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Synthesis, Reactions and Thermal Properties of *endo*-5,12:*endo*-6,11-Dietheno-5,5a,6,11,11a,12-hexahydronaphthacene[1]

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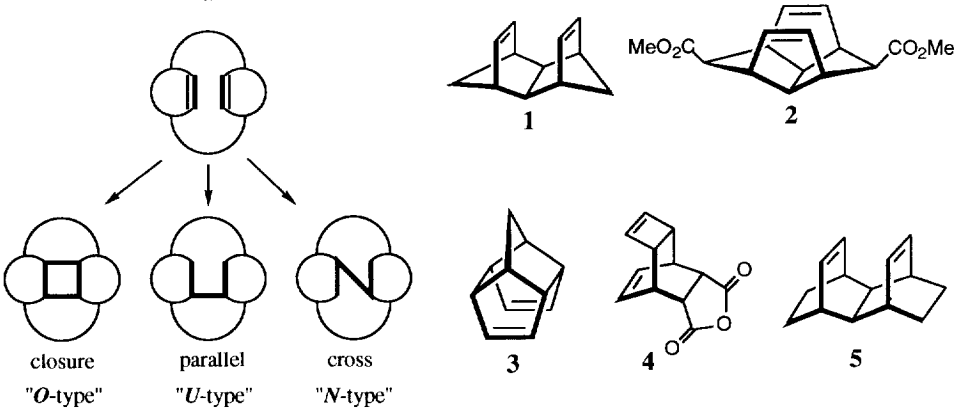
Abstract: The title compound **6** was synthesized in nine steps, starting from the Diels-Alder adduct **21** of ketomethanoethanonaphthalene **20** and *p*-benzoquinone, via 7,8-dimethylidene-diethenoanthracene **10** followed by Diels-Alder reaction with (*E*)-bis(phenylsulfonyl)ethylene and aromatization. Photocyclization of **6** led to **32** via an intramolecular [2+2] cycloaddition. Hydrogenation and epoxidation of **6** gave the corresponding bis-benzo hydrocarbon **33** and bis-epoxide **34**. Bromination of **6** proceeded by transannular reaction to produce *N*-type *exo, endo* dibromide **35b** and *U*-type *exo, exo* dibromide **36b**. Compound **6** underwent thermal decomposition at 210 ± 5 °C to form naphthalene and benzobarrelene.

INTRODUCTION

Rigid polycyclic molecules having two isolated double bonds located in the laticyclic topology[2] and spatially in close proximity have provided suitable frameworks for the study of transannular interactions and reactions.[3] In physicochemical aspect, for example, the orbital interaction through space[4] was demonstrated for *endo,endo*-dimethanonaphthalene skeletal systems (e.g. **1**) by rate enhancements in solvolytic reactions[5] and clearly by the sizable splittings of π-orbitals in photoelectron and electron transmission spectra.[6] Chemically, face-proximate double bonds in these systems may undergo transannular reactions by three modes (Chart 1). Photochemical [2+2] cycloadditions to produce cyclobutane rings (closure, *O*-type) are very facile and well known.[7] Stepwise additions to double bonds usually lead to the transannular bridge formation in either cross (*N*-type) or parallel (*U*-type) manner or both. For examples, a mixture of the *N*-type and *U*-type adducts were isolated from iodination of **1**[8] and bromination of **2**[9], while only the adduct of *N*-type was found in the bromination of **3**[10] and **4**.[11] The same type of electrophilic additions has not been reported for systems having structure as **5**.[12] Our interest in the synthesis of rigid polycyclic hydrocarbons containing π-face-proximate double bonds[13] led us to prepare the previously unknown bisbenzo grafted system of **5**, the title compound **6**. Herein, we report the results of the synthesis, X-ray crystal structure, and some reactions including transannular bromination of **6**. Additionally, the thermal properties of **6** are presented.

