13c** in a similar fashion. The signals for the aromatic protons are shifted to lower field at 7.41 ppm as compared to those of the corresponding 8,16-difluoro[2.2]metacyclophane (**15**) and 8,16-difluoro[2.2]metacyclophane-1,9-diene **6c** at 7.01 and 6.92 ppm, respectively. This would suggest that the former aromatic protons are in a strongly deshielding region of the Br atom on the ethylene bridge and all Br atoms are

(11) Tashiro, M.; Yamato, T. Kobayashi, K. *J. Org. Chem.* **1984**, *49*, 3380.

Scheme II



in an endo arrangement. Therefore, structure **13c'**, where Br atoms are in an exo arrangement, is unlikely. Similarly, the structures of **13a** and **13b** were assigned.

On the basis of the ^{1}H NMR spectrum, **13a–13c** is assigned to be trans addition products. This result should be contrasted to the bromination of [2.2]paracyclophane-1,9-diene with bromine which afforded the corresponding cis addition product.[12]

On the other hand, the reaction of **6f** with bromine gave only 4-bromo-2,7-di-*tert*-butylpyrene (**14a**) in 96% yield under the conditions of 1 min at rt as shown in Table I. No formation of the desired *trans*-10b,10c-dimethoxy-10b,10c-dihydropyrene was observed.

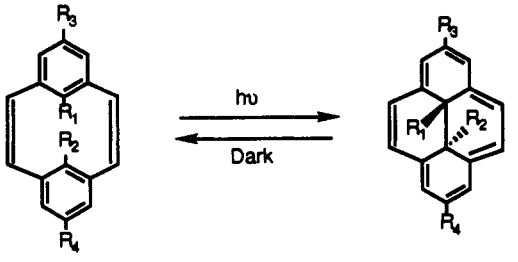
In the case of **6g**, the bromination reaction was also completed within 1 min to afford a mixture of **13g** and 4-bromo-2,7-di-*tert*-butylpyrene (**14a**), whose ratio was determined to be 47:53 by its ^{1}H NMR spectrum. It was also found to be a mixture of cis and trans addition products by its ^{1}H NMR spectrum.

The structure of **14a** was confirmed by ^{1}H NMR spectrum and chemical conversion to the known compound **16** as shown in Scheme V.

Although the detailed mechanism of formation of **14a** is not clear, one might assume the reaction pathway shown in Scheme VI. Bromo cation attacks the bridged double bond of **6f** and **6g** to form intermediate A, from which **14a** might be produced via intermediates B and C. In the case

(12) Singler, R. E.; Cram, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 3512.

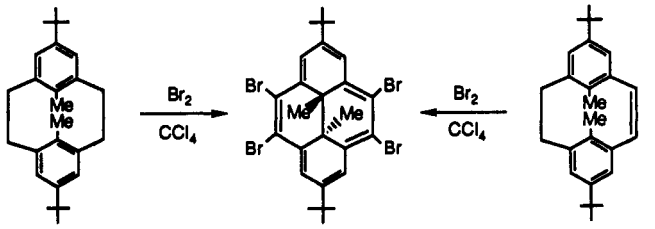
Scheme III



6 b; $R_1 = R_2 = F$, $R_3 = H$, $R_4 = t\text{-Bu}$
c; $R_1 = R_2 = F$, $R_3 = R_4 = t\text{-Bu}$
f; $R_1 = R_2 = OMe$, $R_3 = R_4 = t\text{-Bu}$

