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An Attempted Synthesis of 8-Shaped Circulene: Synthesis and Characterization of [2.2](4,4′)Biphenylo(3,11)dibenzo[*c*, *l*]chrysenophane and Its Cyclophadiene

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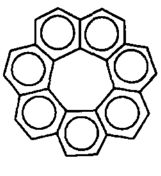
The syntheses of the title compounds are described. The unusually strained structures were supported by their ^{1}H NMR spectra, electronic spectra, and X-ray crystallographic analyses.

As members of cyclophanes,[1] whose two condensed aromatic rings are held together by two ethylene bridges, there have been prepared [2.2]naphthalenophane,[2] [2.2]phnanthrenophane,[3] and [2.2]pyrenophane.[4] Conspicuous features in these compounds are their nonplanar deformed aromatic rings and strong transannular π-electron interactions caused by their intense interfacial crowding of the two condensed aromatic rings. We have been interested in synthetic studies of non-planar polycyclic aromatic molecules, and previous papers from our laboratory have described the syntheses of [7]circulene **1**[5] and [7.7]circulene **2**[6] with a twisted saddle-shaped geometry. An obvious extension of our interests in these non-planar polycyclic aromatic molecules led us to investigate the synthesis of 8-shaped enclosed circulene **3**, a new type of circulene shaped like a figure of eight; this contribution is concerned with the synthesis of [2.2](4,4′)biphenyleno(5,13)dibenzo[*c*,*l*]chrysenophane (**4**) and its diene homologue **5** with the external framework of **3**. In this paper, we describe the synthesis, structures, and properties of **4** and **5**, and an attempted preparation of 8-shaped circulene **3** from **5** (Scheme 1).

Results and Discussion

Synthesis. NBS bromination of dimethyldibenzochrysene **7**[7] afforded the bis(bromomethyl) derivative **8**, which was transformed into dithiol **9** by mercaptization with thiourea. The coupling of **9** and 4,4′-bis(bromomethyl)biphenyl (**10**) was carried out in DMF with cesium carbonate to give the dithiacyclophane **11**, mp 233—234 °C (39% yield). The oxidation of **11** with *m*-chloroperbenzoic acid gave the bis(sulfone) **12**, whose pyrolysis at 550 °C (0.01 Torr, 1 Torr = 133.322 Pa), followed by column chromatography, produced the cyclophane **4** as pale-yellow needles, mp 176—177 °C (34% yield from **11**). The reaction of dithiacyclophane **11** with dimethoxymethylium tetrafluoroborate[8] in dichloromethane yielded the disulfonium salt **13**, whose Stevens rearrangement mediated by sodium hydride provided a 78% yield of the bis(methylthio)cyclophane **14** as a yellow solid. The oxidation of **14** with *m*-chloroperbenzoic acid gave the bis(methyl sulfoxide) **15**, whose pyrolysis at 300 °C (10^{-3} Torr) produced the cyclophadiene **5** as a pale-yellow prisms, mp 185—186 °C (22% yield from **13**). Finally, we carried out an attempted preparation of 8-shaped circulene **3** from **5**. Dehydrogenation of **5** by flash vacuum pyrolysis[9] at 1000 °C at 10^{-3} Torr was observed to afford the dihydro product **6** as pale-orange prisms, mp > 300 °C (10% yield). Structural evidences for **6** mainly came from its ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR is characteristic, having ten sets of AB quartets with the aid of ^{1}H-^{1}H COSY and the ^{13}C NMR exhibiting forty-two peaks, corresponds to the molecular symmetry. This evidence, enhanced by its mass spectrum and its suitable elemental analysis, pointed to dihydrocirculene **6** as the product. We reasoned that the attempted dehydrogenation of the cyclophadiene intermediate **5** directly into 8-shaped circulene **6** failed because of the inherent rigid structure of **6**, incorporating an 8-shaped circular arrangement of ten benzene rings.

