1.60–1.83 (m, 3 H, C*H*(CH_3)$_2$ and CH_2), 0.96 (2d, 6 H, CH_3).

(3*S,5*S**,7*S**)-3,7-Bis(benzoyloxy)-5-hydroxy-8-methylnonanoic Acid δ-Lactone (46b).** The procedure used was identical with that used for the preparation of (3*S**,5*R**,7*S**)-3,7-bis(benzoyloxy)-5-hydroxy-8-methylnonanoic acid δ-lactone (**39b**). Thus, 5.5 mg (27.2 μmol) of *syn,anti*-3,5,7-trihydroxy-8-methylnonanoic acid δ-lactone (**46a**) was treated with 191 mg (1.36 mmol) of benzoyl chloride in the presence of 215 mg (2.72 mmol) of pyridine and the product was purified by flash chromatography on silica gel (15 × 180 mm column, 30% ethyl acetate in hexanes, 8-mL fractions) to give 9.5 mg (85%) of the title compound as a colorless oil: R_f 0.29 (30% ethyl acetate in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) 7.97–8.08 (m, 4 H, aromatic C*H*), 7.38–7.60 (m, 6 H, aromatic C*H*), 5.46 (m, 1 H, C*H*OBz), 5.13 (m, 1 H, C*H*OBz), 4.40 (m, 1 H, C*H*OCOR), 3.00 (dd, 1 H, C*H*HCO$_2$R, J = 6.02, 17.04 Hz), 2.77 (ddd, 1 H, C*H*HCH(OBz)CH$_2$CO$_2$R, J = 3.07, 6.51, 14.10 Hz), 2.71 (dd, 1 H, CH*H*CO$_2$R, J = 6.03, 17.07 Hz), 2.35 (ddd, 1 H, 1CH*H*CHO(OBz)CH$_2$CO$_2$R, J = 5.02, 9.80, 14.62 Hz), 1.92–2.10 (m, 3 H, (CH$_3$)$_2$C*H*CH(OBz)CH_2), 1.80 (ddd, 1 H, CH*H*CH(OBz)-CH$_2$CO$_2$R, J = 7.80, 11.66, 14.13 Hz), 1.01 (2d, 6 H, CH(CH_3)$_2$).

Reduction of 3-Phenylpropyl 7-Hydroxy-3,5-dioxo-8-methylnonanoate (28) with Tetramethylammonium Triacetoxyborohydride. To a solution of 440 mg (1.67 mmol, 20.6 equiv) of tetramethylammonium triacetoxy borohydride in 700 μL of anhydrous acetic acid was added a solution of 27.1 mg (81.0 μmol) of 3-phenylpropyl 7-hydroxy-3,5-dioxo-8-methylnonanoate (**28**) in 300 μL of anhydrous acetic acid. The mixture was stirred at ambient temperature for 30 min. The solution was poured onto ice and the reaction vessel was rinsed onto the ice with 10 mL of dichloromethane. The biphasic mixture was washed with saturated aqueous sodium bicarbonate (2 × 100 mL), the aqueous layers being back extracted with dichloromethane (5 × 10 mL) after each wash. The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo to leave 30.7 mg (113% mass balance) of a colorless solid. The mixture was purified by flash chromatography on silica gel (ethyl acetate, 10 × 180 mm column, 4-mL fractions) to give 9.5 mg (35%) of a colorless oil which contained a 4:1 mixture of anti dihydroxy keto ester **47**. Also isolated was 15.5 mg (56%) of a mixture of triol esters **29–32** as a colorless, crystalline solid. The column was flushed with an additional 200 mL of ethyl acetate which was concentrated to give an additional 1.6 mg of the triol esters. The triols were combined (17.1 mg, 63%) and analyzed by HPLC (Zorbax 5 μm silica, 2% methanol in 70:30 isooctane/dichloromethane, 2 mL/min, λ = 258 nm). The triol esters were present in a ratio of 41:6.1:1:0 (Anti-Anti, **29**: Anti-Syn, **30**: Syn-Anti, **31**: Syn-Syn, **32**). The mixture was separated by flash chromatography on silica gel (3% methanol in 70:30 isooctane/dichloromethane, 15 × 180 mm column, 4-mL fractions) to give 13.6 mg (50%) of the Anti-Anti triol ester **29** as a colorless, crystalline solid.

Acknowledgment. Support was provided by the National Institutes of Health and the National Science Foundation. K.T.C. acknowledges a predoctoral fellowship from the Shell Company Foundation. E.M.C. acknowledges support from the National Science Foundation for a predoctoral fellowship. The NIH BRS Shared Instrumentation Grant Program 1 S10 RR01748-01A1 is acknowledged for providing NMR facilities.

Registry No. 1, 113778-34-0; (±)-**2**, 113778-35-1; (±)-**3**, 113778-36-2; (±)-**3a**, 113778-38-4; (±)-**3b**, 113778-39-5; (±)-**4**, 113778-37-3; (±)-**4a**, 113778-40-8; (±)-**4b**, 113778-64-6; (±)-**7a**, 113778-41-9; (±)-**7b**, 113778-44-2; (±)-**7b** (TBS ether), 113778-82-8; (±)-**8d**, 103729-84-6; (±)-**8a** (acetonide), 113778-76-0; DL-**8b**, 113778-42-0; DL-**8b** (acetonide), 113778-79-3; DL-**8b** (1-TBS ether), 113778-81-7; (±)-**9a**, 103729-88-0; DL-**9b**, 113778-43-1; DL-**9b** (acetonide), 113778-80-6; DL-**6b** (1-TBS ether), 113778-88-4; **12**, 55233-96-0; (±)-**13**, 113778-84-0; (±)-**14**, 113778-45-3; (±)-**15**, 113778-46-4; (±)-**17**, 113778-48-6; (±)-**18**, 113778-87-3; (±)-**20**, 113778-85-1; (±)-**21**, 113778-86-2; **22** (R_1 = Me_2CH; R_2 = $(CH_2)_3Ph$), 109704-49-6; (±)-**27**, 113778-56-6; (±)-**28**, 113778-57-7; (±)-**29**, 113778-58-8; (±)-**30**, 113830-18-5; (±)-**31**, 113830-19-6; (±)-**32**, 113830-20-9; (±)-**33**, 113778-59-9; (±)-**34**, 113778-60-2; (±)-**36**, 113830-25-4; (±)-**37**, 113778-61-3; (±)-**38a**, 113778-47-5; (±)-**38b**, 113778-49-7; (±)-**39a**, 113778-50-0; (±)-**39b**, 113778-51-1; (±)-**40**, 113778-62-4; (±)-**41**, 113778-63-5; (±)-**43**, 113830-21-0; (±)-**44**, 113830-22-1; (±)-**45a**, 113778-52-2; (±)-**45b**, 113778-53-3; (±)-**46a**, 113778-54-4; (±)-**46b**, 113778-55-5; (±)-**47**, 113778-83-9; TBSCl, 18162-48-6; $TBSOSO_2CF_3$, 69739-34-0; $NaBH_4$, 16940-66-2; $NaHB(OAc)_3$, 56553-60-7; Me_4NBH_4, 16883-45-7; Me4NHB(OAc)$_3$, 109704-53-2; $HO(CH_2)_3Ph$, 122-97-4; Me_2CHCHO, 78-84-2; $Zn(BH_4)_2$, 17611-70-0; $Me_2CHCOCH_2CO_2Et$, 7152-15-0; $AcO(CH_2)_3Ph$, 122-72-5; (±)-$Me_2CHCOCH_2CH(OH)CH_2CO_2(CH_2)_3Ph$, 113778-65-7; $Me_2CHCONMe(OMe)$, 113778-69-1; (±)-$Me_2CHCH(OH)CH_2COCHMe_2$, 113778-68-0; $MeCOCHMe_2$, 563-80-4; (±)-*anti*-$Me_2CHCH(OH)CH_2CH(OH)CHMe_2$, 103668-43-5; $EtCOCHMe_2$, 565-69-5; $Bu_2BOSO_2CF_3$, 60669-69-4; (±)-*anti*-$Me_2CHCH(OH)CH(Me)COCHMe_2$, 102285-80-3; (±)-*syn*-$Me_2CHCH(OH)CH(Me)COCHMe_2$, 102285-81-4; (±)-*anti-syn*-$Me_2CHCH(OH)CH(Me)CH(OH)CHMe_2$, 113889-53-5; MeONHMe·HCl, 6638-79-5; $BnOCH_2CO_2Me$, 31600-43-8; $BnOCH_2CONMe(OMe)$, 104863-68-5; Me_2CHCl, 75-29-6; $Me_2CHCOCH_2OBn$, 113778-75-9; (±)-*anti*-$Me_2CHCH(OH)CH(OBn)COCHMe_2$, 113778-70-4; (±)-*syn*-$Me_2CHCH(OH)CH(OBn)COCHMe_2$, 113778-71-5; (±)-*syn-anti*-$Me_2CHCH(OH)CH(OBn)CH(OH)CHMe_2$, 113778-73-7; *syn-syn*-$Me_2CHCH(OH)CH(OBn)CH(OH)CHMe_2$, 113830-24-3; *anti-anti*-$Me_2CHCH(OH)CH(OBn)CH(OH)CHMe_2$, 113830-23-2; DL-*threo*-$MeO_2CCH(OBn)CH(OH)CHMe_2$, 113778-77-1; DL-*erythro*-$MeO_2CCH(OBn)CH(OH)CHMe_2$, 113778-78-2; ACNMe(OMe), 78191-00-1; diketene, 674-82-8; ethyl 4-methyl-3,3-(ethylenedioxy)pentanoate, 27773-04-2; 3,3-(ethylenedioxy)-4-methyl-1-pentanol, 113778-66-8; 3,3-(ethylenedioxy)-4-methylpentanal, 95456-11-4; (±)-3-phenylpropyl 5,5-(ethylenedioxy)-3-hydroxy-6-methylheptanoate, 113778-67-9; *anti-anti*-2,6-dimethyl-4-(phenylmethoxy)-3,5-heptanediol acetonide, 113778-72-6; *syn-anti*-2,6-dimethyl-4-(phenylmethoxy)-3,5-heptanediol acetonide, 113778-74-8; 2,5-dihydro-4-*tert*-butylanisole, 22566-53-6.

