Medium-Sized Cyclophanes, 29[1]

Synthesis and Desulfurization of 2,11-Dithia[3]metacyclo- and 2,11-Dithia[3]paracyclo[3](4,9)pyrenophanes

Takehiko Yamato*[a], Akira Miyazawa[b], and Masashi Tashiro*[c]

Department of Applied Chemistry, Faculty of Science and Engineering, Saga University[a], Honjo-machi 1, Saga-shi, Saga 840, Japan

Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University[b], 6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

Institute of Advanced Material Study, Kyushu University[c], Kasuga-kohen 6-1, Kasuga-shi, Fukuoka 816, Japan

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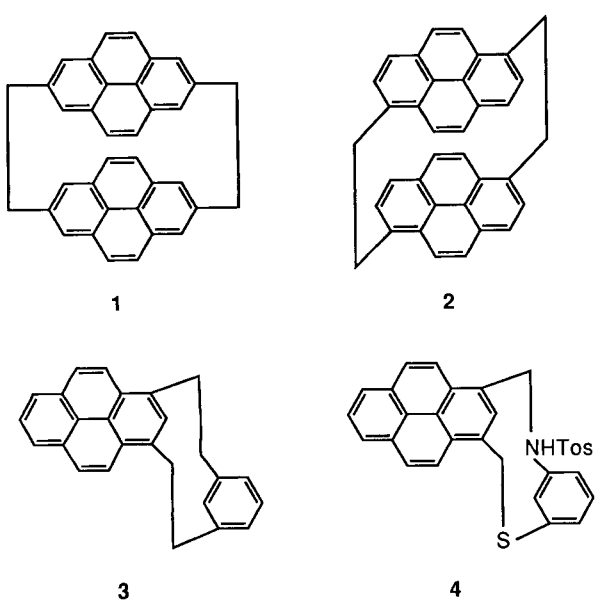
2,11-Dithia[3]metacyclo- (**14b**) and 2,11-dithia[3]paracyclo[3]-(4,9)pyrenophane (**14c**) were obtained by the coupling reactions of 4,9-bis(chloromethyl)pyrene (**12**) with the corresponding bis(mercaptomethyl)benzenes (**13b, c**). Attempted pyrolysis of the disulfones **18b, 18c** to afford [2]metacyclo- (**19b**) and [2]paracyclo[2](4,9)pyrenophane (**19c**) failed. Only the ring cleavage products **16** and **20** were obtained. The sulfur dioxide extrusion by vapor-phase pyrolysis of the corresponding disulfone **18** to the highly strained **19** clearly demonstrates the limits of these preparative ring contraction method. The photolytic desulfurization of **14c** afforded the [2](1,5)naphthaleno[2]paracyclophane analogue **21** instead of [2]paracyclo[1]-(4,9)pyrenophane **21'**. The mechanism of the pyrolysis and photolysis reactions is discussed.

Umemoto et al.[2] first reported on the synthesis of [2.2](1,3)-pyrenophane and another metacyclopyrenophane in 1975, which are important as model compounds of transannular π-electronic interaction of excimer fluorescence[3a–3e]. Later on, Mitchell et al.[4] synthesized the internally substituted dithiametacyclopyrenophanes as precursors for the preparation of highly annelated 10b,10c-dihydro-*trans*-10b,10c-dimethylpyrenes. Recently, Vögtle et al.[5] also synthesized [2.2]cyclophanes containing the pyrene unit to investigate their chiroptical properties (Scheme 1).

Scheme 1



1 2 3 4

All of the previous cases are 2,7-, 1,7-, and 1,3-bridged pyrenophanes. However, 4,9-bridged pyrenophanes have not been synthesized to date. In the above three reports[2,4,5], the construction of the pyrene skeleton requires the transannular reaction of the corresponding bis(bromomethyl)[2.2]metacyclophane with bromine as a key step. Since electrophilic substitution of pyrene itself occurs in the 1-, 3-, 6-, and 8-positions, but not in the other positions (2, 4, 5, 7, 9, and 10)[6a,6b], pyrenes substituted in the latter positions must be prepared in ways other than by direct electrophilic substitution of pyrene itself[7a–c]. For example, Moyle et al.[8] prepared 4,9-diethylpyrene in a low total yield from ethylbenzene in 14 steps using Friedel-Crafts intramolecular acylation to construct a pyrene ring and Hempenius et al.[9] reported on the introduction of methyl groups into the 1-, 2-, and 3-positions, starting from 1*H*-phenalene.

Quite recently, we have described[10] the $AlCl_3$-catalyzed acetylation of 2,7-di-*tert*-butylpyrene (**6**) with acetyl chloride using the *tert*-butyl group as a positional protective group to afford 4,9-diacetyl-2,7-di-*tert*-butylpyrene (**8**) in 75% yield. This compound afforded a convenient starting material for the attempted preparation of 4,9-bridged benzenopyrenophanes.

