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An Attempted Synthesis of [7][7]Circulene: Synthesis and Characterization of Triple-Layered [2.2]Phenanthreno[2.2]naphthalenophenanthrenophane

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The synthesis of the title compound, a triple-layered cyclophane, is described. The unusually strained structure was supported by its ^{1}H NMR spectra, electronic spectra, and X-ray crystallographic analysis.

Although a large number of multi-layered cyclophane molecules,[1] whose two fused aromatic rings are held together by two ethylene bridges, have been prepared, none possessing a polycyclic aromatic molecular framework as the multi-layered position have been reported, except for triple-layered [2.2][2.2]naphthalenophane.[2]

We have been interested in synthetic studies of non-planar polycyclic aromatic molecules, and previous papers from our laboratory describe the syntheses of [7]circulene **1**[3] and [7.7]-circulene **2**[4] with twisted saddle-shaped geometry. An obvious extension of our interests in these non-planar polycyclic aromatic molecules led us to investigate the synthesis of [7]-[7]circulene **3** with two [7]circulene frameworks; this contribution is concerned with the synthesis of [2.2](3,6)(2,7)-phenanthreno[2.2](3,6)(3,6)naphthalenophenanthrenophane **5** (Scheme 1).

In this paper, we describe the synthesis, structure, and properties of triple-layered [2.2]phenanthreno[2.2]-naphthalenophane **5** and its different stacking type isomer **6**, depending on the substitution mode of the bridging ethylenes, and an attempted preparation of the precursor **4** of [7][7]circulene **3** from **5**.

Results and Discussion

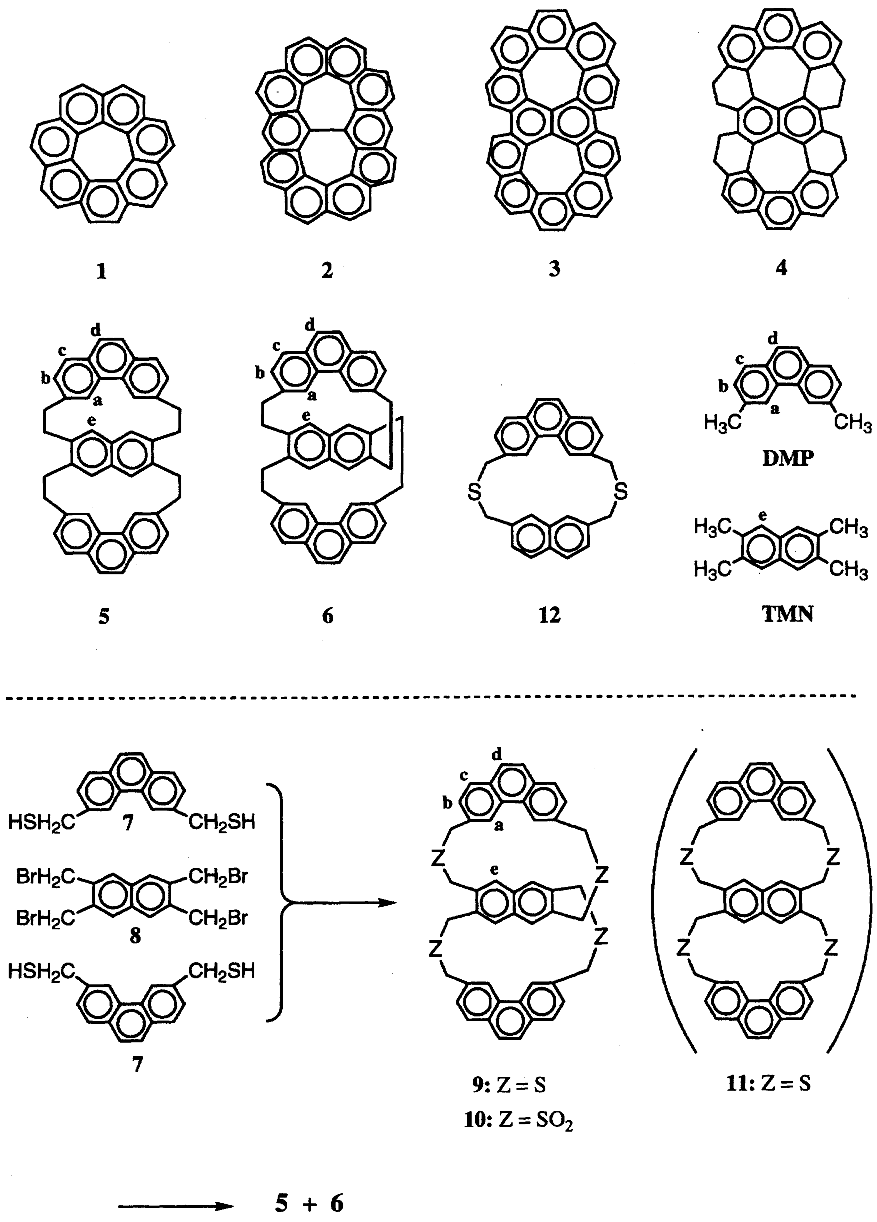
Syntheses of [2.2](3,6)(2,7)Phenanthreno[2.2](3,6)(3,6)naphthalenophenanthrenophane 5 and [2.2](3,6)(2,6)-Phenanthreno[2.2](3, 7)(3, 6)naphthalenophenanthrenophane 6. A termolecular coupling of 2,3,6,7-tetrakis(bromomethyl)naphthalene **8**[2] and 2 equiv of 3,6-bis(mercaptomethyl)phenanthrene **7**[5] was carried out in DMF with cesium carbonate to give the tetrathiacyclophane **9** (mp > 300 °C, 15% yield). Further, their possible isomer **11** with a different substitution mode was not detected. These observation are also compatible with an examination of their molecular models for **9** and **11**, which revealed that the obliquely stacking cyclophane **9** is more stable, apparently reflecting a less hindered geometry than that of **11**. Structural evidence for **9** mainly came from its ^{1}H NMR spectrum. The inner aromatic protons H^a at **9** might be situated just above the outer phenanthrene rings, so that the ^{1}H NMR spectrum shows a characteristic upfield shift at $\delta = 6.23$ as a broad singlet, compared to the corresponding ones ($\delta = 6.72$) of [3.3](2,7)-(3,6)naphthalenophenanthrenophane **12** as a double-layered homologue of **11**.