Synthesis and Molecular Structure of [7]Circulene[1]

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Abstract: The polycyclic aromatic compound with a circular arrangement of seven benzene rings, [7]circulene (**3**), was prepared by treatment of 1,16-dehydro-2,15-diformylhexahelicene (**30**) with low-valent titanium, and its unusual saddle-shaped structure with C_2 symmetry was supported by its X-ray analysis. Preparation, X-ray analysis, and optical stability of dehydro[7]circulene derivatives **17**, **29**, and **30** were also reported.

Within the family of polycyclic aromatic compounds with circular arrangement of benzene rings known as circulene,[2-4] there have been prepared [5]circulene (corannulene) (**1**)[5,6] and [6]-circulene (coronene) (**2**).[7] Conspicuous features in this class of compounds are the existence of three type's of geometry, bowl-

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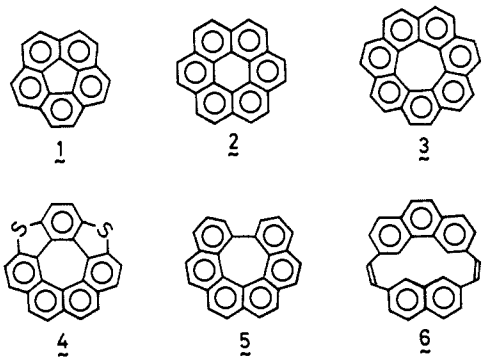
Chart I



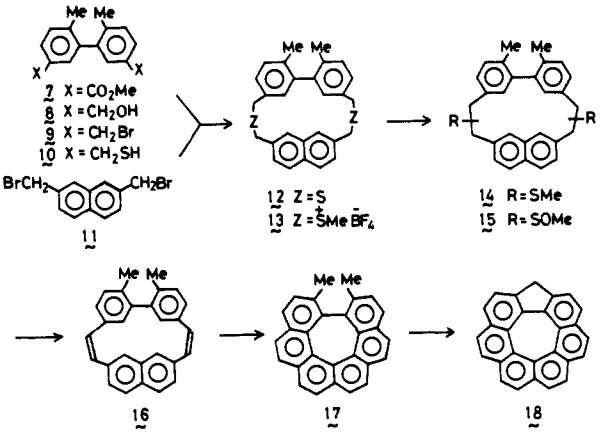
shaped nonplanar, planar, and saddle-shaped nonplanar, each resulting from the number of benzene rings necessary to form the circular arrangement. [5]Circulene (**1**) (C_{5v} symmetry), first reported and studied by Barth and Lawton in 1966, was shown to have a bowl-like shaped geometry by X-ray analysis.[8] On the other hand, [6]circulene (**2**) (D_{6h} symmetry) is a well-known member of the class prepared by Scholl and Mayer in 1932 and has a completely planar structure because of the angular fusion of six benzene rings.[9] [7]Circulene (**3**), the next higher homologue of [6]circulene (**2**), has been of interest for many years because of its anticipated strained and unique saddle-shaped molecular shape with C_2 symmetry as expected from the examination of its molecular model. Although the related compounds of [7]circulene (**3**) such as [7]heterocirculene (**4**)[4] (incorporating thiophene rings) and hexa[7]circulene (**5**)[10] (continguous benzoannelated ring around a central seven-membered ring) have been recorded, the parent carbocyclic structure, [7]circulene (**3**), was still an unknown compound, in spite of an enormous amount of effort in its preparation[4,11] (see Chart I).

We have been interested in the synthetic studies of twisted π-electron systems.[12] and previous papers described the syntheses of various strained cyclophanes with twisted aromatic rings.[13] An obvious extension of our interests in these studies led us to investigate the preparation of highly symmetrical and highly strained polycyclic aromatic molecules, [7]circulene (**3**), as one of a series of our synthetic studies of strained aromatic molecules.[14,15]

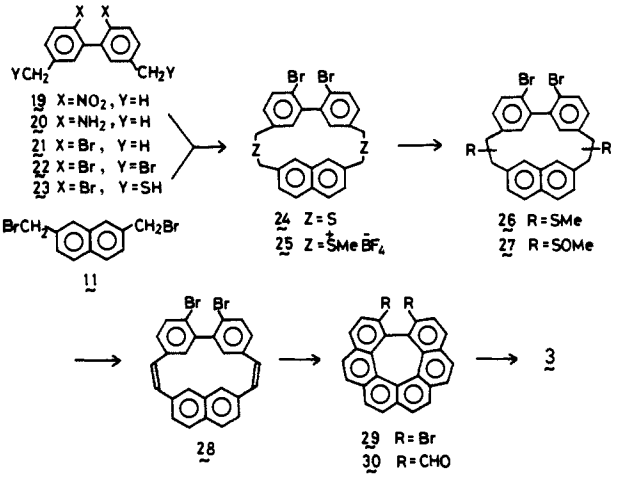
Results and Discussion

We reasoned that Reiss's attempted photocyclization[11] of the cyclophane intermediate **6** directly into [7]circulene (**3**) failed because of the inherent rigid structure of **6**, incorporating both naphthalene and phenanthrene moieties. Thus, we directed our efforts to a two-stage synthetic approach that involves (1) photocyclization of the more flexible biphenylnaphthalene cyclophanes **16** and **28** to the 1,16-dehydrohexahelicenes **17** and **29** and (2) modification of the side chains to secure the missing benzene ring to complete the synthesis.