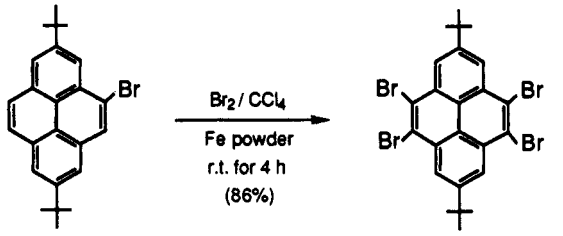
8

Scheme IV



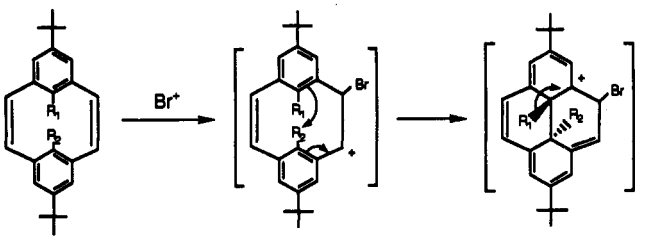
10 12 11

Scheme V



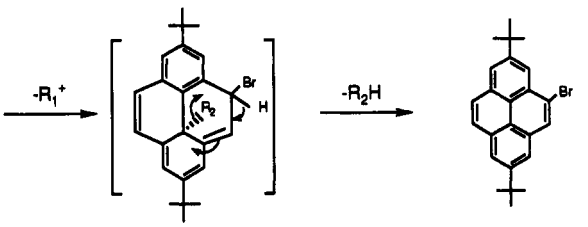
14a 16

Scheme VI



6 A B

f; $R_1 = R_2 = OMe$
g; $R_1 = Me$, $R_2 = OMe$



C 14a

of **6a–6c**, the intermediate B might not be formed by the transannular reaction, so that only the bromine addition product results.

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 as KBr pellets or liquid films 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 9,18-difluorodithia[3.3]metacyclophane (**3a**) was carried out according to the literature.[4] Dithia[3.3]metacyclophane **3b** was prepared according to the route shown in Scheme II. Preparations of the other 9,18-disubstituted dithia[3.3]metacyclophanes **3c–3g** were previously described.[7,13]

Preparation of 6-*tert*-Butyl-9,18-difluorodithia[3.3]-metacyclophane (3b). A solution of 5.08 g (18 mmol) of 2,6-bis(bromomethyl)fluorobenzene (**1a**)[4] and 4.39 g (18 mmol) of 2,6-bis(mercaptomethyl)-4-*tert*-butylfluorobenzene (**2b**)[13] 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 colorless solid, which was recrystallized from hexane to afford 4.59 g (70%) of **3b**: colorless prisms (MeOH); mp 82.5–83.5 °C; NMR ($CDCl_3$) δ 1.14 (9 H, s), 3.36 (4 H, d, J = 15 Hz), 4.62 (4 H, d, J = 15 Hz), 6.54–6.97 (5 H, m); mass spectrum m/e 364 (M^+). Anal. Calcd for $C_{20}H_{22}F_2S_2$: C, 65.90; H, 6.08. Found: C, 65.71; H, 5.97.

Wittig Rearrangement of 3 To Give 4. Typical Procedure. To a solution of 2.99 g (8.20 mmol) of **3b** in 45 mL of dry tetrahydrofuran under nitrogen was added 25.9 mL of 15% hexane solution of *n*-butyllithium (41.0 mmol), with ice cooling. After the reaction mixture was stirred for 10 min at room temperature, 2.58 mL (41 mmol) of methyl iodide was added. The reaction mixture was worked up by addition of H_2O and CH_2Cl_2. The dichloromethane extract was washed with water, dried over Na_2SO_4 and concentrated. The products were purified by filtration through silica gel with 1:1 hexane–benzene to give 2.99 g (93%) of **4b**: colorless prisms (petroleum ether, bp 30–70 °C); mp 145.5–147 °C; IR (KBr) 2960, 1455, 1350, 1175, 770, 735 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (9 H, s), 2.10 (6 H, s), 2.40–2.70 (2 H, m), 2.86–3.10 (2 H, m), 3.86–4.00 (2 H, m), 7.04–7.20 (3 H, m), 7.54–7.72 (2 H, m); mass spectrum m/e 392 (M^+). Anal. Calcd for $C_{22}H_{26}F_2S_2$: C, 67.31; H, 6.68. Found: C, 67.35; H, 6.70.

Similarly, compounds **4a**, **4c**, **4d**, **4f**, and **4g** were prepared. However, similar reaction of **3e** gave a mixture of many products which could not be identified.

4a: yield (95%); colorless prisms (hexane–benzene (1:1)); mp 192–195 °C (lit.[4] mp 193.5–194 °C).

4c: yield (97%); colorless prisms and oil; NMR ($CDCl_3$) δ 1.04–1.42 (18 H, $C(CH_3)_3$), 2.08–2.26 (6 H, SMe), 2.43–2.67 (2 H, CH_2), 2.84–3.06 (2 H, CH_2), 3.60–4.12 (2 H, CH), 7.00–7.24 (2 H, ArH), 7.54–7.74 (2 H, ArH). Anal. Calcd for $C_{26}H_{34}F_2S_2$: C, 69.90; H, 7.64. Found: C, 70.15; H, 7.79.