The oxidation of **9** with *m*-chloroperbenzoic acid gave the tetra(sulfone) **10**, whose pyrolysis at 550 °C (0.01 Torr, 1 Torr = 133.322 Pa), followed by column chromatography, produced the triple-layered cyclophane **6** (mp > 300 °C, colorless plates, 10% yield), together with another triple-layered isomer **5** (mp > 300 °C, colorless needles, 11% yield) with a different substitution mode by a thermal skeletal rearrangement[6] of **6**. The structure of **6** was confirmed by its X-ray crystallographic analysis.

Finally, we carried out an attempted preparation of octahydro[7][7]circulene **4** from **5**. Dehydrogenation of **5** by flush vacuum pyrolysis[7] (1000 °C at 10^{-3} Torr) or 5% Pd/C (300—350 °C) was unsuccessful, invariably giving a polymer as a product.

Spectroscopic Properties of [2.2]Phenanthreno[2.2]-naphthalenophenanthrenophanes 5 and 6. The ^{1}H NMR data (aromatic protons) of **5** and **6** are listed in Table 1, together with those of the reference compounds, 3,6-dimethylphenanthrene (DMP) and 2,3,6,7-tetramethylnaphthlene (TMN). As shown in Table 1, the data of layered cyclophane are characterized by a magnetic anisotropic effect of the adjacent aromatic rings. The remarkable upfield shift ($\Delta\delta = 1.89$—1.58) of aromatic protons of H^a, H^d, and H^e in **6** ($\delta = 6.56$, 7.45, and 5.86) compared to **5** ($\delta = 7.93$, 7.57, and 7.35) and the reference compounds ($\delta = 6.56$, 8.45, and 7.44) clearly indicates an obliquely stacking structure of **6**.

Figure 1 shows the electronic spectra of triple-layered cyclophane **5** and **6**, together with that of the reference compounds, DMP and TNM, in 1,4-dioxane. The electronic spectra of **5** and **6** reveal that these show a dramatic en-



Scheme 1.