Scheme I



Scheme II



Synthesis of [7]Circulene (3). First, we carried out an attempted preparation of [7]circulene (**3**) from 1,16-dehydro-2,15-dimethylhexahelicene precursor (**17**) to complete the synthesis according to the Reiss procedure (Scheme I). Lithium aluminum hydride reduction of 5,5′-dicarbomethoxy-2,2′-dimethylbiphenyl (**7**)[16] afforded the alcohol **8** which was converted to the bis-bromomethyl derivative **9** with phosphorus tribromide, and this was then submitted to the thiourea method under the usual reaction conditions to afford the bis(mercaptomethyl)biphenyl **10**. The coupling of dithiol **10** and 2,7-bis(bromomethyl)naphthalene (**11**)[17] was carried out in *N*,*N*-dimethylformamide with cesium carbonate[18] to give the dithiacyclophane **12**, mp 143–144 °C (54% yield). Reaction of cyclophane **12** with dimethoxycarbonium fluoroborate[19] in dichloromethane yielded the disulfonium salt **13** whose Stevens rearrangement mediated by sodium hydride provided a 93% yield of the bis(sulfide) **14** as an oil. Oxidation of **14** with *m*-chloroperbenzoic acid gave the bis(sulfoxide) **15** whose pyrolysis at 300 °C (0.001 mm) produced the unsaturated cyclophane **16**, as pale orange needles, mp 145–146 °C (45% yield from **14**). A solution of cyclophane **16** containing a trace amount of iodine was irradiated with a high-pressure mercury-quartz lamp[20] in a photolysis tube through which a slow and fine stream of nitrogen was passed. Through monitoring the reaction by UV absorption spectra, it was determined that a 2-h irradiation was enough to afford a maximum yield of 1,16-dehydro-2,15-dimethylhexahelicene (**17**) (57% yield), mp 226–228 °C, pale yellow

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prisms. Its ^1H NMR spectrum showed the expected absorption peaks: a singlet at δ 1.75 for two methyl protons and a multiplet at δ 7.0–7.9 for twelve aromatic protons. Comparison of the UV absorption spectrum of **17** (λ_{max} 245, 269, 275, 282, 308, 325 nm) with that of 1,16-dehydrohexahelicene (**5**)[10] also supports this structure.

An attempt to halogenate the two methyl positions of **17** by use of either NBS or NCS was unsuccessful, invariably giving a polymer as the product. Several other attempts were made to synthesize [7]circulene (**3**). Dehydrogenation of **17** with 5% Pd/C and Pd–S/$BaCO_3$ at 320–330 °C was observed to afford the [7]circulene analogue **18** incorporating a cyclopentadiene unit within the framework (51–65% yield), mp > 300 °C, as yellow plates. The ^1H NMR spectrum revealed that two methyl groups had been lost and showed a new peak at δ 3.99 (2 H, singlet), while the aromatic resonance multiplet resembled that of the starting dimethyl compound **17**. This evidence, enhanced by its mass spectrum and its suitable elemental analysis, pointed to 1,16-dehydro-2,15-methanohexahelicene (**18**) as the product, which seems to be a nearly planar molecule by examination of its molecular model.

In the next approach, we selected as the key intermediate 1,16-dehydro-2,15-dibromohexahelicene (**29**) (see Scheme II) which was easily convertible into the precursor **30** with a suitable substituent for ring closure to give the final benzene ring. 2,2′-Diamino-5,5′-dimethylbiphenyl (**20**), provided by the reduction of 5,5′-dimethyl-2,2′-dinitrobiphenyl (**19**)[21] with tin and concentrated hydrochloric acid, was treated with sodium nitrite to afford the corresponding diazonium salt whose mercuric bromide complex[22] was pyrolyzed at 110 °C to give the 2,2′-dibromo-5,5′-dimethylbiphenyl (**21**), mp 109–110 °C (40% yield from **19**). *N*-Bromosuccinimide bromination of **21** afforded the bis(bromomethyl) derivative **22**, which was converted into the bis(mercaptomethyl)biphenyl **23** by a routine procedure (48% yield from **21**). The coupling reaction of **23** and **11** was carried out following the procedure described for the preparation of **12**, and column chromatography of the reaction product afforded the dithiacyclophane **24** in 56% yield, mp 173–174 °C. The dithiacyclophane **24** was converted into the disulfonium salt **25** whose Stevens rearrangement gave a 95% yield of bis(sulfide) **26** as an oil. Oxidation of **26** with *m*-chloroperbenzoic acid followed by pyrolysis (300 °C, 0.001 mm) produced a 63% yield of the cyclophadiene **28**, mp 213–214 °C. Photocyclization of the diene **28** under a similar condition described for the preparation of **17** led to the formation of 1,16-dehydro-2,15-dibromohexahelicene (**29**), mp 299–301 °C, in 47% yield. Its ^1H NMR spectrum showed the expected absorption at δ 7.82–8.66 (multiplet). UV and MASS spectroscopy confirmed the structure of **29**.

Lithiation of the dibromide **29** with *n*-BuLi in tetrahydrofuran and formylation of the resulting dithio derivative of **29** with dimethylformamide gave, as was expected, the dialdehyde **30** (35% yield, mp 303–305 °C) and 1,16-dehydrohexahelicene (**5**) (4% yield, mp 163–164 °C)[10] as the reductive product of dibromide **29**.

For the introduction of the final benzene ring into circular arrangement, we found that reductive coupling of the dialdehyde **30** with low-valent titanium[23] effected a clean-coupling reaction to produced [7]circulene (**3**). Intramolecular reductive coupling of **30** with $LiAlH_4$ and titanium trichloride in dimethoxyethane completed the outer perimeter and afforded a 35% yield of [7]circulene (**3**) as yellow plates, mp 295–296 °C (from benzene–hexane). The ^1H NMR is characteristic having a single sharp peak at δ 7.45, and the ^{13}C NMR exhibiting three peaks at δ 136.0, 131.1, and 127.5 corresponds to the molecular symmetry. The mass spectrum showed only significant ions at M^+, $M^+ + 1$, and $M^+ + 2$. The UV spectrum of **3** (Figure 1) showed absorption

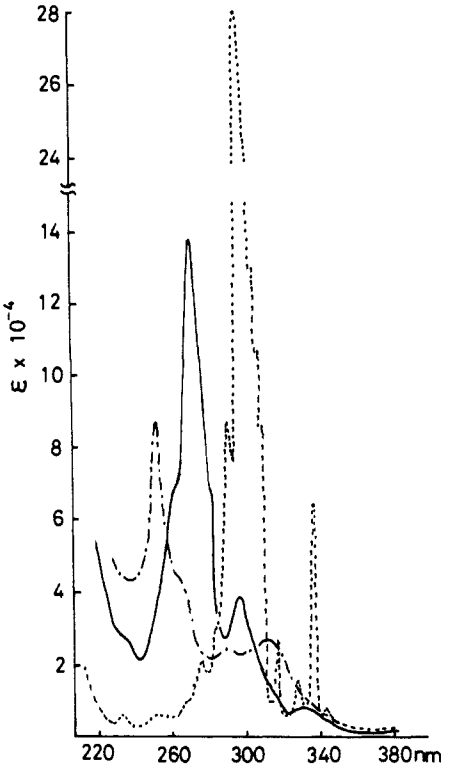

Figure 1. UV spectra of [7]circulene (**3**) (—), 1.16-dehydro-2,15-methanohexahelicene (**18**) (— — —), and [6]circulene (**2**) (– – –) (in cyclohexane).

maxima at 236 sh (log ϵ 4.44), 266 sh (4.86), 275 (5.14), 296 (4.46), 331 (3.91), 383 sh (2.90), and 4.03 (2.83). The remarkable hypsochromic shift (27 nm) with decreasing extinction coefficient of the highest absorption going from the [6]circulene (**2**) to the [7]circulene (**3**) indicates a nonplanar saddle-shaped geometry which is confirmed by its X-ray analysis shown below.