4d: yield (100%); colorless crystals; mp 230–235 °C; IR (KBr) 3040, 2960, 1590, 1460, 1360, 1240, 1170, 1090, 890, 830, 740, 730 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (18 H, s), 2.14 (6 H, s), 2.80–3.30 (4 H, CH_2), 4.33–4.50 (2 H, CHSMe), 7.30–7.37 (2 H, m), 7.85–7.93 (2 H, m); mass spectrum m/e 480, 482 (M^+). Anal. Calcd for $C_{26}H_{34}Cl_2S_2$: C, 64.84, H, 7.12. Found: C, 65.25; H, 7.12.

4f: yield (53%); colorless solid; mp 217–242 °C; IR (KBr) 3040, 1470, 1460, 1420, 1275, 1250, 1100, 1020, 880, 840, 810, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (18 H, s), 2.12 (6 H, s), 2.26–3.00 (4 H, m), 2.88 (6 H, s), 3.88 (2 H, dd, J = 12, 4 Hz), 7.02–7.10 (2 H, m), 7.53–7.61 (2 H, m); mass spectrum m/e 472 (M^+). Anal. Calcd for $C_{28}H_{40}O_2S_2$: C, 71.14; H, 8.53. Found: C, 71.01; H, 8.44.

4g: yield (56%); colorless needles (hexane); mp 201–208 °C; IR (KBr) 2960, 2910, 1475, 1455, 1415, 1355, 1270, 1235, 1095, 1015 cm^{-1}; NMR ($CDCl_3$) δ 0.57 (3 H, s), 1.29 (9 H, s), 1.31 (9 H, s), 2.11 (6 H, s), 2.57 (2 H, dd, J = 12, 11 Hz), 2.81 (3 H, s), 3.10

(13) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1985**, *50*, 2939.

(2 H, dd, J = 4, 12 Hz), 3.88 (2 H, dd, J = 4, 11 Hz), 7.06–7.17 (2 H, m), 7.16–7.70 (2 H, m); mass spectrum m/e 456 (M^+). Anal. Calcd for $C_{28}H_{40}OS_2$: C, 73.63; H, 8.83. Found: C, 73.56; H, 8.84.

Preparation of Bis-Sulfonium Salt 5b. Typical Procedure. A solution of 2.74 g (25.9 mmol) of a mixture of isomers **4b** in 20 mL of dichloromethane was added with stirring to a suspension of 6.5 g (40 mmol) of dimethoxycarbonium tetrafluoroborate[14] in 10 mL of dichloromethane that was maintained at −30 °C under nitrogen. The resulting crystalline precipitate was collected and dried, giving 3.48 g (76%) of **5b** as colorless crystals.

The other bis-sulfonium salts **5a**, **5c**, **5d**, **5f**, and **5g** were obtained from **4a**, **4c**, **4d**, **4f**, and **4g** by this manner, respectively.

Hofmann Elimination of 5 To Give 8,16-Disubstituted [2.2]Metacyclophane-1,9-diene 6. Typical Procedure. To a solution of 500 mg (0.839 mmol) of **5b** in 75 mL of dry tetrahydrofuran was added with stirring 565 mg (5.03 mmol) of potassium *tert*-butoxide. After the reaction mixture was stirred at room temperature under nitrogen for 4 h, benzene was added and the mixture was acidified by the addition of dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, dried, and concentrated. The residue was chromatographed on silica gel with 1:1 hexane–benzene to give 78 mg (31%) of 5-*tert*-butyl-8,16-difluoro[2.2]metacyclophane-1,9-diene (**6b**): pale green prisms (hexane); mp 80 °C dec; IR (KBr) 2960, 1450, 1200, 875, 805, 775, 750, 685 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (9 H, s), 6.39 (4 H, s), 6.82–7.02 (5 H, m); mass spectrum m/e 296 (M^+). Anal. Calcd for $C_{20}H_{18}F_2$: C, 81.06; H, 6.12. Found: C, 80.81; H, 6.06.