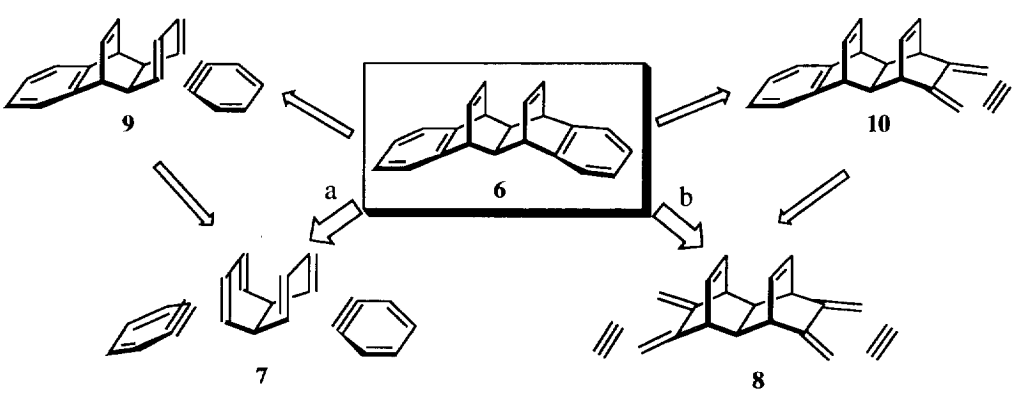
Chart 1



RESULTS AND DISCUSSION

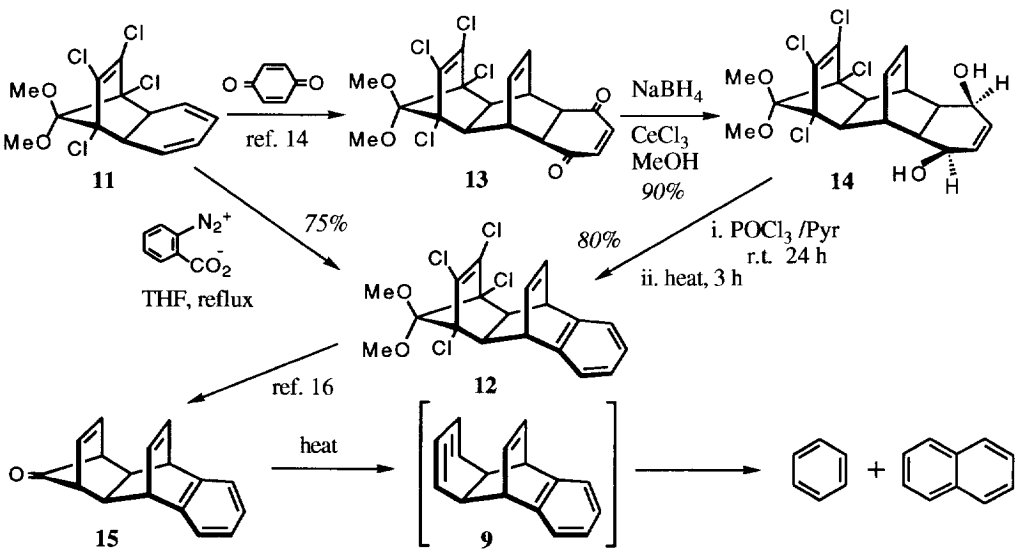
Synthesis. Retrosynthetically, the title compound **6** could conceivably be made directly by a double Diels-Alder cycloaddition of (a) dihydronaphthalene **7** with two equivalents of benzyne or (b) tetracyclic bis-butadiene **8** with two equivalents of acetylene synthon followed by aromatization. Alternatively, the synthesis of **6** could be realized by sequential application of Diels-Alder reactions via intermediate **9** or **10** (Chart 2). For many years, we have demonstrated the application of 1,8,9,10-tetrachloro-11,11-dimethoxy[6.2.1.$0^{2,7}$]undeca-3,5,9-triene (**11**),[14] as a useful synthetic equivalent of dihydronaphthalene **7**[15] to the construction of linearly concatenated bicyclo-[2.2.2]octenes.[13] The underlying synthetic thinking is that a dechlorination-deacetalization-decarbonylation process can be employed to unmask the cyclohexadiene moiety in the first Diels-Alder adduct for constructing the second bicyclo[2.2.2]octene substructure by performing second Diels-Alder reaction with an identical or different dienophile. A high degree of π-facial selectivity has been observed with the cycloadditions yielding only the adducts having two bicyclo-[2.2.2]octene units that are *syn*-concatenated.

Chart 2



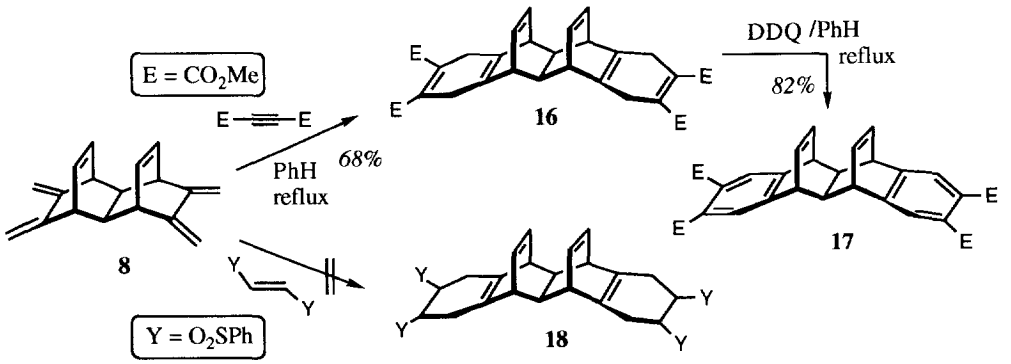
Thus, at the outset we prepared *endo,exo*-1,2,3,4,-tetrachloro-9,10-etheno-1,4-dimethoxymethanoanthracene **12**[16] by the reaction of **11** with benzyne directly or alternatively with *p*-benzoquinone, followed by aromatization of adduct **13** via reduction with sodium borohydride/cerium chloride in methanol and elimination of water from endiol **14** with phosphoryl chloride in pyridine[17] (Scheme 1). Conversion of **12** to 1,4-carbonyl-9,10-ethenoanthracene **15**, a potential equivalent of **9**, was carried out by a dechlorination-deacetalization process according to the reported procedure.[16] This synthetic approach to **6** was abandoned as we could not trap the decarbonylated product of **15** (**9**) using benzyne and *p*-benzoquinone.[18]

Scheme 1



The synthesis of **6** was then decided to be approached by the Diels-Alder reaction of tetracyclic bis-butadiene **8**[13d] with two equivalents of acetylene equivalent. The reactivity of *exo*-cyclic butadiene-fused bicyclo[2.2.1]heptane systems toward [4+2] cycloadditions is well documented.[19] In our hand, bis-butadiene **8** reacted with dimethyl acetylenedicarboxylate (DMAD) in refluxing benzene produced bis-adduct **16** in 68% yield, which was then converted by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to tetramethoxycarbonyl-substituted diethenonaphthacene **17** in 82% yield. However, the desired bis-adduct **18** of bis-butadiene **8** with (*E*)-1,2-bis(phenylsulfonyl)ethylene (*E*-BPSE), which has been used as a convenient acetylene synthon,[20] could not be obtained (Scheme 2). The reactivity of **8** was low at room temperature and in refluxing benzene it gave complicated mixture of products. The unsuccessful result of synthesis of **6** by the direct cycloaddition of **8** with *E*-BPSE led us to seek the approach of sequential application of Diels-Alder reactions via intermediate **10** (Chart 2) and eventually to the success of synthesizing the title compound **6**.