Spectroscopic Properties. The ^{1}H NMR data of **4** and **5** are listed in Table 1, together with that of the reference compounds, 4,4′-dimethylbiphenyl (DMB) and 3,11-dimethyldibenzo[*c*,*l*]chrysene (DMDBC). It is interesting to observe in the ^{1}H NMR data of **4** and **5** four distinctly separated pairs of biphenyl aromatic protons by restricted rotation. Moreover, the remarkable upfield shifts of biphenyl aromatic protons at δ = 5.37, 6.31, 6.87, 7.09, and dibenzochrysene aromatic protons at δ = 7.43 (ArH^a), 8.54 (ArH^g) in **4**, compared



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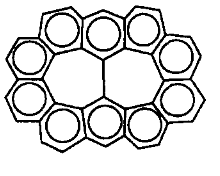

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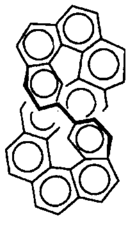

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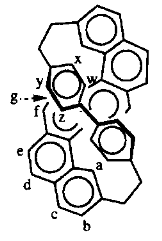

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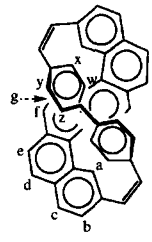

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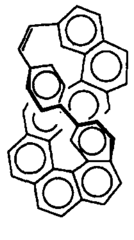

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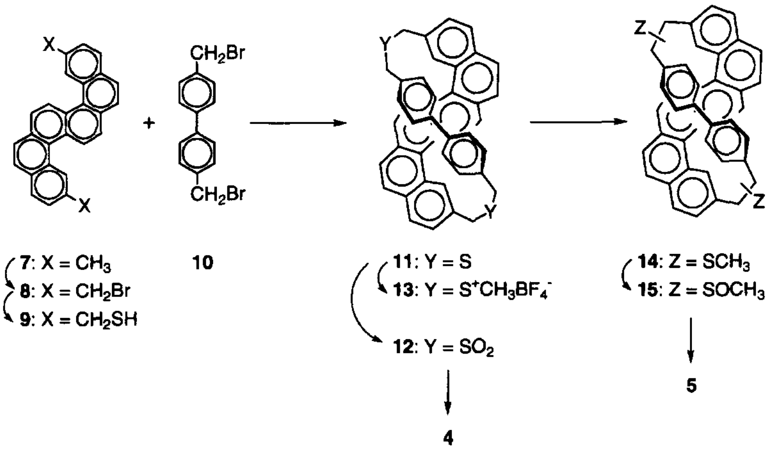

Scheme 1.

to the corresponding ones of DMB at δ = 7.23, 7.47, and ones of DMDBC at δ = 8.85 (ArH^a), 9.12 (ArH^g), clearly indicate an oblique stacking structure of the cyclophane **4**. These upfield shifts are also observed for the cyclophadiene **5**.

Figure 1 records the electronic spectra of **4** and **5** as well as those of the reference compounds, DMB and DMDBC. The transannular π-electron interactions of **4** and **5** can be best understood by those electronic spectra. Compounds **4** and **5** demonstrate the common spectral characteristics of layered cyclophanes, i.e., bathochromism, hyperchromism, and broading[10] compared to that of the standard compound DMDBC. For example, the longest wavelength band of DMDBC appears at 352 nm. In contrast, **4** and **5** have band at 364 and 372 nm, respectively, indicating strong transannular π-electron interactions, as expected from the crystal structures described below.