Syntheses and Chiroptical Properties of Optically Active 1,16-Dehydrohexahelicene Derivatives 5, 17, 29, and 30. 1,16-Dehydrohexahelicene (hexa[7]circulene) (**5**)[10] with C_2 symmetry was predicted, on the basis of the molecular model, to be saddle-shaped and potentially resolvable.[24] While the hydrocarbone **5** has been synthesized, no evidence concerning its chiral properties has yet appeared.[10] Our continuing interest in chiroptical properties of chiral π-electron systems[12] has led us to investigate the preparation and absolute configuration of optically active compounds **5**, **17**, **29**, and **31** as well as their optical stabilities.

1,16-Dehydrohexahelicene (**5**) itself was resolvable at low temperature by chromatographic resolution[25] by using a column packed with (+)-poly(triphenylmethyl methacrylate)[26] (elution with methanol) but was extremely optically labile (half-life, 10 s, at −5 °C) ($\Delta G^{\ddagger}$ 17 Kcal/mol). However, other compounds (**17**, **29**, and **31**) of this type with 2,15-disubstituents could be resolved by the chromatographic method to give optically pure (−)-(M)-**17**, (+)-(P)-**17**, (−)-(M)-**29**, (+)-(P)-**29**, (−)-(M)-**30**, and (+)-(P)-**30**, with $[\alpha]_D$ ($CHCl_3$) −1882°, +1879°, −2110°, +2113°, −1456°, and +1450°, respectively. Comparison of their CD spectra with that of authentic (−)-(M)-hexahelicene[27] established their absolute configurations (Figure 2).

Thermal racemization of their enantiomers (**17**, **29**, and **30**) monitored by polarimetry was examined to have moderate optical

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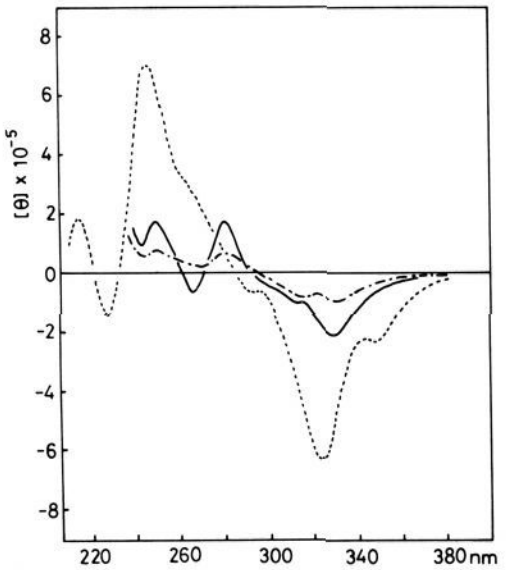

Figure 2. CD spectra of (−)-1,16-dehydro-2,15-dimethylhexahelicene (**17**) (—), (−)-1,16-dehydro-2,15-dibromohexahelicene (**29**) (—·—), and (−)-(*M*)-hexahelicene (– – –) (*in cyclohexane*).

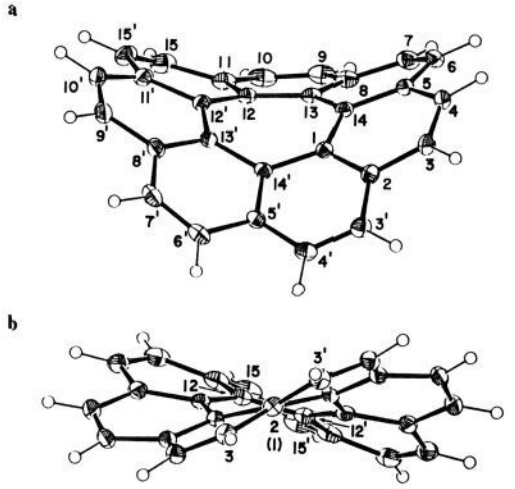

Figure 3. Molecular structure of **3** determined at −110 °C. Thermal ellipsoids for non-hydrogen atoms are drawn at 30% probability level. The hydrogen atoms are shown as the spheres with arbitrary temperature factor of 1.0 Å^2: (a) a view showing saddle-shaped structure and (b) a molecular projection along the crystallographic two-fold axis.

stability, the half-life of racemization being 120 min (at 139 °C in xylene) for the dimethyl derivative (**17**) ($\Delta G^{\ddagger}$ 32 Kcal/mol), 220 min for the dibromide (**29**) ($\Delta G^{\ddagger}$ 33 Kcal/mol), and 100 min for the dialdehyde (**30**) ($\Delta G^{\ddagger}$ 32 Kcal/mol). The capacity of the 2,16-substituents to interfere with passage through the plannar transition state thus seems to be Br > CH_3 > CHO ≫ H. It might be noted that this order roughly parallels the order of size of the groups.[28]

Molecular Structures of [7]Circulene (3) and 1,16-Dehydro-2,15-dibromohexahelicene (29). The molecular structure of [7]circulene (**3**) was determined by the single-crystal X-ray diffraction method at room temperature (at 20 °C) and was

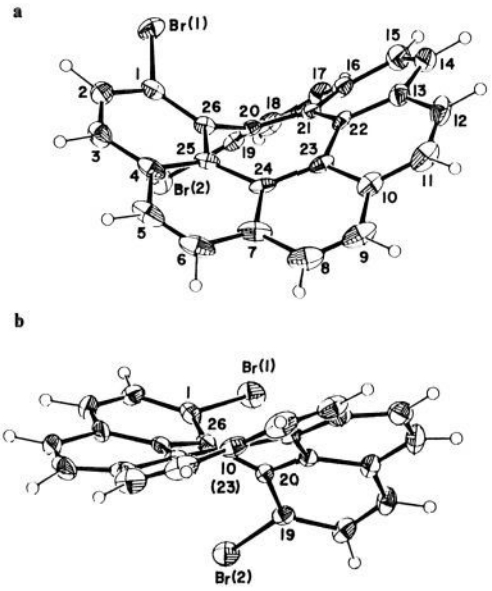

Figure 4. Molecular structure of **29**. Drawing conditions are the same as those in Figure 3: (a) a view showing the saddle-shaped structure and (b) a molecular projection along the noncrystallographic two-fold axis.

communicated previously.[1] In order to obtain structural parameters with higher accuracy, redeterminations of the crystal structure of **3** was carried out at low temperature (at −110 °C). The details of the crystal structure of **3** at room temperature are available as Supplementary Material; however, the discussion hereafter will be made based on the crystal structure of **3** at low temperature. The two different views of the molecular structure of **3** are shown in Figure 3. As expected, the molecule **3** has the unique saddle-shaped structure (Figure 3a). The molecule **3** has a crystallographic two-fold symmetry passing through the C(2) and C(1) atoms and the midpoints of C(12)–C(12′) and C(15)–C(15′) bonds (Figure 3b). The central seven-membered ring is described as the boat form with the base plane defined by C(1), C(14′), C(12), and C(13) atoms, with C(14) atom as the bow and with C(12′) and C(13′) atoms as the stern, or its symmetry equivalent structure related by the twofold axis. The dihedral angles between the base plane and the bow or stern planes are 21.7° and 26.5°, respectively.

The molecular structure of 1,16-dehydro-2,15-dibromohexahelicene (**29**) determined by the X-ray diffraction method is shown in Figure 4 together with the atomic numberings. The molecule has an approximate twofold symmetry axis that coincides with *the C(10)–C(23) bond and the midpoint of the C(20)–C(26) bond.* The molecule **29** is also described as a saddle-shaped structure (Figure 4a) of molecule **3**; however, the deformation of the former is relatively large compared with the rather flat structure of **3**. The seven-membered ring in the center of the molecule is the boat form with the base plane defined by C(20), C(21), C(23), and C(24) atoms, with C(22) atom as the bow and with C(25) and C(26) atoms as the stern, or its alternative one related by noncrystallographic twofold symmetry. The dihedral angles between the base plane and the bow or stern planes are 17.7° and 36.4°, respectively.