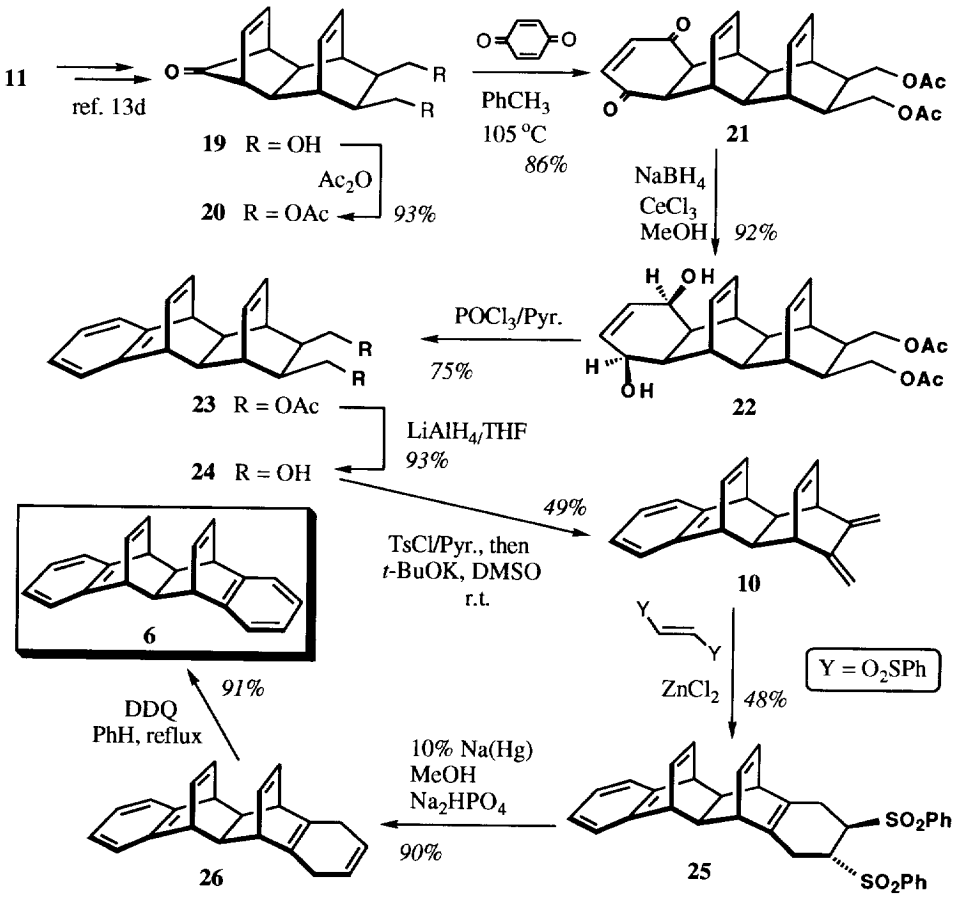
Scheme 2



In Scheme 3, the synthesis of **6** from the readily accessible tetracyclic ketodiol **19**, an intermediate in the synthesis of tetracyclic bis-butadiene **8**,[13d] is outlined. Due to the poor solubility of ketodiol **19**[13d] in methanol which would impede the cerium chloride-mediated reduction of endione moiety with sodium borohydride in the latter stage, diol **19** was converted to its bis-acetate **20** and used as starting material in practice. Reaction of bis-acetate **20** with *p*-benzoquinone in refluxing toluene resulted in slow decarbonylation of **20**, followed by cycloaddition to furnish single cycloadduct **21** in 86% yield after recrystallization from ethyl acetate/hexane. No other stereoisomeric adducts were present in the product mixture as indicated by TLC and ^{1}H NMR spectral analyses. The *syn* orientation of the cyclohexendione moiety with respect to the bridged C=C double bond is expected as in the Diels-Alder reactions of related 1,3-cyclohexadienes with maleic anhydride.[13d,21] It is worth noting that endione **21**, when purified by chromatography on silica gel, underwent partial aromatization to form the corresponding hydroquinone, but could be purified by recrystallization without difficulty. Conversion of endione **21** to the desired benzo-fused tetracyclic bis-acetate **23** was accomplished by reduction of **21** with sodium borohydride/ cerium chloride in methanol, followed by elimination of water from endiol **22** with phosphoryl chloride in pyridine.[17] In the reduction of endione **21** the approach of the metal hydride from the *exo* site of the carbonyl function is clearly less hindered than approach from the *endo* side, and thus endiol **22** was formed as the only product.[14] The thermal instability of hydrocarbon **10** limited the preparation of **10** directly by the pyrolysis of bis-acetate **23**. Therefore, the required 1,2-elimination of bis-acetate to form bis-butadiene **10** was carried out by reduction of **23** with lithium aluminum hydride in THF to afford diol **24** which was then subjected to subsequent bis-tosylation and elimination with potassium *t*-butoxide in DMSO.[13d, 22]

With the acquisition of bis-butadiene **10**, an introduction of ethylene or acetylene equivalent to the *exo*-cyclic 1,3-butadiene unit was called for to the construction of a benzene ring. After several attempts of using 2-chloroacrylyl chloride (an efficient ketene equivalent[23]), phenyl-sulfonylethylene, (*Z*)-BPSE, and (*E*)-BPSE for making 6-membered ring onto **10**, we found that the reaction of **10** with (*E*)-BPSE in hot toluene using $ZnCl_2$ as catalyst gave the best result with

Scheme 3



formation of **25** in 48% yield (Scheme 3). The bis-sulfonate **25** was smoothly reduced with 10% sodium amalgam in methanol according to literature procedures[24] to give the corresponding olefin **26** in 90% yield. Oxidation of olefin **26** with DDQ in refluxing anhydrous benzene afforded the title hydrocarbon **6** in 87% yield after column chromatography on silica gel and recrystallization.