Molecular Structure. The molecular structures of **4** and **5** were determined by the single-crystal X-ray diffraction method at room temperature. Two different views of **4** and **5** are shown in Figs. 2 and 3, respectively. Figures 2a and 3a show top views of the ORTEP drawing. The two aromatic frameworks, biphenyl and dibenzochrysene, diagonally overlap each other and, on the whole, take an obliquely overlapped structure. As can be seen from side views of Figs. 2b and 3b, the dibenzo[*c*,*l*]chrysene rings are bent into a twist form to disperse any strain throughout the fused system; also the nearest non-bonded atomic distances between the neighboring aromatic rings of the biphenyl moiety is 3.07 Å in **4**, and 3.03 Å in **5**. Table 2 lists the dihedral angles between the perihedral benzene rings of the dibenzochrysene moieties in **4** and **5**. Because the largest dihedral angle between mean plane C and mean plane D is 21.5°, a considerable strain exists in it. These values are fairly smaller than that of the bending angles of [2.2](5,13)dibenzochrysenophane (**16**),[11] indicating that the dibenzochrysene part effectively disperses any strain throughout the fused system. In addition, the dihedral angles between the two benzene rings of the biphenyl moieties in **4** and **5** are held at 30° and 27° in a non-coplanar fashion, respectively.

Experimental

General. All of the melting points are uncorrected. IR data were obtained with a JASCO FT-5300 spectrophotometer. ^{1}H and ^{13}C NMR were recorded with a JEOL EX-270 spectrometer and a JEOL JMN/A-500 spectrometer, respectively, with tetramethylsi-

Table 1. ^{1}H NMR Data of **4** and **5** in $CDCl_3$

Compound	Spectral data	
4	2.34—2.43 (2H, m, CH_2)	2.90—2.96 (2H, m, CH_2)
	3.11—3.22 (2H, m, CH_2)	3.33—3.35 (2H, m, CH_2)
	5.37 (2H, d, $J = 7.6$ Hz, ArH^w)	6.31 (2H, d, $J = 7.9$ Hz, ArH^x)
	6.87 (2H, d, $J = 7.6$ Hz, ArH^y)	7.09 (2H, d, $J = 7.9$ Hz, ArH^z)
	7.43 (2H, s, ArH^a)	
	7.48 (2H, d, $J = 7.9$ Hz, ArH^b)	7.66 (2H, d, $J = 8.6$ Hz, ArH^c)
	7.72 (2H, d, $J = 8.5$ Hz, ArH^f)	7.85 (2H, d, $J = 8.6$ Hz, ArH^d)
	7.97 (2H, d, $J = 7.9$ Hz, ArH^e)	8.54 (2H, d, $J = 8.5$ Hz, ArH^g)
5	6.27 (2H, d, $J = 8.1$ Hz, ArH^w)	6.51 (2H, d, $J = 7.9$ Hz, ArH^x)
	6.92 (2H, d, $J = 8.1$ Hz, ArH^y)	7.12 (2H, d, $J = 7.9$ Hz, ArH^z)
	7.00 (4H, s, =CH)	
	7.48 (2H, d, $J = 8.6$ Hz, ArH^b)	7.64 (2H, d, $J = 8.6$ Hz, ArH^c)
	7.70 (2H, d, $J = 8.2$ Hz, ArH^e)	7.79 (2H, d, $J = 8.2$ Hz, ArH^d)
	7.90 (2H, s, ArH^a)	7.92 (2H, d, $J = 7.9$ Hz, ArH^f)
	8.48 (2H, d, $J = 7.9$ Hz, ArH^g)	
DMB	2.39 (6H, s, CH_3)	
	7.23 (4H, d, $J = 7.9$ Hz, ArH)	7.47 (4H, d, $J = 7.9$ Hz, ArH)
DMDBC	2.65 (6H, s, CH_3)	
	7.49 (2H, d, $J = 8.2$ Hz, ArH^b)	7.83 (2H, d, $J = 7.9$ Hz, ArH^d)
	7.90 (2H, d, $J = 8.2$ Hz, ArH^e)	7.92 (2H, d, $J = 8.9$ Hz, ArH^f)
	7.95 (2H, d, $J = 8.9$ Hz, ArH^c)	8.85 (2H, s, ArH^a)
	9.12 (2H, d, $J = 8.9$ Hz, ArH^g)	