Table 1. ^{1}H NMR Data (Aromatic Protons in $CDCl_3$) of Cyclophane **5** and **6**

	5	6	DMP	TMN
H^a	7.93	6.56	8.45	—
H^b	7.44	7.20	7.39	—
H^c	7.76	7.58	7.75	—
H^d	7.57	7.45	7.62	—
H^e	7.35	5.86	—	7.44

hancement in the electronic interaction with a different substitution mode. Compound **6** with the obliquely stacking structure demonstrates the common spectral characteristic of layered cyclophane, i.e., bathochromism, hyperchromism, and broardening,[8] compared to that of DMP and TMN. For example, the longest wavelength bands of DMP and TMN appear at 326 and 333 nm, respectively. In contrast, the layered **6** has its band at 353 and 364 nm, indicating a stronger transannular π-electron interaction expected from the crystal structure described below.

Molecular Structure of [2.2]Phenanthreno[2.2]naphthalenophenanthrenophane 6. The molecular structure of **6** was determined by the single-crystal X-ray diffraction method at room temperature. Two different views of the molecular structure of **6** are shown in Fig. 2. As can be seen from Fig. 2, the three aromatic rings diagonally overlap and are inclined 23.19° and 36.55° to the central naphthalene ring. The central naphthalene ring is distorted into a twist-boat shape, as in other triple-layered cyclophanes.[2] The twist angle of the inner naphthalene, defined by the dihedral angle between the mean planes of two benzene rings, is 12.91°, so that a considerable strain exists in it. The non-bonded distances between the C3 atom and the C29 and C30 atoms are 2.857 and 3.232 Å, respectively.

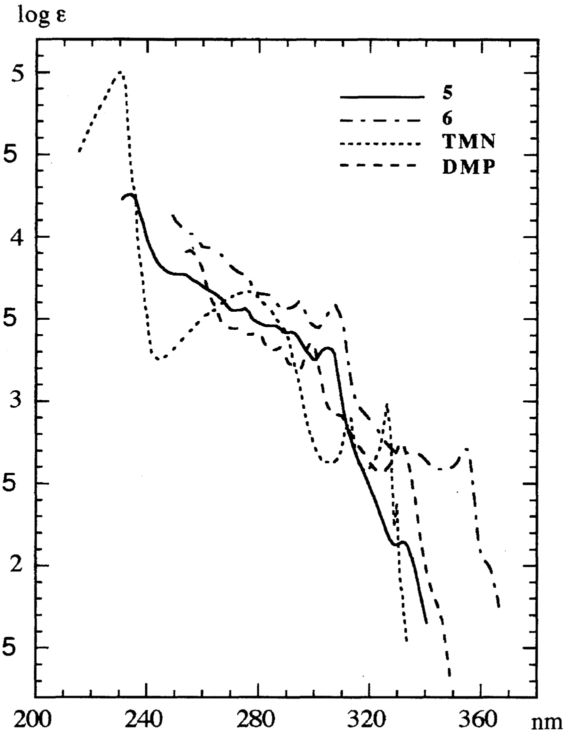


Fig. 1. Electronic spectra of **5**, **6**, DMP, and TMN in 1,4-dioxane.

Experimental

General. All of the melting points are uncorrected. IR data were obtained with a JASCO FT-5300 spectrophotometer. NMR measurements were made on a JEOL EX-270 spectrometer, with tetramethylsilane used as an internal standard. Mass spectra were taken on a JEOL JMS-AX-500 spectrometer. Elemental analyses were performed on a Yanagimoto CHN-Corder, Type II. Visible and ultraviolet spectra were measured with a Shimadzu UV-160 spectrophotometer.