Hydrocarbon **6** formed colorless crystals, mp 204-205 °C, and gave an elemental analysis consistent with a formula of $C_{22}H_{18}$. The structure of **6** was characterized by NMR spectroscopy. The protons of bridged C=C double bonds appear at δ 6.16 ppm as a doublet of doublets (J = 3.3, 4.5 Hz) in the ^{1}H NMR spectrum. The crystal structure of **6** was determined and is shown in Fig. 1, and selected structural parameters are listed in Table 1. The results clearly establish the structure of **6** with two double bonds of etheno-bridges lying in *syn* relationship by a distance of 3.012(1) Å. or 2.993(2) Å.The shorter distance of 2.672(3) Å or 2.699(2) Å between two bridgehead carbon atoms C(1) and C(1a) or C(4) and C(4a), and the nonequivalent bond angles between C(11)-C(1)-C(2) and C(11)-C(1)-C(6) or C(12)-C(4)-C(5) and C(12)-C(4)-C(3) indicate the electronic repulsion of proximal π bonds resulting in bending the benzene ring closer to each other.[25]

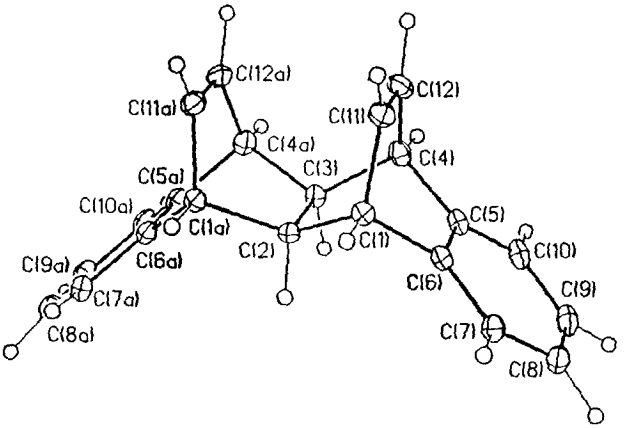
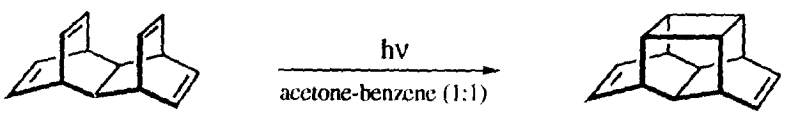


Figure 1. ORTEP Drawing of X-ray Crystallographically Determined Structure of **6**.[26]

Table 1. Selected Structural Parameters for **6**.

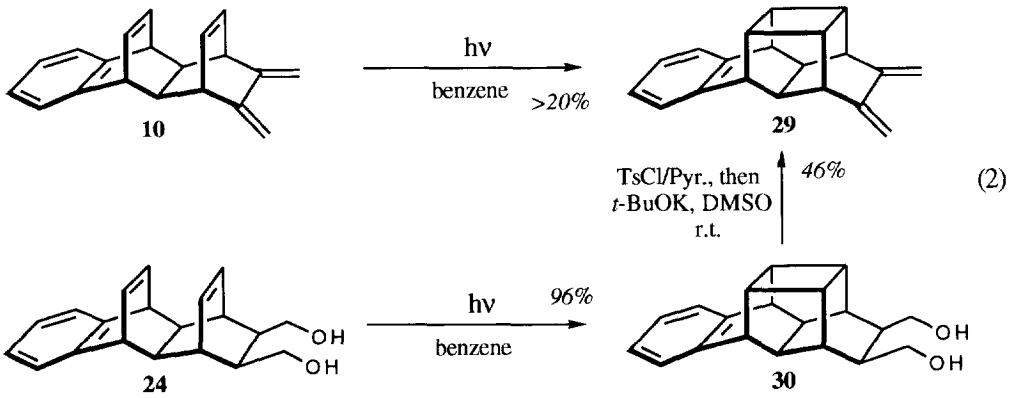
Distances (Å)		Bond Angles (°)	
C(1)-C(1a)	2.699(2)	C(11)-C(1)-C(2)	109.7(1)
C(4)-C(4a)	2.672(3)	C(11)-C(1)-C(6)	106.7(1)
C(11)-C(11a)	3.012(1)	C(12)-C(4)-C(5)	106.9(1)
C(12)-C(12a)	2.993(2)	C(12)-C(4)-C(3)	109.1(1)

Reactions. We[13b] and Prinzbach[27] had previously shown that irradiation of tetracyclo[6.2.2.-$2^{3,6}$.$0^{2,7}$]tetradeca-4,9,11,13-tetraene (**27**), which features two 1,4-homodiene chromorphors and two 1,6-trishomodiene chromorphors with double bonds constrained face-to-face in proximity, proceeded with intercyclic [2+2] photocyclization exclusively and quantitatively to give the cage compound **28** (eq 1). However, when the tetracyclic bis-butadiene **8** was irradiated under the



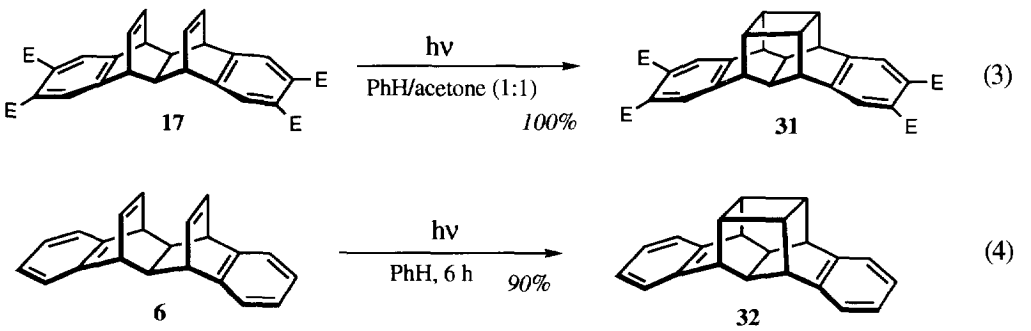
27 **28** (1)

same condition (450-W medium-pressure Hg-lamp/Pyrex filter/acetone-bezene), it polymerized to form insoluble compounds; no desired [2+2] adduct was found. The benzo analogue **10** was less prone to photoinduced polymerization. The initial formation of **29** in yield of 20% was detected by ^{1}H NMR analysis, when **10** was irradiated in benzene for 4 h. But in prolonged irradiation (18 h), the reaction mixture turned brown and gave polymerized material. Compound **29** was synthesized independently from the photocycloadduct **30** obtained from irradiation of diol **24**, followed by the procedure described above (Scheme 3) for the preparation of **10** (eq 2). Again, direct irradiation of pure **29** in benzene for 18 h resulted in polymerization.