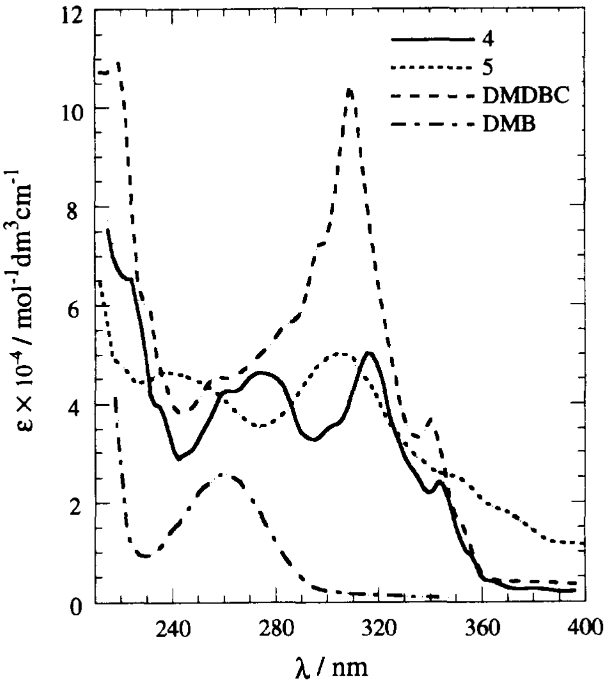

Fig. 1. Electronic spectra of **4**, **5**, **DMDBC**, and **DMB** in 1, 4-dioxane.

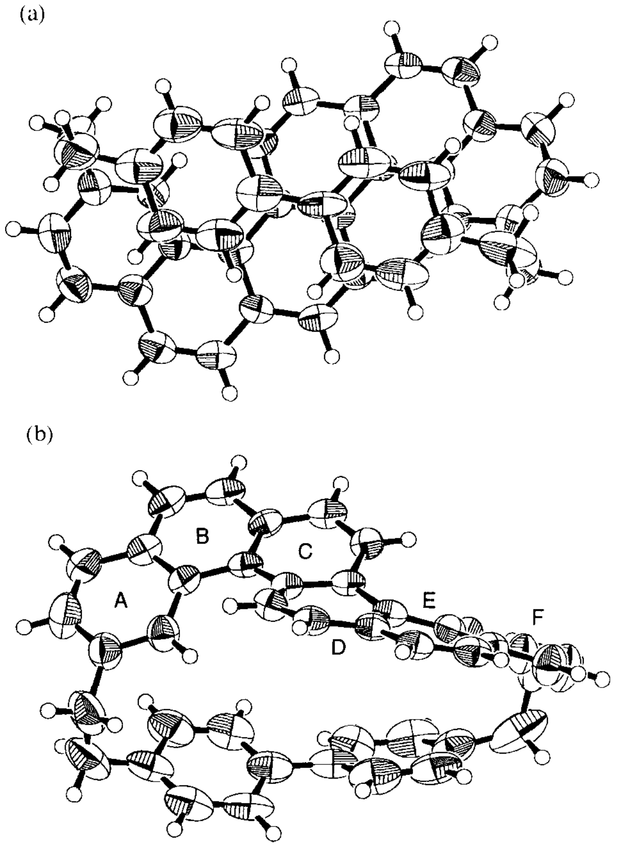

Fig. 2. a) Molecular structure (top view) of cyclophane **4**. b) Molecular structure (side view) of cyclophane **4**.

lane used as an internal standard. Mass spectral data were measured on a JEOL AX-500 spectrometer. Elemental analyses were performed on a Yanagimoto CHN-Corder, Type II. Merck alumina or Merck silica gel was used for column chromatography. Progress of most reactions was followed by TLC with Merck precorted silica gel (1.05735).