Triple Layered Tetrathia[3.3]phenanthreno[3.3]naphthlenophenanthrenophane 9. A solution of 2,3,6,7-tetrakis(bromomethyl)naphthalene (1.65 g, 3.30 mmol) and 3,6-bis(mercaptomethyl)phenanthrene (1.80 g, 6.67 mmol) in DMF (300 ml) was slowly added into a stirred suspension of cesium carbonate (3.0 g, 8.5 mmol) in DMF (700 ml) over a period of 24 h at 50—55 °C under nitrogen. After being stirred at 50—55 °C for 8 h, the mixture was concentrated in vacuum, and the residue was extracted with boiling chloroform. Removal of the solvent afforded a solid which was recrystallized from benzene to give **9** (0.35 g) in 15% yield; mp > 300 °C; *m/z* 845 (M^+); ^{1}H NMR ($CDCl_3$) δ = 3.44 (4H, d, J = 14.5 Hz, CH_2), 3.49 (4H, d, J = 14.5 Hz, CH_2), 3.75 (4H, d, J = 13.0 Hz, CH_2), 4.43 (4H, d, J = 13.0 Hz, CH_2), 6.23 (4H, s, ArH), 6.54 (4H, s, ArH), 7.50 (4H, s, ArH), 7.51 (4H, d, J = 8.0 Hz, ArH), and 7.64 (4H, d, J = 8.0 Hz, ArH). Found: C, 76.82; H, 5.16%. Calcd for $C_{46}H_{36}S_4$: C, 77.05; H, 5.06%.

Tetrathia[3.3]phenanthreno[2.2]naphthlenophenanthrenophane Tetrasulfone 10. The tetrathia cyclophane **9** (0.30 g, 0.42 mmol) and *m*-chloroperbenzoic acid (0.75 g, 0.43 mmol) was dissolved in chloroform (400 ml) at 0 °C. After stirring for 12 h at room temperature, the solution was washed with a 3% sodium carbonate solution and then dried. Removal of the solvent gave a quantitative yield of **10** (0.35 g); mp > 300 °C; IR (KBr) 1110 and 1310 cm^{-1} (SO_2).

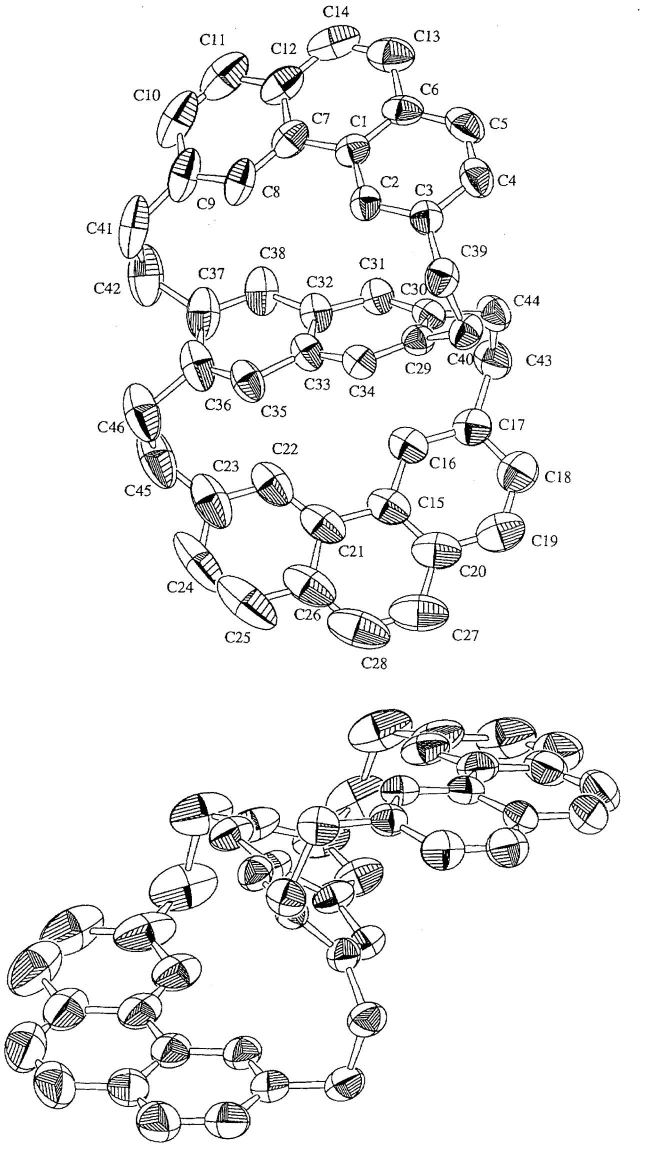


Fig. 2. Molecular structure of cyclophane **6**.