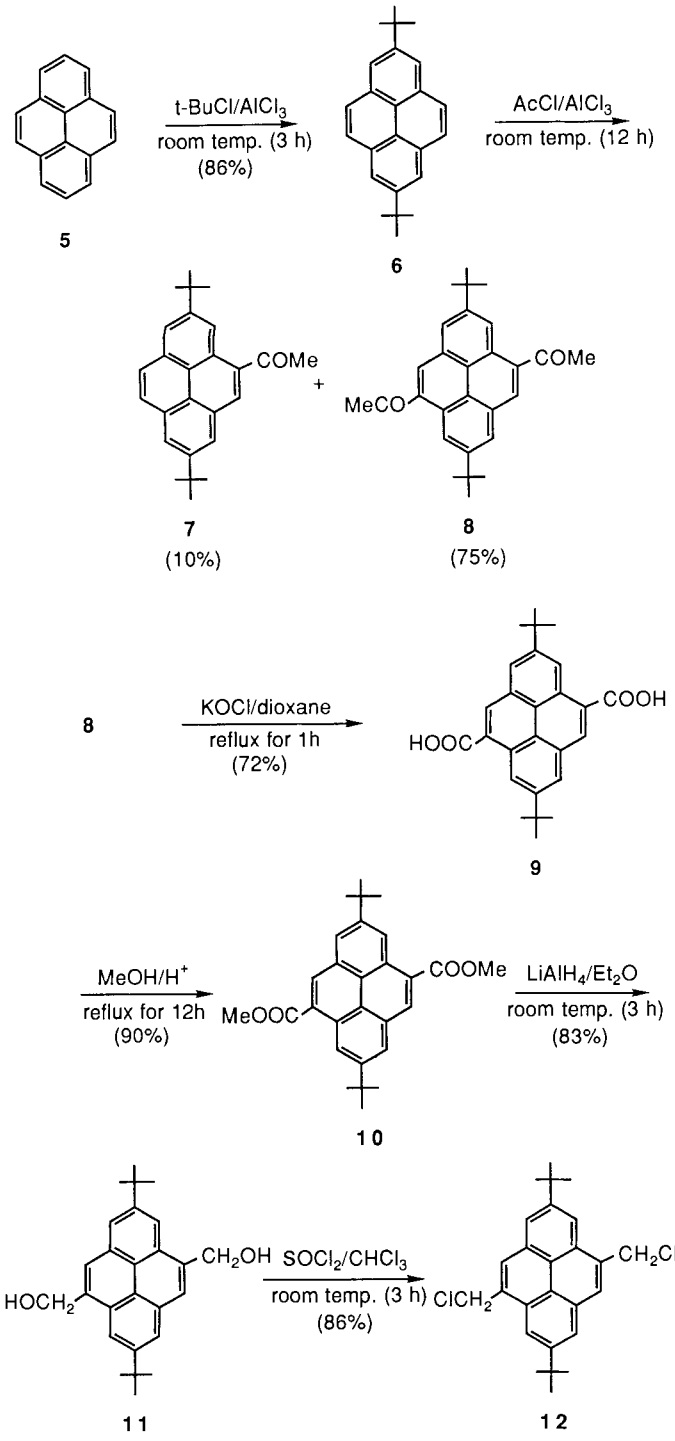
In this paper we report on the first example of the synthesis of 2,11-dithia[3]metacyclo- and 2,11-dithia[3]paracyclo-[3](4,9)pyrenophanes and the attempted desulfurization of these compounds to furnish 4,9-bridged benzenopyrenophanes.

Results and Discussion

A. Synthesis of 2,7-Di-*tert*-butyl-4,9-bis(chloromethyl)-pyrene (12)

The title compound **12** has been prepared according to Scheme 2 from pyrene (**5**) by using the *tert*-butyl function as a positional protective group[11a–h].

Scheme 2



2,7-Di-*tert*-butylpyrene (**6**) was prepared according to the modified *tert*-butylation of pyrene with *tert*-butyl chloride and $AlCl_3$ instead of $AlBr_3$[12], which is not easy to handle. When acetylation of **6** with 10 equiv. of acetyl chloride in the presence of $AlCl_3$ as a catalyst was carried out at room temperature for 12 h, the desired 4,9-diacetyl-2,7-di-*tert*-butylpyrene (**8**) was obtained in 75% yield, along with 4-acetyl-2,7-di-*tert*-butylpyrene (**7**) in 10% yield. No 1-acetylated compound was formed.

Attempted oxidation of **8** with $KMnO_4$ and CrO_3 according to the general procedure failed. Only a large amount of resinous material and unidentified compounds were formed. However, when the haloform reaction of **8** was carried out by using a fourfold excess of potassium hypochlorite, the desired dicarboxylic acid **9** was obtained in 72% yield. The conversion of **9** to **12** was carried out by using standard procedure[13a,13b]. The total yield of **12** from pyrene (**5**) was 30%.

B. Synthesis of 2,11-Dithia[3]benzeno[3](4,9)pyrenophanes (14)

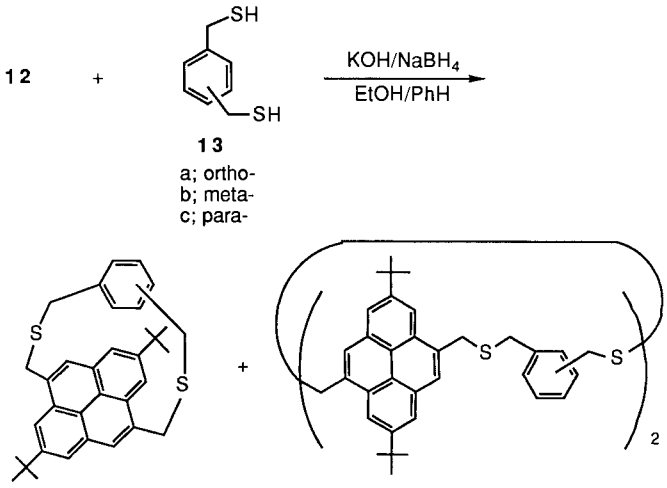
The dithia[3]benzeno[3](4,9)pyrenophanes **14** were synthesized by coupling 2,7-di-*tert*-butyl-4,9-bis(chloromethyl)-pyrene (**12**) with bis(mercaptomethyl)benzenes **13** under high dilution conditions in 10% ethanolic potassium hydroxide in the presence of a small amount of $NaBH_4$ as shown in Scheme 3.

2,11-Dithia[3]metacyclo- (**14b**) and 2,11-dithia[3]paracyclo[3](4,9)pyrenophane (**14c**) were obtained in 29 and 34% yields, respectively. However, no 2,11-dithia[3]orthocyclo[3](4,9)pyrenophane (**14a**) is formed. Only the larger membered tetrathia compound **15a** was obtained in 17% yield. This result seems to be due to the much more strained structure of **14a** by decreasing the size of cyclophane ring.

The structures **14b** and **14c** were readily inferred from their ^{1}H-NMR spectra (Table 1).