Similarly, compounds **6a**, **6c**, **6d**, **6f**, and **6g** were prepared. However, compound **6d** was too labile to isolate only to afford 2,7-di-*tert*-butyl-1-chloropyrene (**7**) in 80% yield.

8,16-Difluoro[2.2]metacyclophane-1,9-diene (6a): yield (70%); colorless prisms (hexane–benzene (1:1)); mp 89 °C dec (lit.[4] mp 89 °C dec).

5,13-Di-*tert*-butyl-8,16-dichloro[2.2]metacyclophane-1,9-diene (6c): yield (73%); pale yellow prisms (MeOH); mp 172–174 °C; IR (KBr) 3040, 2970, 1465, 1360, 1200, 880, 840, 760, 680 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (18 H, s), 6.37 (4 H, s), 6.87 (4 H, d, J = 6 Hz); mass spectrum m/e 352 (M^+). Anal. Calcd for $C_{24}H_{26}F_2$: C, 81.78; H, 7.44. Found: C, 81.61; H, 7.47.

5,13-Di-*tert*-butyl-8,16-dichloro[2.2]metacyclophane-1,9-diene (6d): pale yellow crystals; NMR ($CDCl_3$) δ 1.27 (18 H, s), 6.40 (4 H, s), 6.80 (4 H, s).

5,13-Di-*tert*-butyl-8,16-dimethoxy[2.2]metacyclophane-1,9-diene (6f): yield (60%); pale yellow prisms (hexane); mp 146–149 °C; IR (KBr) 2960, 1475, 1420, 1385, 1360, 1290, 1215, 1120, 1030, 960, 930, 875, 835, 760, 685 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (18 H, s), 3.30 (6 H, s), 6.40 (4 H, s), 6.80 (4 H, s); mass spectrum m/e 376 (M^+). Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82,73; H, 8.65.

5,13-Di-*tert*-butyl-8-methoxy-16-methyl[2.2]metacyclophane-1,9-diene (6g): yield (55%); pale orange needles (hexane); mp 150.5–152.5 °C; IR (KBr) 3010, 2950, 2860, 1465, 1415, 1355, 1280, 1245, 1210, 1190, 1115, 1030, 930, 870, 825, 755, 675 cm^{-1}; NMR ($CDCl_3$) δ 1.24 (18 H, s), 1.42 (3 H, s), 3.35 (3 H, s), 6.25 (2 H, d, J = 11 Hz), 6.48 (2 H, d, J = 11 Hz), 6.72 (4 H, s); mass spectrum m/e 360 (M^+). Anal. Calcd for $C_{26}H_{32}O$: C, 86.62; H, 8.95. Found: C, 86.85; H, 9.09.

Bromination of 6a–6c. Typical Procedure. To a solution of 240 mg (1 mmol) of **6a** in 80 mL of carbon tetrachloride was added 480 mg (3 mmol) of bromine in 20 mL of carbon tetrachloride with stirring at room temperature. After 15 min the reaction mixture was poured into a large amount of ice–water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over $MgSO_4$ and evaporated in vacuo, and the residue was recrystallized from hexane–benzene (1:1) to afford 532 mg (95%) of **1,2,9,10-tetrabromo-8,16-difluoro[2.2]metacyclophane (13a)**: colorless prisms (hexane–benzene (1:1); mp 300 °C dec; IR (KBr) 2980, 1597, 1570, 1465, 1270, 1230, 1202, 1192, 1170, 1070, 970, 860, 755, 740 cm^{-1}; NMR (DMSO-d_6) δ 5.92 (4 H, d, J = 2 Hz), 7.21 (2 H, dd, J = 8.1, 7.2 Hz), 7.50–7.72 (4 H, m); mass spectrum m/e 556, 558, 560, 562, 564 (M^+). Anal. Calcd for $C_{16}H_{10}F_2Br_4$: C, 34.33; H, 1.80. Found: C, 34.60; H, 2.03.

Compounds **13b** and **13c** were also obtained in this manner in 85% and 90% yields, respectively.