The important structural parameters of molecules **3** and **29** are summarized in Table I. The torsional angles around the C–C bonds of the central seven-membered ring are compared in Table Ia to describe the conformation of the ring precisely. The remarkable difference is found in the torsional angles around the C(12)–C(12′) bond in **3** and the corresponding bond of C(20)–C(26) in **29**, the former being 33.1° while the latter being 64.6°. This may be caused by the strong steric repulsion between the two neighboring bromine atoms. The nonbonded distance between the bromine atoms is 3.571 (1) Å, which is shorter than the sum of the Pauling's van der Waals' radius for bromine (1.95 Å). Some short constants are also found between the bromine atoms and

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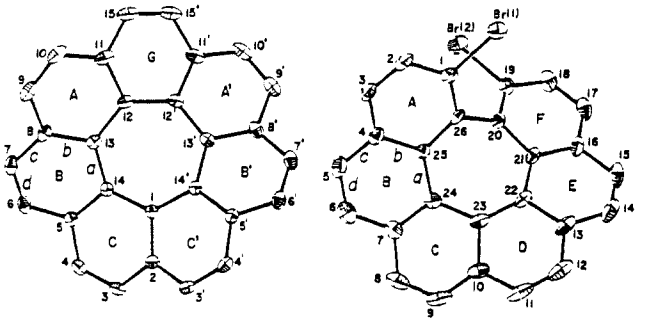
(30) Ashida, T. HBLS-V: *The Universal Crystallographic Computing System-Osaka*; The Computation Center, Osaka University, 1979.
(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, p 71.

Table I. Important Structural Parameters in Molecules **3** and **29**



(a) Torsional Angles (ϕ/deg)[a]

3		29	
C–C bond	ϕ/deg	C–C bond	ϕ/deg
C(12)–C(13)	−6.3	C(26)–C(25)	−22.7
C(13)–C(14)	−31.9	C(25)–C(24)	−24.8
C(14)–C(1)	21.5	C(24)–C(23)	16.1
C(1)–C(14′)	21.5	C(23)–C(22)	24.8
C(14′)–C(13′)	−31.9	C(22)–C(21)	−18.1
C(13′)–C(12′)	−6.3	C(21)–C(20)	−35.0
C(12′)–C(12)	33.1	C(20)–C(26)	64.6

(b) Dihedral Angles (θ/deg)[b]

3		29	
benzene ring	θ/deg	benzene ring	θ/deg
A–B	16.4	A–B	10.2
B–C	23.1	B–C	19.4
C–C′	16.0	C–D	11.1
A–G	19.6	D–E	23.0
		E–F	14.6
mean	19.2	mean	15.7

(c) Mean Atomic Deviations (Δd/Å)[c]

3		29	
benzene ring	Δd/Å	benzene ring	Δd/Å
A	0.063	A	0.048
B	0.065	B	0.059
C	0.060	C	0.048
G	0.065	D	0.055
		E	0.050
		F	0.058

(d) C–C Bond Distances (l/Å)[d]

3		29	
bond type	l/Å	bond type	l/Å
a	1.453–1.467	a	1.410–1.484
	1.461		1.443
b	1.427–1.432	b	1.391–1.458
	1.430		1.422
c	1.417–1.427	c	1.362–1.456
	1.422		1.410
d	1.342–1.345	d	1.310–1.362
	1.344		1.337

[a] Around the C–C bonds in central seven-membered ring. [b] Between the peripheral benzene rings. [c] From the least-squares plane of peripheral benzene rings. [d] In the peripheral benzene rings (upper; range, lower; mean).

benzene carbons: Br(1)··C(19) = 3.182 (6), Br(1)··C(20) = 3.142 (6), Br(2)··C(1) = 3.275 (6), and Br(2)··C(26) = 3.182 (6) Å, the sum of van der Waals' radii for these atoms being 3.65 Å.

Table Ib lists the dihedral angles between the peripheral benzene rings of molecules **3** and **29**. The mean dihedral angles between the neighboring benzenes are 19.2° and 15.7°, respectively. Even in molecule **29**, the out-of-plane deformation of each naphthalene fragment is not so large as to result in the large dihedral angle between benzene rings A and F. Related to the result, the mean atomic deviations from the least-squares plane for each benzene ring are summarized in Table Ic. The values show that the out-of-plane deformations of the benzene rings are averaged in all the peripheral rings, which show the similar mean atomic deviations between 0.048 and 0.065 Å in these molecules.

The unique structural features are found from the examination of the C–C bond distances of peripheral benzene rings and are summarized in Table Id. The C–C bonds in molecule **3** are separated into four types based on its chemical structure: (a) the innermost, which are in the central seven-membered ring, (b) the middle, which are the bonds in common with two fused benzene rings, (c) the outer, which are the outer bonds next to type b bond, and (d) the outermost. The mean bond distance of type d is the shortest and that of type a is the longest; the former is close to the localized C–C double bond distance, while the latter is close to the single bond distance between the sp^2 carbons. According to the examination of Kekule's formula for molecule **3**, the fact may be reasonable. However, the type b bond is longer than the type c bond in contrary to the expectation from the Kekule's formula. This fact may result from the larger out-of plane deformation of the type b bond than that of type c bond; the mean torsional angle for type b and c bonds are 12.0° and 9.6°, respectively. The similar feature is also observed in the molecule **29** even though the ranges for each type of bond are larger than the corresponding values for molecule **3**.

Experimental Section

5,5′-Bis(hydroxymethyl)-2,2′-dimethylbiphenyl (8). A solution of 5,5′-dicarbomethoxy-2,2′-dimethylbiphenyl (**7**)[16] (4.6 g, 15.4 mmol) in dry tetrahydrofuran (35 mL) was added to a suspension of $LiAlH_4$ (2.0 g, 53 mmol) in dry tetrahydrofuran (75 mL). The mixture was refluxed with stirring for 8 h, and the excess reducing agent was decomposed with water (5 mL). After the insoluble aluminum hydroxide was removed by filtration from the reaction mixture, the filtrate was concentrated under vacuum. The resulting solid was recrystallized from benzene–hexane to give **8** (3.4 g, 91%), mp 147–148 °C: IR (KBr) 3375, 3290 cm^{-1} (ν_{OH}). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.41; H, 7.53.

5,5′-Bis(bromomethyl)-2,2′-dimethylbiphenyl (9). To a stirred solution of **8** (22.7 g, 11.2 mmol) in dry tetrahydrofuran (40 mL) was added dropwise a solution of phosphorus tribromide (2.4 g, 8.8 mmol) in dry ether (20 mL) at room temperature. After the reaction mixture was stirred for 4 h at room temperature, water (50 mL) was slowly added. The organic phase was washed with dilute sodium bicarbonate solution and with water and then dried. Removal of the solvent afforded a solid which was recrystallized from hexane to yield **9** (3.8 g, 94%), mp 82–83 °C; MS, *m/e* 368 (M^+). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.20; H, 4.83. Found: C, 52.16; H, 4.36; Br, 43.48.

5,5′-Bis(mercaptomethyl)-2,2′-dimethylbiphenyl (10). A mixture of **9** (5.4 g, 14.7 mmol), thiourea (2.46 g, 14.7 mmol), and 95% ethanol (200 mL) was refluxed with stirring for 13 h. The resulting diisothiuronium salt was collected by filtration and dissolved in 6% sodium hydroxide solution (500 mL). After refluxing under nitrogen for 8 h, the solution was allowed to cool and then acidified with 6 N hydrochloric acid (60 mL). The resulting product was extracted with ether, and the ether extract was washed with water and then dried. After removal of the solvent, the residue was chromatographed on neutral alumina. Elution with chloroform yielded **10** (3.5 g, 88%) as an oil; MS, *m/e* 274 (M^+); IR (film) 2570 cm^{-1} (ν_{SH}).