The internal proton of 2,11-dithia[3]metacyclo[3]-(4,9)pyrenophane (**14b**) shows an upfield shift at $\delta = 3.97$ due to the ring current of the opposite pyrene ring[14a,14b]. Thus, the internal proton of **14b** is observed at the highest field in the known dithia[3.3]cyclophanes. For the methylene protons in **14b**, two AB systems are observed at $\delta = 2.78$ ($J_{AB} = 16.5$ Hz) and 4.58 ($J_{AB} = 11.7$ Hz). The signal for the

Scheme 3

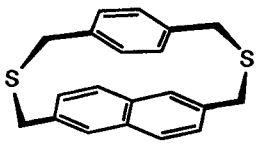


14	Yield		15	Yield
a	0%	ortho-	a	17%
b	29%	meta-	b	trace
c	34%	para-	c	trace

Table 1. Chemical shifts δ of the protons of pyrene and benzene ring and methylene protons of 2,11-dithia[3]metacyclo- (**14b**) and 2,11-dithia[3]paracyclo[3](4,9)pyrenophane (**14c**) ($CDCl_3$, $SiMe_4$ as a reference, 270 MHz)

Compd.	Pyrene protons 1,6-H	3,8-H	5,10-H	Benzene protons	Methylene protons
14b	7.92	8.33	7.70	3.97 (9-H) 6.15 (6-H) 6.44 (5,7-H)	2.72, 2.84 (J_{AB} = 16.5 Hz) 4.23, 4.92 (J_{AB} = 11.7 Hz)
14c	8.01	8.30	7.70	5.38 (5,9-H) 5.51 (6,8-H)	3.13, 3.39 (J_{AB} = 16.1 Hz) 4.22, 4.66 (J_{AB} = 13.0 Hz)
16	8.12	8.24	7.87		

former methylene protons is observed at higher field than that of the known dithia[3.3]cyclophanes. This phenomenon can be deduced from a molecular model of **14b**, in which the ring current of the opposite pyrene ring is extended to the bridging methylene protons. No change of the AB systems of the $-CH_2-S-CH_2-$ bridge in **14b** was observed between −100 and 120°C. Therefore, the conformation of **14b** in solution is rigid, and the signals of the methylene bridge do not coalescence below 120°C. The same phenomenon was observed for the AB systems of the $-CH_2-S-CH_2-$ bridge in **14c** in its dynamic ^{1}H-NMR spectrum. The benzene protons of 2,11-dithia[3]paracyclo[3](4,9)-pyrenophane (**14c**) show an upfield shift at δ = 5.38 and 5.51 due to the stronger ring current of the opposite pyrene ring than that of the naphthalene ring in 2,13-dithia[3]-(2,6)naphthaleno[3]paracyclophane (**17**) (δ = 6.27 and 6.42), which was prepared by Haenel[15] in 1982.



C. UV Spectra of 2,11-Dithia[3]benzeno[3](4,9)-pyrenophanes 14

The UV spectra of 2,11-dithia[3]metacyclo[3]-(4,9)pyrenophane (**14b**) and 2,11-dithia[3]paracyclo[3]-(4,9)pyrenophane (**14c**) in chloroform are shown in Figure 1. Bathochromic shifts in **14b**, **c** in comparison with 2,7-di-*tert*-butyl-4,9-dimethylpyrene (**16**) were observed (Figure 1). These bathochromic shifts are ascribed to a transannular interaction between the pyrene ring and the benzene ring leading to an increase of the strain of these systems[16]. The difference in the bathochromic shifts between **14b** and **14c** is supposed to depend on their modes[16].

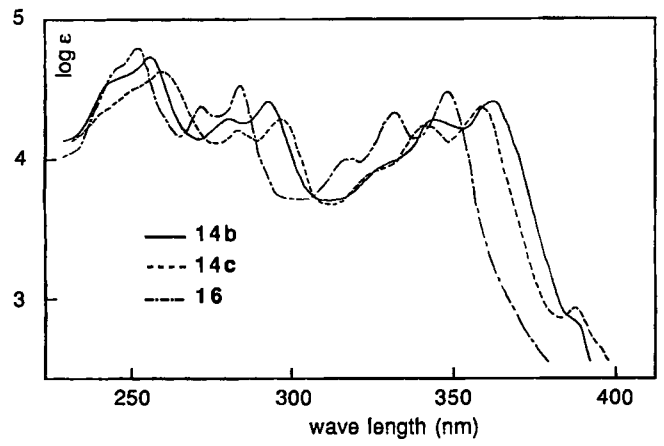
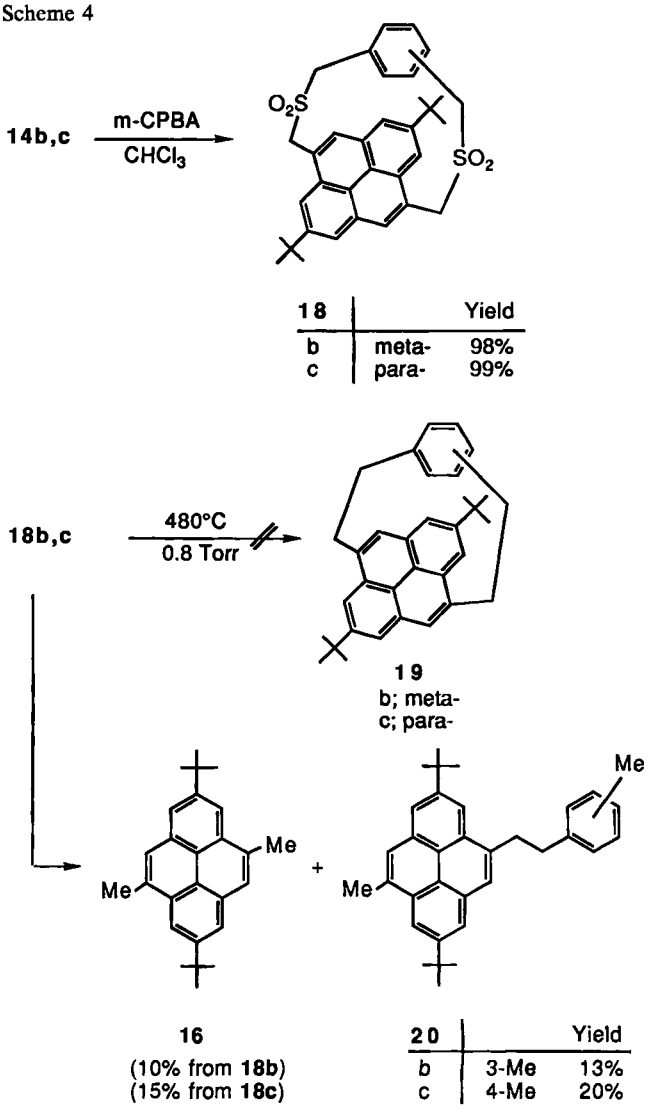