3,11-Bis(bromomethyl)dibenzo[*c*,*l*]chrysene (8). 3,11-Dimethyldibenzo[*c*,*l*]chrysene (**7**)[11] (1.25 g, 3.5 mmol) was refluxed with *N*-bromosuccimide (1.34 g, 7.5 mmol) and a catalytic amount of benzoyl peroxide in 60 ml of carbon tetrachloride for 3 h. After

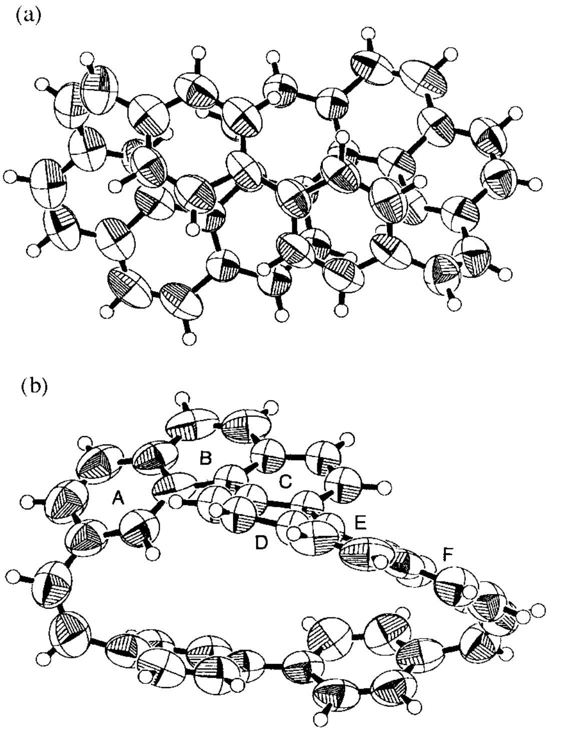

Fig. 3. a) Molecular structure (top view) of cyclophadiene **5**. b) Molecular structure (side view) of cyclophadiene **5**.

Table 2. Dihedral Angles (°) between Two Benzene Rings of the Dibenzochrysene Moieties

	A–B	B–C	C–D	D–E	E–F	A–F
4	11.0	9.2	21.5	9.4	11.6	62.5
5	13.6	9.6	21.5	9.5	11.4	65.6
16	10.4	9.4	18.2	7.7	11.2	58.5

removal of succinimide by filtration, the filtrate was concentrated. The remainder was recrystallized from benzene–hexane to give light-yellow fine crystals of **8** (1.54 g, 85%); mp 229—231 °C; *m/z* (FAB) 514 (M$^+$); ^{1}H NMR (CDCl$_3$) δ = 4.84 (4H, s, CH$_2$), 7.70 (2H, d, J = 8.6 Hz, ArH), 7.90—7.95 (6H, m, ArH), 8.00 (2H, d, J = 8.6 Hz, ArH), 8.06 (2H, d, J = 8.6 Hz, ArH), and 9.08 (2H, d, J = 8.9 Hz, ArH).

Dibenzo[*c*,*l*]chrysene-3,11-bis(methanethiol) (9). A mixture of **8** (0.69 g, 1.34 mmol), thiourea (0.23 g, 3.00 mmol), and DMSO (20 ml) was stirred for 10 h. The resulting thiouronium salt was collected by filtration and dissolved in a 6% sodium hydroxide solution (30 ml). After refluxing under nitrogen for 8 h, the solution was allowed to cool and then acidified with 6 M (1 M = 1 mol dm^{-3}) hydrochloric acid with ice-cooling. The resulting solid was collected by filtration and recrystallized from chloroform to give light-yellow scales of **9** (0.46 g, 82%); mp 121—122 °C; IR (KBr) 2570 cm^{-1} (SH); *m/z* (FAB) 420 (M$^+$); ^{1}H NMR (CDCl$_3$) δ = 1.98 (2H, t, J = 7.3 Hz, SH), 4.04 (4H, d, J = 7.3 Hz, CH$_2$), 7.78 (2H, d, J = 8.2 Hz, ArH), 7.93 (4H, s, ArH), 7.99 (2H, d, J = 8.6 Hz, ArH), 8.05 (2H, d, J = 8.2 Hz, ArH), 8.94 (2H, s, ArH), and 9.07 (2H, d, J = 8.6 Hz, ArH).