(2)

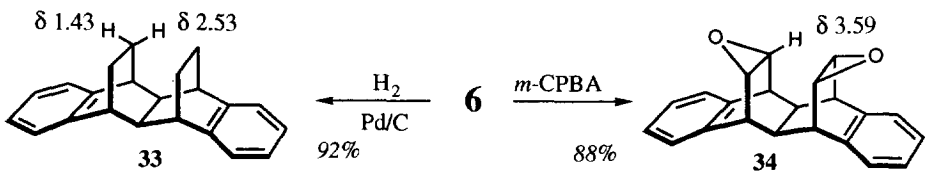
Bis-benzoannulated analogues **17** and **6** displayed photochemical property similar to that of tetraene **27**, undergoing [2+2] photoclosure to form quantitatively the corresponding caged adducts. Thus irradiation of **17** in benzene-acetone (1:1) afforded adduct **31** (eq 3). When a solution of bis-benzo **6** (the title compound) in benzene was irradiated under nitrogen atmosphere using a 450-W medium-pressure mercury lamp (Pyrex filter) for 6 h, the reaction produced bis-benzo fused hexacycle **32** quantitatively (eq 4).



(3)

(4)

As shown in eq 5, hydrogenation of bis-benzo hydrocarbon **6** at 50 °C reduced the parallel C=C double bonds of **6** to give **33** in quantitatively yield. The geminal protons on the ethano-bridges of **33** were clearly identified by DEPT and HETCOR spectra to appear at δ 2.53 ppm (*endo* protons) and δ 1.43 ppm (*exo* protons).[28] The chemical shift difference of 1.1 ppm for these geminal protons is due to steric influence of proximate nuclei.[29] Epoxidation of hydrocarbon **6**

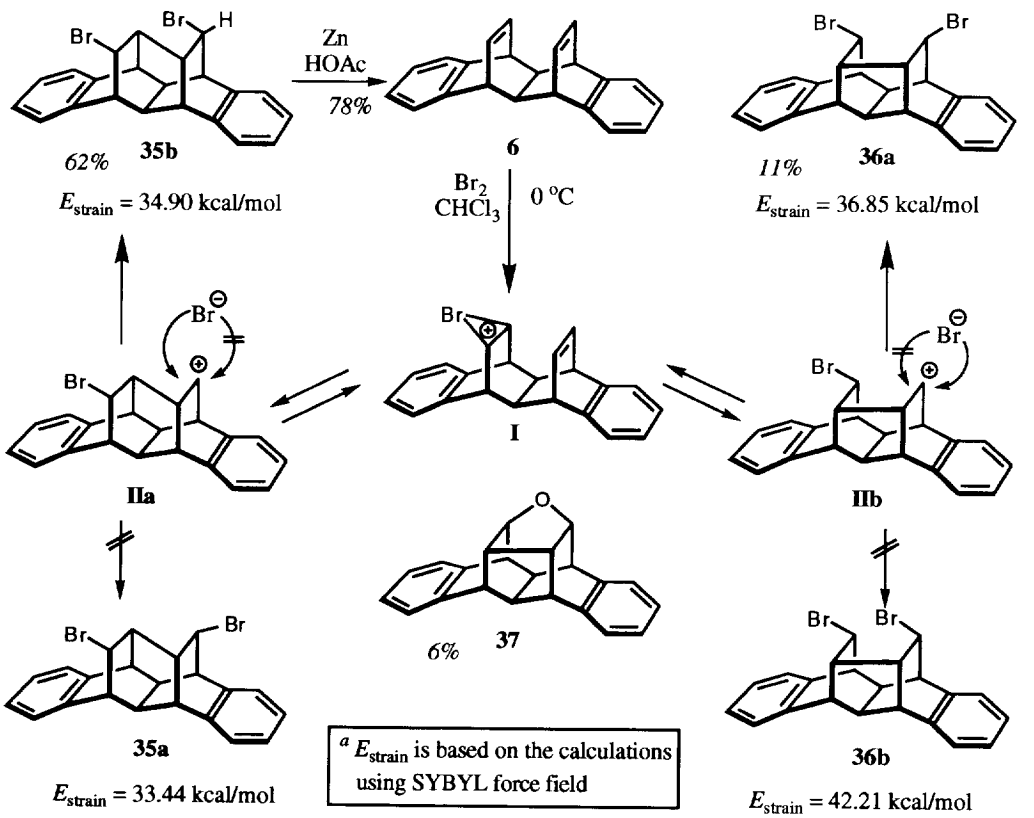


(5)

with *m*-chloroperbenzoic acid (*m*-CPBA) was carried out by published procedures.[30] Thus, in methylene chloride, hydrocarbon **6** reacted with two equivalents of *m*-CPBA to furnish bis-epoxide **34** in 88% yield. The ^{1}H-NMR data of the product **34** indicated that reaction occurred stereospecifically with two oxygen atoms entering exclusively from the benzene-ring sides of molecule.[31]

Bromination of hydrocarbon **6** in a solution of chloroform at 0 °C produced, after separation by chromatography on silica gel, two isomeric addition products with molecular formula $C_{22}H_{18}Br_2$ and an oxygen-containing product with molecular formula $C_{22}H_{18}O$ (Scheme 4). The major dibromide (62% yield), mp 170-171 °C, displayed a complex ^{1}H NMR spectrum and a ^{13}C NMR spectrum of 22 lines for all carbon atoms, indicating the lack of symmetry in the molecule. Mechanistically anticipating that bromination occured transannularly to give dibromide of either *N*-type or *U*-type framework, only the dibromides with *exo*, *endo* (or *syn*, *anti* with respect to benzene ring) stereochemistry of carbon-bromine bonds would be consistent with the NMR spectral data. Based on the examination of molecular model and force field calculations (*vide infra*), the *N*-type dibromide **35b** rather than the U-type dibromide **36b** would appear to be more likely to be formed. To confirm the structural assignment, the single-crystal X-ray structure of **35b** was analyzed and