Figure 1. UV spectra of 2,11-dithia[3]metacyclo- (**14b**), 2,11-dithia[3]paracyclo[3](4,9)pyrenophane (**14c**), and **16** (chloroform)

D. Vapor-Phase Pyrolysis of 2,11-Dithia[3]benzeno[3]-(4,9)pyrenophane *S,S,S',S'*-Tetraoxides (18b,c)

Oxidation of **14b**, **c** with *m*-chloroperbenzoic acid (*m*-CPBA) furnished the corresponding sulfones **18b**, **c** in almost quantitative yields (Scheme 4).

Scheme 4

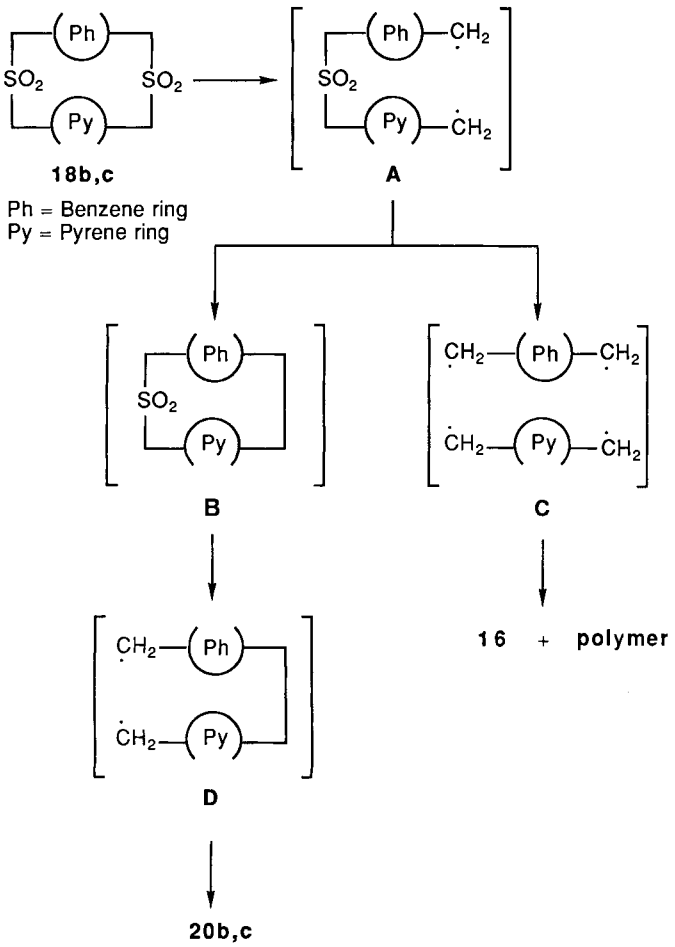


Attempted pyrolysis of **18b**, **c** under reduced pressure (0.8 Torr) carried out according to the reported method[17a–c] failed. The formation of the desired [2.2]cyclophanes **19b**, **c** was not observed. Only the ring cleavage and reduction products **16** and **20b**, **c** were obtained in 10–20% yields (Scheme 4).

These results strongly suggest that the sulfur dioxide extrusion by vapor-phase pyrolysis of the disulfones **18b, c** leading not to the highly strained [2]metacyclo[2](4,9)pyrenophane (**19b**) and [2]paracyclo[2](4,9)pyrenophane (**19c**) clearly demonstrate the limits of these preparative ring contraction method. The structure of **19c** formally corresponds to that of [8](2,6)naphthalenophane which is connected in the 2,6-positions of the naphthalene ring with the benzene ring. An X-ray crystallographic study[18] of [8]paracyclophane shows that the benzene ring is bent in a boat-like form, and that the deviation of the angle from planarity is 9°. Therefore, due to the expansion of the benzene ring with the naphthalene ring, the naphthalene moiety of **19c** is thus more strongly tilted than the benzene ring of [8]paracyclophane. The same phenomenon has also been observed in the preparation of [2](2,6)naphthaleno[2]paracyclophane by the disulfone pyrolysis[15].

The reaction pathway of the disulfone pyrolysis of **18b, c** leading to the ring cleavage products **16** and **20b, c** is shown in Scheme 5.

Scheme 5

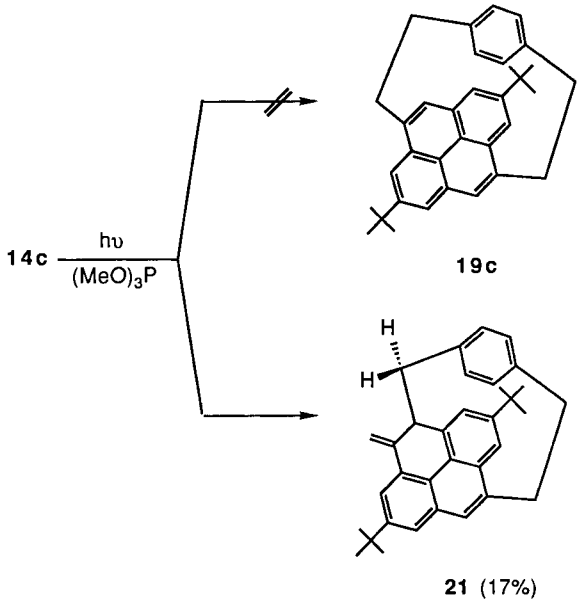


Thus, the diradicalic intermediate **A**[19] may generate a C–C bond to give [3.2]benzenopyrenophane **B** which may undergo further sulfur dioxide extrusion to form the diradicalic intermediate **D**. Intermediate **D** does not undergo intramolecular C–C coupling to afford [2.2]benzenopyrenophane (**19**) due to the highly strained structure of the product, but rather disproportionation to furnish **20b, c** (Scheme 4). The same reaction pathway for the formation of **16** via the intermediate **C** is proposed.