Triple-Layered [2.2]Phenanthreno[2.2]naphthlenophenanthrenophane 5 and 6. The tetra(sulfone) **10** (0.33 g, 0.39 mmol) was pyrolyzed at 550 °C under a vacuum (0.01 Torr) using a slow stream of nitrogen, and the pyrolysate was subjected to silica column chromatography. Elution with benzene–hexane (1 : 2) yielded **6** followed by **5**. Compound **6** was recrystallized from benzene, 24 mg (10%); colorless plates; mp > 300 °C; *m/z* 588 (M^+); ^{1}H NMR ($CDCl_2CDCl_2$) δ = 2.59 (8H, bs, CH_2), 2.82 (4H, bs, CH_2), 3.15 (4H, bs, CH_2), 5.86 (4H, s, ArH), 6.56 (4H, bs, ArH), 7.20 (4H, d, J = 8.2 Hz, ArH), 7.45 (4H, s, ArH), and 7.58 (4H, d, J = 8.2 Hz, ArH); UV (1,4-dioxane) λ_{max} (ε) 258 (9800), 266 (7500), 275 (5500), 284 (4400), 296 (3900), 307 (3900), 310sh (3000), 318 (790), 336 (480), 348 (400), 353 (480), and 364 nm (90). Found: C, 93.78; H, 6.16%. Calcd for $C_{46}H_{36}$: C, 93.84; H, 6.16%.

Compound **5** was recrystallized from benzene–hexane, 25 mg (11%); colorless needles; mp > 300 °C; *m/z* 588 (M^+); ^{1}H NMR ($CDCl_2CDCl_2$) δ = 2.63 (8H, bs, CH_2), 3.28 (4H, bs, CH_2), 3.55 (4H, bs, CH_2), 7.35 (4H, s, ArH), 7.44 (4H, d, J = 7.6 Hz, ArH), 7.57 (4H, s, ArH), 7.76 (4H, d, J = 7.6 Hz, ArH), and 7.93 (4H, s, ArH); UV (1,4-dioxane) λ_{max} (ε) 234 (17400), 238sh (14400), 276

(3500), 278 (2800), 292 (2500), 305 (2100), 315 (520), and 334 nm (130). Found: C, 93.76; H, 6.22%. Calcd for $C_{46}H_{36}$: C, 93.84; H, 6.16%.

Dithia[3.3](2,7)(3,6)naphthalenophenanthrenophane 12. Starting from 3,6-bis(bromomethyl)phenanthrene and 2,7-bis(mercaptomethyl)naphthalene, the cyclophane **12** was prepared by the same method as that described for the preparation of **9**; 33% yield; mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ = 3.62 (4H, s, CH_2), 3.65 (4H, s, CH_2), 6.72 (2H, s, ArH), 7.42 (2H, s, ArH), 7.72 (2H, dd, J = 8.6 and 1.7 Hz, ArH), 7.76 (2H, s, ArH), 7.81 (2H, d, J = 1.7 Hz, ArH), 7.86 (2H, d, J = 8.4 Hz, ArH), and 7.94 (2H, d, J = 8.3 Hz, ArH).

X-Ray Crystallographic Sructure Analysis of Compound 6. Recrystallisation from benzene at room temperature gave colorless single crystals. X-Ray diffraction data were collected at 20 °C on a Rigaku AFC-7R diffractometer with Mo $K\alpha$ radiation (λ = 0.71069 Å). The structure was solved and refined by using the program package teXsan.[9]

Crystal Data: $C_{46}H_{36}$, M = 588.79, monoclinic, space group $P2_1/n$ (No. 14), a = 14.419(4), b = 16.205(5), c = 14.854(5) Å, β = 113.87(2)°, V = 3173(1) Å^3, Z = 4, D_c = 1.232 g cm^{-3}, crystal dimensions 0.50×0.30×0.30 mm, F(000) = 1248.00, μ(Mo $K\alpha$) = 0.69 cm^{-1}.

Data Collection, Structure Solution, and Refinement. A total of 7852 reflections were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°; 7564 reflections were unique (R_{int} = 0.034). The structure was solved by direct methods (SAPI 91)[10] and refined by a full-matrix least-squares method with 524 variables and 2663 observed reflections [$I > 3.0\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The final R- and R_w- values were 0.044 and 0.040, respectively. The standard deviation of an observation of unit weight was 1.75. The maximum peak and the minimum peak in the final difference map were 0.09 and −0.08 e$^-$ Å^{-3}, respectively.

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