Dithiacyclophane 11. To a stirred suspension of cesium carbonate (1.96 g, 6.0 mmol) and dry DMF (1000 ml), a mixture of **9** (2.40 g, 5.68 mmol) and 4,4′-bis(bromomethyl)biphenyl **10** (1.93 g, 5.68 mmol) in dry DMF (100 ml) was added 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 **11** (1.33 g, 39%); mp 233—234 °C; *m/z* (FAB) 598 (M$^+$); ^{1}H NMR (CDCl$_3$) δ = 3.59 (2H, d, J = 15.5 Hz, CH$_2$), 3.84 (2H, d, J = 15.5 Hz, CH$_2$), 4.12 (2H, d, J = 15.2 Hz, CH$_2$), 4.19 (2H, d, J = 15.2 Hz, CH$_2$), 6.14 (4H, d, J = 8.3 Hz, ArH of biphenyl unit), 6.82 (4H, d, J = 8.3 Hz, ArH of biphenyl unit), 7.83 (2H, d, J = 8.9 Hz, ArH), 7.86 (2H, s, ArH), 7.89 (2H, d, J = 8.6 Hz, ArH), 7.94 (2H, d, J = 8.9 Hz, ArH), and 8.76 (2H, d, J = 8.6 Hz, ArH). Found: C, 84.41; H, 5.10%. Calcd for $C_{42}H_{30}S_2$: C, 84.24; H, 5.05%.

Dithiacyclophane *S*,*S*′-Bis(dioxide) 12. The dithiacyclophane **11** (0.15 g, 0.25 mmol) and *m*-chloroperbenzoic acid (0.19 g, 1.10 mmol) were dissolved in chloroform (50 ml) at 0 °C. After stirring for 12 h at room temperature, the solution was washed with a 3% sodium hydrogencarbonate solution and then dried. Removal of the solvent gave a quantitative yield of **12** (0.21 g); mp $>$ 300 °C; IR (KBr) 1320 and 1110 cm^{-1} (SO$_2$).

[2.2](4,4′)Biphenylo(3,11)dibenzo[*c*,*l*]chrysenophane (4). The disulfone **12** (0.20 g, 1.33 mmol) was pyrolyzed at 550 °C under a vacuum (0.01 Torr) using a slow stream of nitrogen, and the pyrolysate was subjected to alumina column chromatography. Elution with benzene–hexane (1 : 1) gave **4** (46 mg, 34%), which was recrystallized from benzene; yellow needles; mp 176—177 °C; *m/z* (FAB) 562 (M$^+$); UV (1,4-dioxane) λ_{max} (ε) = 224 (64700), 235sh (39300), 246 (29600), 260sh (41900), 275 (45800), 302sh (34900), 317 (50700), 343 (23500), 352 (15600), and 364 nm (4500). Found: C, 94.47; H, 5.53%. Calcd for $C_{44}H_{30}$: C, 94.34; H, 5.66%.

***S*,*S*′-Dimethyldithioniacyclophane Bis(tetrafluoroborate) 13.** To a stirred solution of dithiacyclophane **11** (1.26 g, 2.14 mmol) in dry dichloromethane (140 ml) was added dropwise dimethoxycarbonium tetrafluoroborate[8] (5.0 ml) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 24 h. After the addition of a small quantity of ethanol, the resulting solid was collected, washed with dichloromethane, and then dried to yield **13** (quantitative) as a yellow powder; mp $>$ 300 °C. The product was used without further purification.