E. Photolytic Desulfurization of 2,11-Dithia[3]paracyclo[3](4,9)pyrenophane (14c)

The photodesulfurization of **14c** was carried out in trimethyl phosphite with irradiation by a 100-W high-pressure mercury lamp at room temperature for 33 h to give [2]-(1,5)naphthaleno[2]paracyclophane (**21**) containing a 4*H*-5-pyrenylidene skeleton (Scheme 6). The desired [2]paracyclo-[2](4,9)pyrenophane (**19c**) was not formed. This result is also attributable to the highly strained structure of [2]paracyclo-[2](4,9)pyrenophane (**19c**) as mentioned previously.

Scheme 6



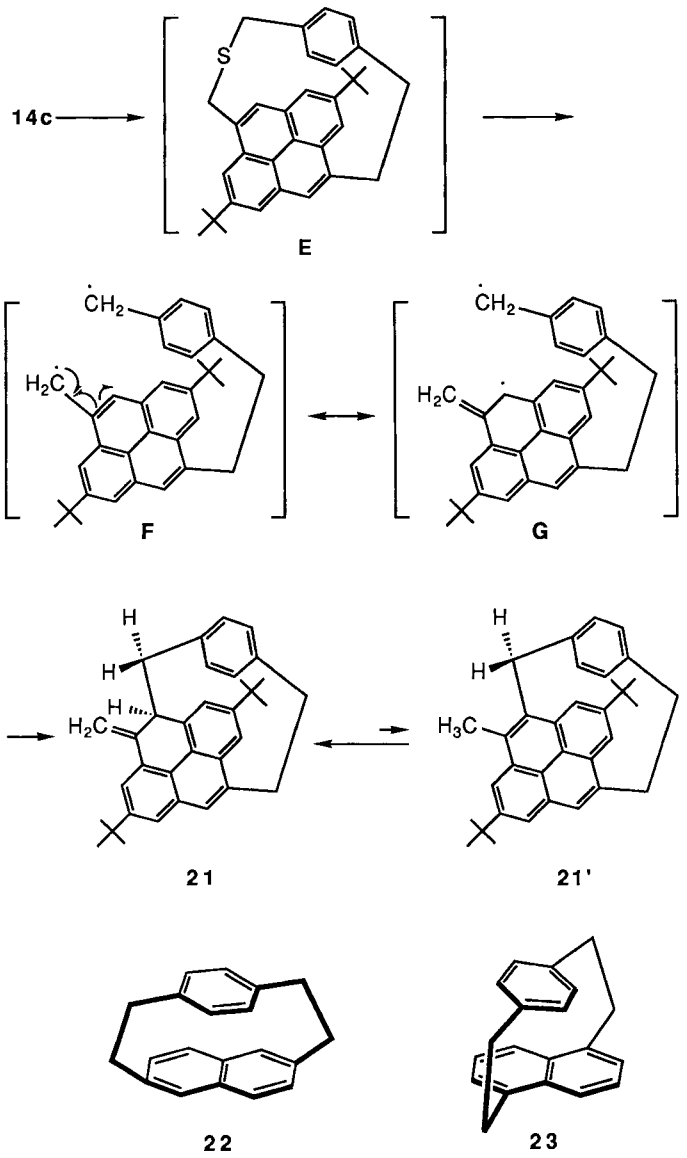
The structure of **21** was determined on the basis of its elemental analysis and spectral data. The ^{1}H-NMR spectrum in $CDCl_3$ shows four double doublets at higher fields (δ = 5.20, 5.37, 5.51, and 5.87) for non-equivalent benzene protons and a singlet at δ = 5.34 and 5.76 for *exo*-methylene protons. The ^{13}C-NMR spectrum of **21** shows signals due to four kinds of methylene carbon atoms (δ = 32.2, 36.0, 47.1, and 109.6), one of which is observed at considerably lower field than others being assigned to an *exo*-methylene carbon.

The formation of **21** can be explained most simply as proceeding via the diradicalic intermediate **F** and its resonance form **G**. The coupling of the diradicalic intermediate **F** affording **19c** does not occur due to the highly strained structure of product **19c**. Instead, the coupling reaction of the diradicalic intermediate **G** furnishes the less strained **21**. Further conversion of **21** to **21′** by aromatization has not been observed (Scheme 7).

Thus, compound **21** is considered to be a [2]naphthaleno[2]paracyclophane analogue of **22** and **23**. On the other hand, the valence tautomer **21′** is regarded as the much more strained [2.1](4,10)-

benzenopyrenophane analogue which cannot be constructed by means of a molecular model.

Scheme 7



Conclusions

We have prepared 2,11-dithia[3]benzeno[3](4,9)pyrenophanes (**14**) and have investigated their different modes of non-bonded transannular interaction between the pyrene ring and the benzene ring for the first time. Although the attempted synthesis of [2]benzeno[2](4,9)pyrenophanes (**19**) has been unsuccessful, the photolytic desulfurization of **14c** affords the [2](1,5)naphthaleno[2]paracyclophane analogue **21**. Further studies of the chemical properties of **21** are in progress.

Experimental

All melting and boiling points are uncorrected. — IR (KBr or NaCl): Nippon Denshi JIR-AQ2OM. — ^{1}H NMR: Nippon Denshi JEOL FT-270, in $CDCl_3$, TMS as reference. — UV: Hitachi 220A spectrophotometer. — MS: Nippon Denshi JMS-01SA-2. — Elemental analysis: Yanaco MT-5.