Scheme 4[a]



[a] E_{strain} is based on the calculations using SYBYL force field

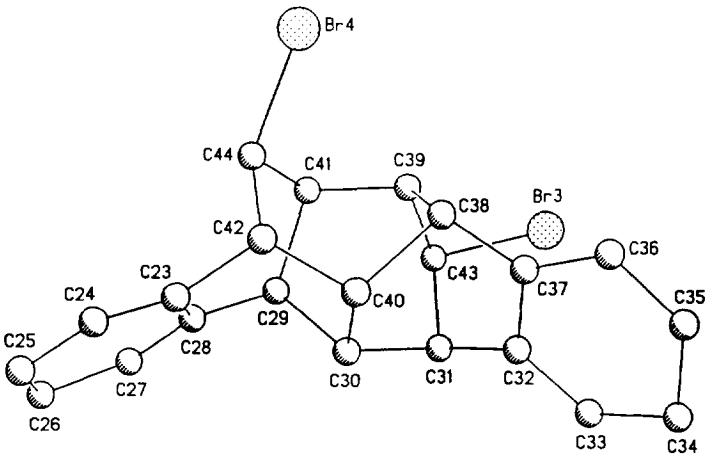


Figure 2. Crystal Structure of **35b.** Hydrogen Atoms Have Been Omitted for Clarity.[26]

is shown in Fig. 2, which clearly shows that two bromine atoms are located to have *exo*- and *endo*-stereochemistry. When treatment with zinc in acetic acid, dibromide **35b** underwent 1,4-debromination to regenerate hydrocarbon **6** in good yield (78%). The second isomeric dibromide, obtained in yield of 11%, exhibited a less complex ^{1}H NMR spectrum and a ^{13}C NMR spectrum of 12 lines for 22 carbon atoms, indicating the presence of a plane symmetry element in the molecule. Among three possible dibrominated products of *U*-type, only *exo, exo* and *endo, endo* dibromides would be consistent with the NMR spectral data. Sterically and mechanistically, structure **36a** with *exo, exo* (or *syn, syn*) stereochemistry of carbon-bromine bonds would be the choice of the two (Scheme 4). An oxygen-containing product, isolated in small amounts and various yields (~6%), showed a ^{1}H NMR spectrum having six groups of signals due to non-aromatic hydrogens and a ^{13}C NMR spectrum of 12 lines for 22 carbon atoms, indicating the presence of a plane symmetry element in the molecule. The spectral data led us to suggest structure **37** for this side product, which may arised from reaction intermediates **IIb** due to trace amount of water present in the raction mixture.

The electrophilic addition to a molecule having two face-proximate double bonds to produce a transannular cross (*N*-type) or parallel (*U*-type) bridged product is likely be under product development control with a product-like transition state. Based on this assumption, the course of reaction has been rationalized by Ösawa *et al.* with the aid of the empirical force field calculations to depend on the thermodynamic stability of the products.[32] A difference larger than 10 kcal/mol in calculated strain energies between neutral hydrocarbon skeletons of *N*-type and *U*-type adducts would dictate the exclusive formation of the more stable product.[32] In our hand, calculations on hydrocarbon skeletons of **35** and **36** using SYBYL force field[33] revealed that *N*-type (E_S = 35.83 kcal/mol) is more stable than*U*-type (E_S = 39.76 kcal/mol) by a strain energy of only 3.93 kcal/mol.[34] This amount of strain energy difference is about equal to the difference between

exo,exo dibromides **35a** (E_s = 33.44 kcal/mol) and **36a** (E_s = 36.85 kcal/mol). Accordingly both *N*-type and *U*-type addition products were expected by Ösawa's rationalization and indeed observed experimentally. SYBYL force field calculations of dibromides also revealed that inversion of one carbon-bromine bond from *exo* to *endo* stereochemistry increases a strain energy of 5.36 kcal/mol in the case of *U*-type dibromide (**36a** →**36b**), but only 1.46 kcal/mol in *N*-type dibromide (**35a** →**35b**) (Scheme 4). That only the *exo,endo* dibromide **35b** rather than the more stable stereoisomer **35a** was isolated from the bromination of **6** is probably due to kinetically controlled recapture of carbocation **IIa** (Scheme 4) in which the bromide ion approaches **IIa** from *endo (anti)* side would suffer the repulsion of benzo group.

Thermal properties. On heating (sealed tube/120 °C[13b] or perchlorobutadiene/160 °C[25]), tetracyclic tetraene **27** underwent [4+2] cycloreversion cleanly to benzene and barrelene. Higher temperature (210 °C ± 5 °C) was needed to effect thermal decomposition of bis-benzo fused hydrocarbon **6**, at which benzobicyclo[2. 2. 2]octatriene (benzobarrelene) and naphthalene were observed in a ratio of 1:1. Increasing the temperature up to 280 °C ± 5 °C, total decomposition of **6** resulted and naphthalene was the only isolated product. The obligatory exclusion of acetylene from **6** to form naphthacene was not detected. In contrast to the thermal properties of **6**, hydrocarbon **33** was not decomposed at 380 °C for 4 hours in a sealed tube.

EXPERIMENTAL SECTION

All solvents were dried and distilled by standard procedures. Melting points were determined with an capillary melting point apparatus (Thomas-Hoover) or micro melting point apparatus (Yanaco) and are uncorrected. Infrared (IR) spectra were recorded with a Perkin-Elmer 682, 1725X spectrometers or Bio-RAD FTs 40 spectrometer. NMR spectra were recorded with a Varian Unity-300 or VXR-300FT spectrometer and were obtained using $CDCl_3$ as solvent (unless otherwise indicated) and tetramethylsilane (for ^1H NMR), $CDCl_3$ (for ^{13}C NMR) as internal references (0 δ, 77.0 δ). The multiplicity of ^{13}C NMR signals taken from DEPT analysis refers to the number of attached H's (i.e., s = C, d = CH, t = CH_2, q = CH_3). Mass spectra were obtained on a JEOL JMS-SX/SX 102A, JMS-HX 110 or JMS-D100 mass spectrometer at 12 eV. Elemental microanalyses were performed by Analytical Center operated by the Cheng-Kung University, Tainan, Taiwan.