18,22-Dimethyl-2,13-dithia[3.3](3,3′)biphenyl(2,7)naphthalenophane (12). To a stirred suspension of cesium carbonate (4.9 g, 15 mmol) in *N,N*-dimethylformamide (2 L) was added, in a period of 12 h, a mixture of bis(bromomethyl)naphthalene (**11**)[17] (4.58 g, 15 mmol) and **10** (4 g, 15 mmol) in *N,N*-dimethylformamide (500 mL) at 50–55 °C. After being refluxed 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–hexane to give **12** (3.5 g, 54%): mp 134–144 °C; MS, *m/e* 426 (M^+); IR (KBr) 3040, 3010, 2910, 1630, 1600, 1510, 1480, 1420, 1350, 1235, 1145, 915, 845, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (s, 6 H), 3.51 (d, J = 14.2 Hz, 2 H), 3.82 (d, J = 14.2 Hz, 2 H), 3.91 (s, 4 H), 6.27 (d, J = 1.5 Hz, 2 H), 7.06–7.70 (m, 10 H). Anal. Calcd for $C_{28}H_{26}S_2$: C, 78.89; H, 6.15. Found: C, 78.73; H, 6.11.

Bis(methyl tetrafluoroborate) Salt 13 of Dithiacyclophane 12. The dithiacyclophane **12** (1.8 g, 4.2 mmol) in dry dichloromethane (170 mL) was added dropwise to dimethoxycarbonium tetrafluoroborate[19] (2.5 mL, excess) at −15 °C with stirring. The solution was allowed to warm to room temperature and stirred for 24 h. After the addition of a small quantity of ethanol, the resulting solid was filtered, washed with methylene chloride, and dried to yield **13** (quantitative) as a white powder, mp > 350 °C. The product was used without further purification.

Stevens Rearrangement of the Salt 13. The salt **13** (3.4 g, 5.3 mmol) was suspended in dry tetrahydrofuran (280 mL) with excess sodium

hydride under nitrogen, and the mixture was stirred at 50–55 °C for 3 days. Water (300 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 hexane–benzene (2:1) gave a mixture of structural and stereoisomers of **14** (2.3 g, 93%) as an oil: MS, *m/e* 454 (M^+); ^1H NMR ($CDCl_3$) δ 1.7–2.0 (m, 6 H), 2.02–2.30 (m, 6 H), 2.41–4.58 (m, 6 H), 6.90–7.80 (m, 12 H).

16,20-Dimethylbis(methylthio)[2.2](3,3′)biphenyl(2,7)naphthalene *S,S′*-Dioxide (15). The cyclophane **14** (2.7 g, 5.9 mmol) and *m*-chlorobenzoic acid (2.05 g, 12 mmol) were dissolved in chloroform (400 mL) at 0 °C. After stirring for 12 h at room temperature, the solution was washed with 5% dilute sodium bicarbonate solution and then dried. Removal of the chloroform gave a quantitative yield of **15** (2.9 g) as a pale yellow glass: IR ($CHCl_3$) 1035 cm^{-1} (strong $\nu_{S=O}$).

16,20-Dimethyl[2.2](3,3′)biphenyl(2,7)naphthalenophane-1,11-diene (16). The disulfoxide **15** (0.5 g, 1.03 mmol) was pyrolyzed at 300 °C under vacuum (0.002 mm), and the pyrolysate was subjected to silica gel column chromatography. Elution with hexane–benzene (4:1) gave **16** (0.17 g, 45%), which when recrystallized from hexane–benzene gave the following: mp 143–144 °C; MS *m/e* 358 (M^+); IR (KBr) 3010, 1605, 1485, 1330, 935, 905, 850, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (s, 6 H), 6.46–7.97 (m, 16 H). Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.84; H, 6.14.

1,16-Dehydro-2,15-dimethylhexahelicene (7,8-Dimethylbenzo[*no*]naphtho[2,1,8,7-*ghij*]pleiadene) (17). A solution of the diene **16** (0.3 g, 0.84 mmol) in spectroscopic grade cyclohexane (500 mL) containing iodine (3 mg) was placed in a photolysis tube, and a slow, fine, stream of nitrogen was passed through the solution during the reaction. After 3-h irradiation with a high-pressure mecury lamp (Halos ET-300),[20] the solvent was removed in vacuo, leaving a yellow solid, which was subjected to column chromatography over neutral alumina. Elution with benzene afforded **17** (140 mg, 47%) which was recrystallized from benzene–hexane to give yellow prisms: mp 226–228 °C; MS, *m/e* 354 (M^+); IR (KBr) 3050, 2920, 1605, 1585, 1440, 1280, 1190, 845, 820, 790, 750, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 7.0–7.9 (m, 12 H); UV (C_6H_{12}) λ_{max} 220 nm (log ε 4.76), 236 sh (4.75), 243 (4.74), 268 (4.72), 277 sh (4.65), 304 (4.59), 321 (4.48), 345 (3.90). Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.80; H, 5.18.

1,16-Dehydro-2,15-methanohexahelicene (Indeno[2,3,4,5-*nopq*]naphtho[2,1,8,7-*ghij*]pleiadene) (18). The hydrocarbon **17** (50 mg, 0.014 mmol) was mixed with 5% palladium on carbon (10 mg) under nitrogen, and the mixture was heated at 320 °C for 0.5 h. Chloroform (10 mL) was added to the reaction mixture, and the catalyst was removed. The filtrate was free of solvent, and the residue was chromatographed on neutral alumina. Elution with benzene yielded **18** (33 mg, 65%) which was recrystallized from benzene to give yellow needles: mp 260 °C dec; MS, *m/e* 338 (M^+); IR (KBr) 3050, 1390, 1330, 1250, 1185, 915, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.99 (s, 2 H), 7.52–7.83 (m, 12 H); UV (C_6H_{12}) λ_{max} 249 nm (log ε 4.95), 265 sh (4.65), 292 (4.40), 313 (4.45), 343 sh (3.97). Anal. Calcd for $C_{27}H_{14}$: C, 95.83; H, 4.17. Found: C, 95.77; H, 4.20.

2,2′-Diamino-5,5′-dimethylbiphenyl (20). To a stirred mixture of 5,5′-dimethyl-2,2′-dinitrobiphenyl (**19**)[21] (120 g, 0.441 mol), toluene (250 mL), and concentrated hydrochloric acid (500 mL) was added slowly tin powder (200 g). The reaction mixture was refluxed with stirring for 5 h, and 2 N NaOH solution (500 mL) was slowly added. The organic phase was washed with water and then dried. Removal of the solvent followed by distillation in vaccuo afforded **20** (65 g, 70%): bp 165–170 °C (0.2 mm); IR (film) 3440, 3350 cm^{-1} (ν_{NH}).

2,2′-Dibromo-5,5′-dimethylbiphenyl (21). To the cold diazonium solution, prepared as usual from diamine **20** (30 g, 0.14 mol), water (300 mL), concentrated sulfuric acid (150 mL), and 20% sodium nitrite solution (150 mL), was added with stirring a cold mixture of mercuric bromide (210 g, 0.58 mol) and potassium bromide (200 g, 1.68 mol) in water (300 mL). The yellow insoluble complex which separated immediately was collected by filtration, washed with water and acetone, and dried. The thermal decomposition of mercuric bromide salt was carried out according to the procedure of Dauben and Saegebarth.[22] The dried mercuric bromide salt (140 g) was finely ground, added in several portions through a wide rubber tube to a flask with a reflux condenser containing dimethylaniline (240 mL), and heated to 110–120 °C. After each addition of the complex, the mixture was heated for 2 h to complete the reaction. The organic matter was taken into benzene and washed with dilute acid and alkali, and then the benzene was removed. The residue was chromatographed on neutral alumina. Elution with hexane yielded **21** (28.8 g, 60%) which was recrystallized from hexane to give white needles, mp 109–110 °C; MS, *m/e* 340 (M^+); ^1H NMR ($CDCl_3$) δ 2.35 (s, 6 H), 6.95–7.62 (m, 4 H). Anal. Calcd for $C_{14}H_{12}Br_2$: C, 49.44; H, 3.56. Found: C, 49.44; H, 3.51.