2,7-Di-tert-butylpyrene (**6**): To a solution of 8.0 g (40.0 mmol) of pyrene (**1**) and 200 ml of *tert*-butyl chloride was added 8.0 g (60.0 mmol) of powdered $AlCl_3$ at 0°C. After the reaction mixture had been stirred at room temp. for 3 h, it was poured into a large amount of ice/water and extracted with CH_2Cl_2 (2 × 250 ml). The combined CH_2Cl_2 extracts were washed with water (2 × 200 ml), dried with Na_2SO_4, and the solvent was evaporated in vacuo to leave a residue, which was chromatographed on silica gel (hexane as an eluent) to give a colorless solid. Recrystallization from ethanol afforded 10.0 g (31.8 mmol, 86%) of **6** as colorless prisms, m.p. 209–211°C (ref.[20] 210–212°C).

Acetylation of **6** *with Acetyl Chloride:* To a solution of 10.0 g (32.0 mmol) of **6** in 300 ml of CH_2Cl_2 was added at −5°C with stirring 4.3 g (32.0 mmol) of powdered $AlCl_3$ and then 25 g (320 mmol) of acetyl chloride. After stirring of the reaction mixture at room temp. for 12 h, it was poured into a large amount of ice/water and extracted with CH_2Cl_2 (2 × 250 ml). The combined CH_2Cl_2 extracts were washed with water (2 × 200 ml), dried with Na_2SO_4, and the solvent was evaporated in vacuo to leave a residue, which was chromatographed on silica gel with hexane/benzene (1:1) as the eluent to give 1.1 g (3.09 mmol, 10%) of *4-acetyl-2,7-di-tert-butylpyrene* (**7**) as brown prisms, m.p. 121–122°C (ref.[11g] 121–122°C), and 9.5 g (23.9 mmol, 75%) of *4,9-diacetyl-2,7-di-tert-butylpyrene* (**8**) as pale yellow prisms ($CHCl_3$), m.p. 311°C. — IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1670 (C=O). — ^{1}H NMR ($CDCl_3$): δ = 1.60 (18H, s), 2.95 (6H, s), 8.32 (2H, d, J = 1.8 Hz), 8.63 (2H, s), 9.40 (2H, d, J = 1.8 Hz). — MS (75 eV), *m/z*: 398 [M^+]. — $C_{28}H_{30}O_2$ (398.6): calcd. C 84.38, H 7.59; found C 84.38, H 7.66.

2,7-Di-tert-butylpyrene-4,9-dicarboxylic Acid (**9**): To a stirred suspension of 18 g (12.5 mmol) of calcium hypochloride in 25 ml of hot water was added a solution of 13 g (94 mmol) of potassium carbonate and 3.7 g (66 mmol) of potassium hydroxide in 60 ml of water. To the prepared aqueous solution of potassium hypochlorite was added a solution of 7.0 g (18 mmol) of **8** in 90 ml of dioxane. After stirring the reaction mixture was refluxed for 1 h, then worked up by the addition of water (50 ml) and $CHCl_3$ (50 ml). The organic layer was separated and the alkaline solution acidified with 10% hydrochloric acid to pH 1. The resulting precipitate was filtered, washed with water and dried in vacuo to give 5.1 g (12.7 mmol, 72%) of **9** as a pale yellow powder, m.p. >300°C. — IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3300, 2900, 1690, 1270. — MS (75 eV), *m/z*: 402 [M^+].

Dimethyl 2,7-Di-tert-butylpyrene-4,9-dicarboxylate (**10**): To a suspension of 5.0 g (12.4 mmol) of **9** in 500 ml of MeOH was added with stirring 5 ml of concd. sulfuric acid, and the reaction mixture was refluxed for 12 h. After cooling to room temp. it was extracted with $CHCl_3$. The organic extract was washed with water, dried with Na_2SO_4, and concentrated. The residue was subjected to silica gel column chromatography (eluent hexane/benzene, 1:1). Recrystallization from hexane/benzene (1:1) afforded 4.8 g (11.2 mmol, 90%) of **10** as colorless prisms, m.p. 271–272°C. — IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 1720, 1465, 1260, 1205, 1080. — ^{1}H NMR ($CDCl_3$): δ = 1.60 (18H, s), 4.12 (6H, s), 8.33 (2H, d, J = 1.8 Hz), 8.90 (2H, s), 9.53 (2H, d, J = 1.8 Hz). — MS (75 eV), *m/z*: 430 [M^+]. — $C_{28}H_{30}O_4$ (430.6): calcd. C 78.11, H 7.02; found C 77.75, H 6.96.

2,7-Di-tert-butyl-4,9-bis(hydroxymethyl)pyrene (**11**): To a suspension of 1.37 g (36 mmol) of $LiAlH_4$ in 100 ml of Et_2O was added at room temp. with stirring a solution of 5.0 g (11.6 mmol) of **10** in 100 ml of Et_2O, and the reaction mixture was stirred for 3 h at room temp. To this mixture was added a small amount of ethyl acetate at 0°C; subsequently, it was poured into a large amount of

ice/water and extracted with CH_2Cl_2 (3 × 200 ml). The combined extracts were washed with water (200 ml), 10% aqueous HCl (200 ml), and water (2 × 200 ml), dried with Na_2SO_4, and concentrated in vacuo. The residue was recrystallized from $CHCl_3$ to afford 3.6 g (9.63 mmol, 83%) of **11** as colorless prisms ($CHCl_3$), m.p. 302°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3250, 2950, 1600, 1480, 1260, 1080. – ^1H NMR ($CDCl_3$): δ = 1.58 (18H, s), 5.39 (4H, s), 8.11 (2H, s), 8.23 (2H, d, J = 1.8 Hz), 8.43 (2H, d, J = 1.8 Hz). – MS (75 eV), m/z: 374 [M^+]. – $C_{26}H_{30}O_2$ (374.5): calcd. C 83.38, H 8.07; found C 83.76, H 8.01.