(1α,2α,3β,6β,7α,8α,9α,10α,13α,14α)-3,4,5,6-Tetrachloro-10,13-dihydroxy-17,17-dimethoxypentacyclo[6.6.2.1^{3,6}.0^{2,7}.0^{9,14}]heptadeca-4,11,15-triene (14).

To a 0.4*M* methanolic solution of cerium chloride prepared by dissolving $CeCl_3 \cdot 7H_2O$ (7.8 g) in methanol (50 mL) was added ground enedione **13**[14] (1 g, 2.2 mmol) and the resulting suspension was stirred with cooling in an ice-water bath. Sodium borohydride (0.5 g) was then added carefully in portions over a period of about 30 min.. The resulting milky reaction mixture was stirred for additional 2 h at ambient temperature and then quenched with ice-water (20 g) followed

by the addition of CH_2Cl_2 (20 mL). After stirring for 10 min., the aqueous layer was separated and further extracted with CH_2Cl_2 (20 mL x 3). The combined organic layers were washed with brine (20 mL x 3), dried (Na_2SO_4), and filtered. The filtrate was evaporated under reduced pressure leaving a off-white solid which was recrystallized from $CHCl_3$-cyclohexane to give enediol **14** as colorless crystals (0.9 g, 90%): mp 175-176 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.08 (br s, 2H), 2.65 (br s, 2H), 2.76 (s, 2H), 2.87 (dd, $J_1 = J_2$ = 3.9 Hz, 2H), 3.50 (s, 3H), 3.57 (s, 3H), 4.20 (br s, 2H), 6.05 (dd, J = 4.5, 3.3 Hz, 2H), 6.38 (dd, J = 3.9, 2.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 33.37 (d), 46.77 (d), 51.49 (q), 51.86 (d), 52.73 (q), 64.94 (d), 77.20 (s), 113.97 (s), 126.56 (d), 127.71 (s), 136.27 (d); MS (EI) *m/z* (rel. intensity) 456/454/452 (M^+,weak), 421 (5), 419 (13), 417 (14), 415 (3), 257 (32), 255 (97), 253 (100), 209 (15), 207 (16), 86 (52), 57 (13). Anal. Calcd for $C_{19}H_{20}Cl_4O_4$: C, 50.22; H, 4.44. Found: C, 50.23; H, 4.43.

(1α,2α,3β,6β,7α,8α)-3,4,5,6-Tetrachloro-13,13-dimethoxy-9,10-benzotetracyclo-[6.2.2.1^{3,6}.0^{2,7}]trideca-4,9,11-triene (12).

Method 1. A mixture of **11**[14] (345 mg, 1 mmol) and benzenediazonium-2-carboxylate hydrochloride (185 mg, 1 mmol) in THF (10 mL) was heated under reflux for 3 h. To the cooled mixture was added a solution of 0.4 g of KOH in 10 mL of water. The mixture was extracted with CH_2Cl_2 (15 mL x 3), and the combined extracts were washed with water (5 mL x 3), 10% HCl (5 mL x 3), and brine (50 mL x 3). The organic phase was dried over $MgSO_4$, filtered, and evaporated in vacuum to afford a crude product of **12** (315 mg, 75%). ***Method 2.*** To a solution of endiol **14** (0.58 g, 1.27 mmol) in dry pyridine (4 mL) cooled with an aid of ice-water bath was added dropwise phosphoryl chloride (0.97 g, 5.73 mmol) at 0 °C. After the addition was complete, the resulting yellow solution was stirred at room temperature for 24 h and then heated at 80 -90 °C for another 3 h. The reaction mixture was cooled and crushed ice (15 g) was added, and the mixture was extracted with CH_2Cl_2 (15 mL x 3). The combined extracts were washed with water (5 mL x 3), 15% HCl (5 mL x 3), and brine (50 mL x 3). The organic phase was dried (Na_2SO_4), filtered, and evaporated in vacuum to give crude product (0.42 g, 80%) which was purified by recrystallization from chloroform-methanol to afford pure **12** as colorless crystals: mp 152 °C (lit.[16] 156-157 °C). ^{1}H NMR spectral data is consistent with the reported one.[16]

(1α,2α,3α,10α,11α,12α)-6,7,15,16-Tetra(methoxycarbonyl)hexacyclo[10.6.2.2^{3,10}.-0^{2,11}.0^{4,9}.0^{13,18}]docosan-4(9),6,13(18),15,19,21-hexaene (16).

A solution of tetracyclic hydrocarbon **8** (0.101 g, 0.431 mmol) and dimethyl acetylene-dicarboxylate (0.183 g, 1.29 mmol) in toluene (2 mL) was heated in a sealed tube at 85 °C for 8 h. Toluene was then evaporated in vacuo to leave crude product of **16**. Column chromatography on silica gel with ethyl acetate-hexane (10:90) as eluent afforded **16** (0.152 g, 68%) as a white solid: mp 149-150 °C (Et_2O); R_f 0.75 (3:2 ethyl acetate/hexane); IR (KBr) 2953, 1734, 1647, 1436, 1325, 1255, 1062, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 2H), 2.91 (m, 4H), 3.07 (m, 8H), 3.76 (s, 12H), 5.93 (dd, J = 4.4, 3.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 29.82 (t), 44.65 (d), 46.85 (d), 52.16 (q), 132.43 (d), 133.20 (s), 136.50 (s), 168.50 (s); MS(EI) *m/z* (rel. intensity) 518 (M^+, 2), 487 (8), 486 (8), 459 (33), 272 (27), 240 (71), 214 (100), 213 (90), 128 (79), 127 (57); HRMS calcd for $C_{30}H_{30}O_8$ (M^+)

518.1941, Found: 518.1936; Anal. Calcd for $C_{30}H_{30}O_8$: C, 69.49; H, 5.83. Found: C, 69.22; H, 5.93.