1,2,9,10-Tetrabromo-5-*tert*-butyl-8,16-difluoro[2.2]metacyclophane (13b): colorless prisms (hexane–benzene (1:1)); mp >300 °C; IR (KBr) 2980, 1597, 1570, 1465, 1280, 1230, 1202, 1192, 1170, 1070, 970, 860, 755, 740 cm^{-1}; mass spectrum m/e 556, 558, 560, 562, 564 (M^+). Anal. Calcd for $C_{20}H_{18}F_2Br_4$: C, 39.00; H, 2.95. Found: C, 39.34; H, 3.14.

1,2,9,10-Tetrabromo-5,13-di-*tert*-butyl-8,16-difluoro[2.2]metacyclophane (13c): colorless prisms (hexane–benzene (1:1)); mp >300 °C; IR (KBr) 3040, 2960, 1590, 1480, 1360, 1200, 1165, 830, 790, 760, 695 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (18 H, s), 5.40 (4 H, d, J = 2 Hz), 7.34 (4 H, d, J = 5.2 Hz); mass spectrum m/e 668, 670, 672, 674, 676 (M^+). Anal. Calcd for $C_{24}H_{26}F_2Br_4$: C, 42.89; H, 3.90. Found: C, 43.10; H, 3.94.

Bromination of 6f. To a solution of 360 mg (1 mmol) of **6f** in 80 mL of carbon tetrachloride was added 480 mg (3 mmol) of bromine in 20 mL of carbon tetrachloride with stirring at room temperature. After 1 min, the reaction mixture was treated as described above to afford 380 mg (96%) of **14a**: colorless prisms (MeOH); mp 130–132 °C; IR (KBr) 3040, 2950, 2900, 1600, 1470, 1450, 1355, 1260, 1210, 995, 880, 870, 790, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (9 H, s), 1.60 (9 H, s), 8.00 (2 H, s), 8.10 (1 H, d, J = 1.8 Hz), 8.19 (1 H, d, J = 1.8 Hz), 8.22 (1 H, d, J = 1.8 Hz), 8.38 (1 H, s), 8.59 (1 H, d, J = 1.8 Hz); mass spectrum m/e 392, 394 (M^+). Anal. Calcd for $C_{24}H_{25}Br$: C, 73.28; H, 6.41. Found: C, 73.67; H, 6.75.

Bromination of 6g. To a solution of 45 mg (0.12 mmol) of **6g** in 20 mL of carbon tetrachloride was added 0.02 mL (0.4 mmol) of bromine in 5 mL of carbon tetrachloride with stirring at room temperature. After 1 min, the reaction mixture was treated as described above to afford 72 mg of a mixture of **13g** and **14a** as colorless crystals and the ratio of **13g** and **14a** was determined to be 47:53 by its NMR spectrum.

Bromination of 14a to 16. To a solution of 100 mg (0.26 mmol) of **13a** in 50 mL of carbon tetrachloride was added 100 mg of iron powder and 0.09 mL of bromine in 5 mL of carbon tetrachloride with stirring at room temperature. After 4 h, the reaction mixture was treated as described above to afford colorless solid which was recrystallized from hexane to give 164 mg (86%) of **16**: pale yellow prisms (hexane); mp 286–288 °C (lit.[6] mp 287–288 °C).

Registry No. **1a**, 25006-86-4; **2b**, 77180-50-8; **3a**, 25117-62-8; **3b**, 137059-70-2; **3c**, 92661-24-0; **3d**, 96929-84-9; **3f**, 137171-05-2; **3g**, 137171-06-3; **4a**, 137056-79-2; **4b**, 137056-80-5; **4c**, 137056-81-6; **4d**, 137056-82-7; **4f**, 76446-99-6; **4g**, 76447-02-4; **5a**, 137056-84-9; **5b**, 137056-86-1; **5c**, 137056-88-3; **5d**, 137056-90-7; **5f**, 137056-92-9; **5g**, 137056-94-1; **6a**, 137172-07-7; **6b**, 13712-08-8; **6**, 92661-23-9; **6d**, 137059-71-3; **6f**, 137059-72-4; **6g**, 137171-07-4; **7**, 78751-85-6; **13a**, 137059-73-5; **13b**, 137059-74-6; **13c**, 137059-75-7; **13f**, 137059-76-8; **13g**, 137059-77-9; **14a**, 137059-78-0; **14b**, 137059-79-1; **14c**, 1732-26-9; **16**, 76466-34-7.

(14) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.