2,7-Di-tert-butyl-4,9-bis(chloromethyl)pyrene (**12**): To a solution of 4.8 g (12.8 mmol) of **11** in 200 ml of $CHCl_3$ were added at room temp. with stirring 3.3 g (28 mmol) of thionyl chloride and a small amount of pyridine, and the reaction mixture was stirred for 3 h at room temp. It was subsequently poured into a large amount of ice/water. The organic layer was washed with 10% aqueous $NaHCO_3$ (100 ml) and water (2 × 100 ml), dried with Na_2SO_4, and concentrated in vacuo. The residue was recrystallized from hexane to afford 4.5 g (10.9 mmol, 86%) of **12** as colorless prisms (hexane), m.p. 250–253°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 1605, 1460, 1250. – ^1H NMR ($CDCl_3$): δ = 1.56 (18H, s), 5.28 (4H, s), 8.13 (2H, s), 8.23 (2H, d, J = 1.8 Hz), 8.49 (2H, d, J = 1.8 Hz). – MS (75 eV), m/z: 410, 412 [M^+]. – $C_{26}H_{28}Cl_2$ (411.4): calcd. C 75.91, H 6.86; found C 76.26, H 6.80.

Cyclization of **12** *and* **13** *to Dithiapyrenophanes* **14**. *Typical Procedure:* A solution of 2.0 g (4.9 mmol) of **12** and 834 mg (4.9 mmol) of 1,3-bis(mercaptomethyl)benzene (**13b**) in 100 ml of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 1.0 g (17.8 mmol) of KOH and 200 mg (5.0 mmol) of $NaBH_4$ in 3.0 l of ethanol. When the addition was complete (6 h), the reaction mixture was concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (500 ml). The CH_2Cl_2 extract was concentrated in vacuo, and the residue was separated by silica gel column chromatography (hexane/$CHCl_3$, 1:1). Recrystallization from hexane/$CHCl_3$ (1:1) afforded 722 mg (1.4 mmol, 29%) of *15,20-di-tert-butyl-2,11-dithia[3]metacyclo[3](4,9)pyrenophane* (**14b**) as colorless prisms (hexane/$CHCl_3$, 1:1), m.p. 234–237°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2970, 1600, 1390, 1355, 1240, 1220. – ^1H NMR ($CDCl_3$): δ = 1.61 (18H, s), 2.72 (2H, d, J = 16.5 Hz), 2.84 (2H, d, J = 16.5 Hz), 3.97 (1H, s), 4.23 (2H, d, J = 11.7 Hz), 4.92 (2H, d, J = 11.7 Hz), 6.15 (1H, t, J = 7.7 Hz), 6.44 (2H, dd, J = 7.7/1.6 Hz), 7.70 (2H, s), 7.92 (2H, d, J = 1.8 Hz), 8.33 (2H, d, J = 1.8 Hz). – MS (75 eV), m/z: 508 [M^+]. – $C_{34}H_{36}S_2$ (508.8): calcd. C 80.27, H 7.13; found C 80.11, H 7.15.

Compound **14c** was synthesized in the same manner as described above for **14b**. However, an attempted cyclization of **12** with 1,2-bis(mercaptomethyl)benzene (**13a**) to afford **14a** failed. Only dimer **15a** was obtained in 17% yield.

15,20-Di-tert-butyl-2,11-dithia[3]paracyclo[3](4,9)pyrenophane (**14c**): Colorless prisms (hexane/$CHCl_3$, 1:1), m.p. 258–261°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2970, 1600, 1390, 1355, 1240, 1220. – ^1H NMR ($CDCl_3$): δ = 1.64 (18H, s), 3.13 (2H, d, J = 16.1 Hz), 3.39 (2H, d, J = 16.1 Hz), 4.22 (2H, d, J = 13.0 Hz), 4.66 (2H, d, J = 13.0 Hz), 5.38 (2H, dd, J = 7.9/1.8 Hz), 5.51 (2H, dd, J = 7.9/1.8 Hz), 7.70 (2H, s), 8.01 (2H, d, J = 1.8 Hz), 8.30 (2H, d, J = 1.8 Hz). – MS (75 eV), m/z: 508 [M^+]. – $C_{34}H_{36}S_2$ (508.8): calcd. C 80.27, H 7.13; found C 80.29, H 7.03.

15,20,37,42-Tetra-tert-butyl-2,11,24,32-tetrathia[3]orthocyclo[3](4,9)pyreno[3]orthocyclo[3](4,9)pyrenophane (**15a**): Colorless prisms (hexane/$CHCl_3$, 1:1), m.p. 272–274°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2970, 1600, 1390, 1355, 1240, 1220. – ^1H NMR ($CDCl_3$): δ = 1.45 (36H, s), 3.44 (8H, s), 3.63 (4H, d, J = 12.8 Hz), 3.75 (4H, d, J = 12.8 Hz), 7.15 (8H, m), 7.33 (4H, s), 7.90 (4H, d, J = 1.8 Hz), 7.92 (4H, d, J = 1.8 Hz). – MS (75 eV), m/z = 1016 [M^+]. – $C_{68}H_{72}S_4$ (1017.6): calcd. C 80.27, H 7.13; found C 80.29, H 7.03.

15,20-Di-tert-butyl-2,11-dithia[3]metacyclo[3](4,9)pyrenophane S,S,S′,S′-Tetraoxide (**18b**): To a solution of 500 mg (0.98 mmol) of **14b** in 100 ml of $CHCl_3$ was added 870 mg (5.0 mmol) of *m*-chloroperbenzoic acid. After the reaction mixture had been stirred at room temp. for 6 h, it was washed with a 10% aqueous $NaHCO_3$ solution (2 × 30 ml), water (2 × 30 ml), and brine (30 ml), dried with Na_2SO_4 and concentrated in vacuo. The residue was recrystallized from $CHCl_3$ to give 550.1 mg (0.96 mmol, 98%) of **18b** as colorless prisms ($CHCl_3$), m.p. >300°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 1600, 1300, 1100. – MS (75 eV), m/z: 572 [M^+]. – $C_{34}H_{36}S_2O_4$ (572.8): calcd. C 71.30, H 6.34; found C 71.37, H 6.39.