Stevence Rearrangement of the Salt 13. The salt **13** (1.36 g, 1.69 mmol) was suspended in dry tetrahydrofuran (140 ml) with excess sodium hydride under nitrogen, and the mixture was stirred at 50—55 °C for 3 d. Water (120 ml) was carefully added under cooling, and the separated product was extracted with chloroform. The chloroform phase was washed with water, and then dried. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene–hexane (1 : 2) gave a mixture of structural and stereoisomers of **14** (0.81 g, 78%) as a yellow solid; *m/z* (FAB) 628 (M$^+$).

Bis(methylthio)[2.2](4, 4′)biphenylo(3, 11)dibenzo[*c*,*l*]chrysenophane *S*,*S*′-Bis(oxide) (15). The cyclophane **14** (0.81 g, 1.29 mmol) and *m*-chloroperbenzoic acid (0.45 g, 2.60 mmol) were dissolved in chloroform (200 ml) at 0 °C. After stirring for 12 h at room temperature, the solution was washed with a 3% sodium hydrogenecarbonate solution and then dried. Removal of the solvent gave a quantitative yield of **15** (0.85 g) as a yellow solid; IR (KBr) 1035 cm^{-1} (SO).

[2.2](4,4′)Biphenyleno(3,11)dibenzo[*c*,*l*]chrysenophadiene (5). The bis(sulfoxide) **15** (0.84 g, 1.33 mmol) was pyrolyzed at 300 °C under vacuum (0.01 Torr) and the pyrolysate was subjected to silica-gel column chromatography. Elution with benzene–hexane (1 : 1) gave **5** (0.15 g, 22%), which was recrystallized from benzene; yellow prisms; mp 185—186 °C; *m/z* (FAB) 530 (M$^+$); UV (1,4-

dioxane) $\lambda_{\max}$ (ε) = 218sh (48500), 244 (46300), 308 (49800), 348 (25300), and 372 nm (17100). Found: C, 94.89; H, 5.11%. Calcd for $C_{42}H_{26}$: C, 95.06; H, 4.94%.

Flash Vacuum Pyrolysis of Cyclophadiene 5. The cyclophadiene **5** (0.05 g, 0.09 mmol) was pyrolyzed at 1000 °C under vacuum (10^{-3} Torr) using a slow stream of nitrogen, and the pyrolysate was subjected to alumina column chromatography. Elution with benzene–hexane (1 : 1) afforded a yellow solid which was recrystallized from benzene to give **6**; mp 226—227 °C; *m*/*z* (FAB) 528 (M^+); ^{1}H NMR ($CDCl_3$) δ = 8.51 (1H, d, J = 8.6 Hz), 8.06 (1H, d, J = 8.7 Hz), 8.04 (1H, d, J = 8.7 Hz), 8.02 (1H, d, J = 8.1 Hz), 7.96 (1H, d, J = 8.1 Hz), 7.95 (1H, d, J = 8.8 Hz), 7.90 (1H, d, J = 8.8 Hz), 7.84 (1H, d, J = 8.5 Hz), 7.82 (1H, d, J = 8.6 Hz), 7.73 (1H, d, J = 8.2 Hz), 7.69 (1H, s), 7.61 (1H, d, J = 8.5 Hz), 7.46 (1H, d, J = 8.6 Hz), 7.44 (1H, d, J = 8.5 Hz), 7.36 (1H, s), 7.33 (1H, d, J = 8.5 Hz), 7.25 (1H, d, J = 8.2 Hz), 7.17 (1H, d, J = 8.0 Hz), 7.04 (1H, d, J = 11.2 Hz, CH=CH), 7.01 (1H, d, J = 11.2 Hz, CH=CH), 6.93 (1H, d, J = 8.6 Hz), 6.83 (1H, d, J = 8.0 Hz), 6.34 (1H, d, J = 7.8 Hz), and 6.06 (1H, d, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 140.98, 137.71, 136.94, 134.51, 132.84, 132.73, 132.21, 132.10, 131.67, 130.96, 130.69, 130.57, 129.98, 129.73, 129.23, 129.20, 129.01, 128.41, 128.37, 128.33, 128.32, 127.83, 127.63, 127.56, 127.35, 127.33, 127.28, 127.24, 127.17, 127.09, 126.53, 126.52, 126.49, 126.45, 126.01, 125.80, 125.61, 125.57, 125.22, 125.03, 123.82, and 123.33. Found: C, 95.38; H, 4.60%. Calcd for $C_{42}H_{24}$: C, 95.42; H, 4.58%.