2,2′-Dibromo-5,5′-bis(bromomethyl)biphenyl (22). A mixture of **21** (14 g, 42 mmol), *N*-bromosuccinimide (16.5 g, 92 mmol), benzoyl peroxide (100 mg), and CCl_4 (200 mL) was heated to reflux for 3 h. Removal of the deposited succinimide followed by concentration of the filtrate in vacuo gave a residue which was chromatographed over silica gel. Elution with hexane–benzene (10:1) gave **22** (18 g, 87%), which was converted to the thiol **23** without further purification: MS, *m/e* 497 (M^+); ^1H NMR ($CDCl_3$) δ 4.42 (s, 4 H), 7.2–7.7 (m, 6 H).

2,2′-Dibromo-5,5′-bis(mercaptomethyl)biphenyl (23). The preparation of **23** was carried out by the same method as described for the preparation of **10**, utilizing **22** (10 g, 20 mmol) and thiourea (3.34 g, 44 mmol). The product was chromatographed over neutral alumina (chloroform eluent) to provide the dithiol **23** (4.5 g, 55%): MS, *m/e* 404 (M^+); IR (film) 2560 cm^{-1} (ν_{SH}).

18,22-Dibromo-2,13-dithia[3.3](3,3′)biphenyl(2,7)naphthalenophane (24). Preparation of **24** was carried out by the same method described for the preparation of **12**, utilizing dithiol **23** (3 g, 7.4 mmol) and bis(bromomethyl)naphthalene **11** (2.3 g, 7.4 mmol). The product was chromatographed over silica gel, and elution with hexane–benzene (2:1) furnished the thiacyclophane **24** (2.3 g, 56%) which was recrystallized from hexane–benzene: mp 173–174 °C; MS, *m/e* 556 (M^+); IR (KBr) 3050–3010, 1460, 1420–1400, 1225, 1030, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.46 (d, *J* = 15.0 Hz, 2 H), 3.76 (d, *J* = 15.0 Hz, 2 H), 3.87 (s, 4 H), 6.11 (d, *J* = 3.0 Hz, 2 H), 7.02–7.75 (m, 10 H). Anal. Calcd for $C_{26}H_{20}Br_2S_2$: C, 56.12; H, 3.62. Found: C, 56.23; H, 3.58.

Bis(methyl tetrafluoroborate) Salt 25 of Dithiacyclophane 24. The cyclophane **24** (2 g, 3.6 mmol) was treated with dimethoxycarbonium tetrafluoroborate as described for the preparation of **13** and yielded the salt **25** (2.7 g, 98%) as a white powder, mp > 360 °C. The product was used without further purification.

Stevens Rearrangement of the Salt 25. Excess sodium hydride (1.8 g) was added gradually to a stirred suspension of **25** (2.7 g, 3.5 mmol) in dry tetrahydrofuran (200 mL) under nitrogen and stirred at 50–55 °C for 2 days. After a usual workup, the product was chromatographed on silica gel (hexane–benzene (2:1) eluent) to give **26** (1.4 g, 67%) as an oil: MS, *m/e* 584 (M^+); ^1H NMR ($CDCl_3$) δ 1.91–2.12 (m, 6 H), 2.4–4.5 (m, 6 H), 6.8–7.6 (m, 12 H).

16,20-Dibromobis(methylthio)[2.2](3,3′)biphenyl(2,7)naphthalene *S,S′*-Dioxide (27). *m*-Chloroperbenzoic acid (0.52 g, 3 mmol) was added to a stirred solution of **26** (1.07 g, 1.5 mmol) in chloroform (60 mL) at 0 °C and stirred for 12 h at room temperature. The routine workup gave a quantitative yield of **27** (1.2 g) as a pale yellow glass: IR ($CHCl_3$) 1035 cm^{-1} (strong, $\nu_{S=O}$).

16,20-Dibromo[2.2](3,3′)biphenyl(2,7)naphthalenophane-1,11-diene (28). The pyrolysis of the disulfone **27** (0.5 g, 0.8 mmol) was carried out in the same manner as described for **16**, providing a 63% yield of **28** (0.25 g): mp 213–215 °C; MS, *m/e* 488 (M^+); ^1H NMR ($CDCl_3$) δ 6.52–8.08 (m); UV (C_6H_{12}) λ_{max} 333 nm (log ε 3.72), 290 sh (4.21). Anal. Calcd for $C_{26}H_{16}Br_2$: C, 63.96; H, 3.30. Found: C, 64.21; H, 3.26.

1,16-Dehydro-2,15-dibromohexahelicene (7,8-Dibromobenzo[*no*]naphtho[2,1,8,7,-*ghij*]pleiadene) (29). A solution of **28** (150 mg, 0.31 mmol) in cyclohexane (500 mL) containing a small amount of iodine was irradiated with a 300 W high-pressure mercury lamp (HALOS EH-300)[20] in an atmosphere of nitrogen for 2 h. Removal of the solvent followed by column chromatography on alumina (benzene eluent) afforded **29** (70 mg, 42%) which was recrystallized from benzene–hexane to give pale yellow prisms: mp 299–301 °C; MS, *m/e* 484 (M^+); IR (KBr) 3050, 3010, 1590, 1465, 1403, 1255, 1182, 1114, 1082, 985, 965, 908, 842, 810, 780, 750, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82–8.66 (m, ArH); UV (C_6H_{12}) λ_{max} 245 nm (log ε 4.80), 270 sh (4.72), 277 (4.73), 312 (4.48), 326 (4.40). Anal. Calcd for $C_{26}H_{12}Br_2$: C, 64.49; H, 2.50; Br, 33.01. Found: C, 64.68; H, 2.46; Br, 32.91.

1,16-Dehydro-2,15-diformylhexahelicene (7,8-Diformyl[*no*]naphtho-[2,1,8,7-*ghij*]pleiadene) (30). *n*-Butyllithium (1.6 M solution in hexane) (0.25 mL, 0.4 mmol) was added dropwise under nitrogen by syringe to a stirred solution of **29** (70 mg, 0.14 mmol) in dry tetrahydrofuran (5 mL) at −78 °C. After stirring at this temperature for 30 min, dry dimethylformamide (0.5 mL, 6.5 mmol) was added dropwise and stirred for 1 h. The solution was warmed to room temperature where stirring was continued for 30 min. Saturated aqueous ammonium chloride (10 mL) was added to quench the reaction. The reaction mixture was extracted with chloroform and washed with brine and then dried. Removal of the solvent afforded a solid which was chromatographed on silica gel. Elution of the column with benzene–hexane (1:1) afforded the 1,16-dehydrohexahelicene **5**[10] (6 mg, 13%) which was recrystallized from benzene–hexane to give mp 163–164 °C. Further elution with benzene furnished **30** (56 mg, 54%), which when recrystallized from benzene gave mp 303–305 °C: MS, *m/e* 382 (M^+); IR (KBr) 1684 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 7.86–8.34 (m, 12 H), 8.61 (s, 2 H). Anal. Calcd for

$C_{28}H_{14}O_2$: C, 87.94; H, 3.69. Found: C, 88.12; H, 3.61.