15,20-Di-tert-butyl-2,11-dithia[3]paracyclo[3](4,9)pyrenophane S,S,S′,S′-Tetraoxide (**18c**) was prepared in the same manner as described above in 99% yield. Colorless prisms ($CHCl_3$), m.p. >300°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 1600, 1310, 1100. – MS (75 eV), m/z: 572 [M^+]. – $C_{34}H_{36}S_2O_4$ (572.8): calcd. C 71.30, H 6.34; found C 71.57, H 6.29.

Pyrolysis of Sulfone **18**. – *Typical Procedure:* Sulfone **18b** (300 mg, 0.52 mmol) was pyrolyzed at 480°C/0.8 Torr according to refs.[17a–c]. The sublimed product was collected and chromatographed on silica gel with hexane as an eluent to give 18 mg (0.053 mmol, 10%) of **16** and 30 mg (0.067 mmol, 13%) of **20b**.

2,7-Di-tert-butyl-4,9-dimethylpyrene (**16**): Colorless prisms (EtOH), m.p. 210–213°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2950, 2900, 1600, 1350, 1260. – ^1H NMR ($CDCl_3$): δ = 1.58 (18H, s), 2.88 (6H, s), 7.87 (2H, s), 8.12 (2H, d, J = 1.5 Hz), 8.24 (2H, d, J = 1.5 Hz). – MS (75 eV), m/z: 342 [M^+]. – $C_{26}H_{30}$ (342.5): calcd. C 91.17, H 8.83; found C 90.01, H 8.69.

2,7-Di-tert-butyl-4-methyl-9-(2-m-tosylethyl)pyrene (**20b**): Colorless prisms (EtOH), m.p. 158–159°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2960, 2850, 1600, 1390, 1360, 1230. – ^1H NMR ($CDCl_3$): δ = 1.59 (18H, s), 2.39 (3H, s), 2.90 (3H, s), 3.21 (2H, m), 3.55 (2H, m), 7.20 (4H, m), 7.89 (1H, s), 7.93 (1H, s), 8.13 (1H, d, J = 1.8 Hz), 8.16 (1H, d, J = 1.8 Hz), 8.26 (1H, d, J = 1.8 Hz), 8.37 (1H, d, J = 1.8 Hz). – MS (75 eV), m/z = 446 [M^+]. – $C_{34}H_{38}$ (446.7): calcd. C 91.42, H 8.58; found C 91.52, H 8.74.

Similarly, pyrolysis of sulfone **18c** afforded **16** and **20c** in 15 and 20% yield, respectively.

2,7-Di-tert-butyl-4-methyl-9-(2-p-tosylethyl)pyrene (**20c**): Colorless prisms (EtOH), m.p. 212–213°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2960, 2850, 1600, 1390, 1360, 1230. – ^1H NMR ($CDCl_3$): δ = 1.58 (9H, s), 1.59 (9H, s), 2.37 (3H, s), 2.90 (3H, s), 3.20 (2H, m), 3.55 (2H, m), 7.19 (2H, d, J = 8.1 Hz), 7.25 (2H, d, J = 8.1 Hz), 7.89 (1H, s), 7.92 (1H, s), 8.13 (1H, J = 1.8 Hz), 8.15 (1H, d, J = 1.8 Hz), 8.26 (1H, d, J = 1.5 Hz), 8.36 (1H, d, J = 1.5 Hz). – MS (75 eV), m/z: 446 [M^+]. – $C_{34}H_{38}$ (446.7): calcd. C 91.43, H 8.57; found C 91.21, H 8.28.

Photodesulfurization of **14c**: A solution of 200 mg (0.39 mmol) of **14c** in 50 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 33 h during which time nitrogen was bubbled through the solution. The solvent was distilled under reduced pressure, and 50 ml of water was added to the residue. The mixture was extracted with $CHCl_3$ (3 × 30 ml), and the combined extracts were washed with brine (30 ml), dried with Na_2SO_4, and concentrated. The residue was subjected ot silica gel column chromatography (eluent hexane). Recrystallization from hexane afforded 30 mg (0.067 mmol, 17%) of **21** as colorless prisms (hexane), m.p. 190–192°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2970, 1600,

1470, 1360, 1250. – ^{1}H NMR ($CDCl_3$): δ = 1.43 (9H, s), 1.47 (9H, s), 2.35 (1H, m), 2.95 (3H, m), 3.14 (1H, m), 3.48 (1H, m), 4.34 (1H, d, J = 8.8 Hz), 5.20 (1H, dd, J = 1.9/7.6 Hz), 5.34 (1H, s), 5.37 (1H, dd, J = 1.9/7.6 Hz), 5.51 (1H, dd, J = 1.9/7.6 Hz), 5.76 (1H, s), 5.87 (1H, dd, J = 1.9/7.6 Hz), 7.23 (1h, d, J = 1.8 Hz), 7.28 (1H, s), 7.42 (1H, d, J = 1.8 Hz), 7.59 (1H, d, J = 1.8 Hz), 7.87 (1H, d, J = 1.8 Hz). – ^{13}H NMR ($CDCl_3$): δ = 31.4, 31.6, 32.2, 34.6, 34.9, 36.0, 47.1, 50.6, 109.6, 118.5, 118.6, 122.7, 122.9, 124.8, 125.7, 125.9, 126.0, 126.2, 127.4, 128.3, 129.8, 130.5, 131.0, 135.9, 136.1, 136.2, 136.3, 147.1, 148.7, 148.8. – ^{13}H NMR-DEPT ($CDCl_3$): positive δ = 31.5, 31.6, 50.6, 118.5, 118.6, 122.7, 122.9, 124.8, 125.7, 126.2, 127.4, 128.3 negative δ = 32.2, 36.0, 47.1, 109.6. – MS (75 eV), m/z: 444 [M^+]. – $C_{34}H_{36}$ (444.7): calcd. C 91.84, H 8.16; found C 91.45, H 8.11.

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