X-Ray Crystallographic Structure Analysis of Compound 4. Recrystallization from benzene–ethanol 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.[12]

Crystal Data: $C_{42}H_{30}\cdot C_6H_6$, M_w = 612.81, triclinic, space group $P\bar{1}$ (#2), a = 13.31(2), b = 13.39(3), c = 12.18(2) Å, α = 105.3(1)°, β = 105.5(1)°, γ = 113.3(1)°, V = 1706(8) Å^3, Z = 2, D_c = 1.193 g cm^{-3}, crystal dimensions 0.25×0.20×0.20 mm, F (000) = 648.00, μ(Mo $K\alpha$) = 0.67 cm^{-1}.

Data Collection, Structure Solution, and Refinement. A total of 6897 reflections were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°; 6554 reflections were unique (R_{int} = 0.074). The structure was solved by direct methods (SIR 92)[13] and refined by a full-matrix least-squares method with 403 variable parameter and 6549 observed reflections [$I > 0$]. All carbon atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The final $R2-$ ($wR2$-) and R1 $-$ ($wR1-$) values were 0.193 (0.245) and 0.092 (0.217), respectively. 2154 of reflections [$I > 2.0\sigma(I)$] were used to calculate $R1$. The goodness-of-fit indicator was 1.63. The maximum peak and the minimum peak in the final difference map were 0.63 and -0.84 e$^-$ Å^{-3}, respectively.

X-Ray Crystallographic Structure Analysis of Compound 5. Recrystallization from benzene–methanol at room temperature gave pale-yellow single crystals. Data collection of X-ray diffraction and a structure analysis were performed in the same way for compound **4**.

Crystal data: $(C_{42}H_{26}\cdot C_6H_6)_2$, M_w = 1217.56, triclinic, space group $P\bar{1}$ (#2), a = 15.55(3), b = 17.02(1), c = 14.26(2) Å, α = 105.50(7)°, β = 110.7(1)°, γ = 93.41(1)°, V = 3341(8) Å^3, Z = 2, D_c = 1.210 g cm^{-3}, crystal dimensions 0.30×0.30×0.15 mm, F (000) = 1280.00, μ (Mo $K\alpha$) = 0.68 cm^{-1}.

Data Collection, Structure Solution, and Refinement. A total of 9893 reflections were collected using the ω–2θ scan technique to a maximum 2θ value of 50.0°; 9418 reflections were unique (R_{int} = 0.024). The structure was solved by direct methods (MULTAN 88)[14] and refined by a full-matrix least-squares method with 681 variable parameter and 9401 observed reflections [$I > 0$]. The carbon atoms of the central naphthalene part in the dibenzochrysene moiety were refined isotropically to reduce the number of variables, while the other carbon atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The final $R2-$ ($wR2-$) and $R1-$ ($wR1-$) values were 0.149 (0.213) and 0.088 (0.191), respectively. 3515 of reflections [$I > 2.0$ $\sigma(I)$] were used to calculate $R1$. The goodness-of-fit indicator was 1.82. The maximum peak and the minimum peak in the final difference map were 0.54 and -0.59 e$^-$ Å^{-3}, respectively.

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