[7]Circulene (Dinaphtho[2,1,8,7-*ghij*:2′,1′,8′,7′-*nopq*]pleiadene) (3). $LiAlH_4$ (6 mg, 0.158 mmol) was added to a stirred solution of titanium trichloride (100 mg, 0.648 mmol) in dry dimethoxyethane (3 mL) under argon. The resultant black mixture was refluxed with stirring for 30 min. To the mixture, a solution of **30** (30 mg, 0.079 mmol) in dry dimethoxyethane (10 mL) was added dropwise, and then the mixture was refluxed with stirring for 4 h. The reaction mixture was passed through Hyflo Spercel and washed with benzene. The filtrate was concentrated, and the residue was chromatographed on silica gel. Elution with benzene yielded **3** (10 mg, 35%) which was recrystallized from benzene–hexane to give yellow plates, mp 295–296 °C; MS, *m/e* (rel intensity) $M^+ + 2$ 352 (12); $M^+ + 1$ 351 (30), M^+ 350 (100); IR (KBr) 3050, 1620, 1262, 1186, 845, 840, 811, 742, 734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (s, ArH); ^{13}C NMR ($CDCl_3$) δ 127.5, 132.1, 136.0; UV (C_6H_{12}) λ_{max} 236 sh nm (log ϵ 4.44), 266 sh (4.86), 275 (5.14), 296 (4.46), 331 (3.91), 388 sh (2.90), 403 (2.83). Anal. Calcd for $C_{28}H_{14}$: C, 95.97; H, 4.03. Found: C 95.88; H, 4.00.

Optically Active 1,16-Dehydro-2,15-dimethylhexahelicene (17). Optical resolution of (±)-**17** was achieved by HPLC technique with a column packed with (+)-poly(triphenylmethyl methacrylate)[26] on silica gel as described.[25] A solution of (±)-**17** (10 mg) in methanol (15 mL) was injected on the column (30 × 2.2 (i.d.) mm) and eluted with methanol to give the first eluted (−)-isomer followed by the (+)-isomer. The procedure was repeated to process a total of 50 mg of **17**, and recrystallization of the resolved enantiomeric compounds from benzene–hexane afforded optically pure (M)-(−)-**17** and (P)-(+)-**17**, respectively. (M)-(−)-**17** (19 mg): mp 221–223 °C, $[\alpha]_D^{25}$ −1882° ($CHCl_3$), CD (C_6H_{12}) $[\theta] \times 10^{-5}$ (λ, nm) +1.30 (240), +1.87 (249), −0.69 (266), +1.74 (281), −0.89 (315), −2.17 (328). (P)-(+)-**17** (18 mg): mp 220–222 °C, $[\alpha]_D^{25}$ +1879° ($CHCl_3$).

Optically Active 1,16-Dehydro-2,15-dibromohexahelicene (29). Optical resolution of (±)-**29** (50 mg) was carried out and described for the preparation of optically active **17**. (M)-(−)-**29** (18 mg): mp 291–292 °C, $[\alpha]_D^{25}$ −2110° ($CHCl_3$), CD(C_6H_{12}) $[\theta] \times 10^{-4}$ (λ, nm) +4.32 (267), +5.84 (279), −6.51 (308), −7.32 (325). (P)-(+)-**29** (18 mg): mp 292–293 °C, $[\alpha]_D^{25}$ +2113° ($CHCl_3$).

Optically Active 1,16-Dehydro-2,15-diformylhexahelicene (30). (±)-**30** (70 mg) was separated into the enantiomers by HPLC technique by using the chiral column described above. (M)-(−)-**30** (30 mg): mp 294–296 °C, $[\alpha]_D^{25}$ −1456° ($CHCl_3$), CD(C_6H_{12}) $[\theta] \times 10^{-4}$ (λ, nm) +2.16 (249), +2.46 (282), −0.86 (312), −2.24 (328). (P)-(+)-**30** (280 mg): mp 294–296 °C, $[\alpha]_D^{25}$ +1458° ($CHCl_3$).

Chromatographic Resolution of 1,16-Dehydrohexahelicene (Hexa[7]circulene) (5). The chromatography on the (+)-poly(triphenylmethyl methacrylate) column was accomplished on a JASCO UV-100-UV detector and DIP-181 polarimeter (365 nm) detector. The chromatogram of resolution of (±)-**5** was carried out at −5 °C by using methanol as eluant. The UV detector showed two peaks. The (−)-isomer was eluted first followed by the (+)-isomer. The (−)-isomer was eluted first followed by the polarimeter and was stopped when it showed the maximum negative rotation, and the decrease of the optical rotation was followed to estimate racemization rate. Rapid racemization proceeded, and its half-life period was an estimated 10 s at −5 °C.

Crystallographic Data. All X-ray experiments were carried out on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell parameters were determined by a least-squares fit to 2θ values of 24, 25, and 30 strong higher angle reflections for **3** (room temperature), **3** (low temperature), and **29**, respectively.

[7]Circulene (**3**): monoclinic, space group $C2/c$, $Z = 4$, $F(000) = 728$, at 20 °C; $a = 13.106$ (2) Å, $b = 11.664$ (2) Å, $c = 11.015$ (3) Å, $\beta = 95.67$ (1)°, $V = 1675.5$ (5) Å^3, $D_m = 1.380$, $D_c = 1.390$ g cm^{-3}, μ(Mo Kα) = 0.86 cm^{-1}, at −110 °C; $a = 13.072$ (4) Å, $b = 11.604$ (4) Å, $c = 10.935$ (6) Å, $\beta = 95.39$ (3)°, $V = 1651.4$ (12) Å^3, $D_c = 1.409$ g cm^{-3}, μ(Mo Kα) = 0.87 cm^{-1}.

1,16-Dehydro-2,15-dibromohexahelicene (**29**): monoclinic, space group $P2_1/c$, $a = 10.716$ (2) Å, $b = 7.338$ (2) Å, $c = 22.844$ (4) Å, $\beta = 97.02$ (2)°, $V = 1783.0$ (5) Å^3, $Z = 4$, $D_m = 1.776$, $D_c = 1.804$ g cm^{-3}, $F(000) = 952$, μ(Mo Kα) = 49.7 cm^{-1}.

Collection and Reduction of Intensity Data. The X-ray diffraction data were measured by using crystals shaped with dimensions of 0.3 × 0.3 × 0.3 mm for each crystal. Two types of X-ray generator were used for the experiments: conventional type (40 kV, 30 mA) for **3** (room temperature), rotating anode type (40 kV, 200 mA) for **3** (low temperature) and **29**. The low temperature was attained by the gas flow method of liquid nitrogen. The integrated intensities were measured by the θ–2θ scan technique at a 2θ scan rate of 4 deg min^{-1} for **3** (room temperature) and 8 deg min^{-1} for **3** (low temperature) and **29**. The scan width was $\Delta 2\theta = (2.0 + 0.70 \tan \theta)°$. The background intensities were measured at both ends of a scan for 7.5 s [**3** (room temperature)], for 5 s [**3** (low temperature)], or for 4 s [**29**], respectively. No significant intensity decay of the standard reflections was observed for any of the crystals used. The number of intensities collected up to 2θ of 60° was 2449, 2412, and 3912 for **3** (room temperature), **3** (low temperature), and **29**, respectively. The intensity data were corrected for the usual Lorentz and polarization effects, but an absorption correction was not applied.

Determination and Refinement of the Structure. The crystal structure of **3** was solved by the direct method,[29] while that of **29** was solved by the conventional heavy atom method. The crystal structures were refined by the block-diagonal least-squares method.[30] The atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[31] After anisotropic refinement of the non-hydrogen atoms, all hydrogen atoms were located in the difference Fourier maps and were refined isotropically. The weighting function used in the final stage of refinement was $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$ for nonzero reflections and $w = c$ for zero reflections. The final R indices defined by $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ were 0.094 (nonzero reflections) for **3** (room temperature), 0.105 for **3** (low temperature), and 0.105 for **29**, respectively. The weighted R indices defined by $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.129 for **3** (room temperature) with the weighting parameters of $a = 0.0303$, $b = 0.0014$, and $c = 0.1825$, 0.085 for **3** (low temperature) with $a = 0.0218$, $b = 0.0001$, and $c = 0.2068$, and 0.081 for **29** with $a = -0.4630$, $b = 0.0094$, and $c = 0.0371$, respectively.

All calculations were carried out on an ACOS S900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka Universisty.

Supplementary Material Available: General information from the Experimental Section and full lists of atomic coordinates, thermal parameters, bond distances, and bond angles for **3** at room temperature and low temperature and **29** (7 pages). Ordering information is given on any current masthead page.