(1α,2α,3α,6α,7α,8α)-4,5:9,10-Bis(3,4-dimethoxycarbonylbenzo)tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene (17).

A mixture of **16** (85.0 mg, 0.164 mmol) and DDQ (0.103 g, 0.453 mmol) in dry benzene (3 mL) was refluxed under N_2 for 3 h. Evaporation of benzene left a residue which was subjected to column chromatography on silica gel (3:97 ethyl acetate/benzene as eluent) to afford pure **17** (69.4 mg, 82%) as a white solid: mp 210-211 °C (ethyl acetate/hexane); R_f 0.45 (1:1 ethyl acetate-benzene); IR (KBr) 3030, 2982, 1728, 1610, 1570, 1432, 1289, 1132, 1053, 718 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 2H), 3.80 (m, 4H), 3.88 (s, 12H), 6.11 (dd, *J*=4.4, 3.0 Hz, 4H), 7.44 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 43.99 (d), 44.48 (d), 52.43 (q), 123.2 (d), 129.0 (s), 132.7 (d), 149.6 (s), 168.6 (s); MS(EI, 70 ev) *m/z* (rel. intensity) 514 (M^+, 14), 483 (13), 482 (12), 270 (24), 257 (82), 244 (21), 239 (42), 226 (35), 213 (100); HRMS calad for $C_{30}H_{26}O_8$ (M^+) 514.1628; Found: 514.1627.

(1α,2α,3β,6β,7α,8α,9α,10α)-9,10-Di(acetoxymethyl)tetracyclo[6.2.2.1^{3,6}.0^{2,7}]trideca-4,11-dien-13-one (20).

Acetic anhydride (15 mL) was added dropwise under N_2 to a stirring solution of the diol **19**[13d] (10.50 g, 42.68 mmol) in triethylamine (40 mL) cooled at 5 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 18h. The resulting brown solution was washed with cold water (60 mL) and extracted with dichloromethane (60 mL x 3). The organic layers were combined and washed with 10% HCl (20 mL), saturated $NaHCO_3$ (20 mL x 3), and brine (30 mL), and then dried over anhydrous $MgSO_4$. The residue obtained after evaporation of the solvent was triturated with cold ether/hexane (3:1) to afford crude product as white solids. purification of crude product by flash column chromatography (silica gel, 10-20% ether-hexane as eluent) furnished diacetate **20** (13.1 g, 93%) as a white solid: mp 122-123 °C (ether/hexane); R_f: 0.43 (3:2, ether/hexane); IR (KBr) 1752, 1725, 1235, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.05 (s, 6H), 2.25 (m, 2H), 2.51 (d, *J* = 1.2 Hz, 2H), 2.72 (br, s, 2H), 2.98 (m, 2H), 3.71 (m, 2H), 3.84 (dd, *J* = 10.5, 5.7 Hz, 2H), 5.72 (dd, *J* = 3.6, 4.5 Hz, 2H), 5.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 20.95 (q), 35.15 (d), 36.68 (d), 42.31 (d), 51.61 (d), 63.47 (t), 128.5 (d), 131.9 (d), 170.9 (s), 199.8 (s); MS (EI,12 eV) *m/z* 210 (M^+-2HOAc); MS (FAB) *m/z* (rel. intensity): 331 (M^++H), 271 (25), 229 (38), 211 (31), 183 (23), 104 (97), 91 (27). Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.72. Found: C, 69.06; H, 6.66.

(1α,2α,3α,4α,5α,6α,7α,8α,9α,14α)-4,5-Di(acetoxymethyl)pentacyclo[6.6.2.2^{3,6}.0^{2,7}.0^{9,14}]octadeca-11,15,17-trien-10,13-dione (21).

A solution of diacetate **20** (5.00 g, 15.15 mmol) in toluene (30 mL) was purged with N_2 for 1 h and then added with freshly sublimated *p*-benzoquinone (1.64 g, 15.19 mmol). The reaction mixture was stirred and heated at 100 °C for another 14 h under N_2. After that period, the solvent was removed under reduced pressure to leave yellowish solids of product. Purification by flash column chromatography (silica gel, 5~10% EtOAc/Hexane as eluent) resulted in partial aromatization of benzoquinone moiety of dione **21**. The sample of **21** was therefore purified by

several recrystallization from ethyl acetate/hexane at 0 °C to provide pure **21** as a pale white solid (5.36 g, 86%): mp 148-149 °C (EtOAc/hexane); R_f: 0.43 (1:1, EtOAc/hexane); IR (KBr) 3010, 1724, 1702, 1604, 1240, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (s, 6H), 2.20 (s, 2H), 2.24 (m, 2H), 2.58 (br, 2H), 2.97 (s, 2H), 3.14 (br, 2H), 3.69 (m, 2H), 3.89 (dd, 2H, *J* = 10.8, 5.4 Hz), 5.77 (m, 4H), 6.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 20.75 (q), 37.48 (d), 40.33 (d), 41.73 (d), 41.79 (d), 50.38 (d), 63.57 (t), 131.3 (d), 131.7 (d), 142.0 (d), 170.6 (s), 198.5 (s); MS(EI) *m/z* (rel. intensity) 410 (M^+, 11), 290 (100), 158 (54), 104 (38), 78 (76); HRMS calad for $C_{24}H_{26}O_6$ (M^+) 410.1715, Found: 410.1729. Anal. Calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found: C, 69.95; H, 6.63. The isomerized product **21a** (10-15% yield) obtained from the silica gel column was recrystallized from CH_2Cl_2/hexane as a white solid: mp 195-197 °C (CH_2Cl_2/hexane); R_f: 0.43 (1:1, EtOAc/hexane); IR (KBr) 3404, 1718, 1495, 1270 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.06 (s, 6H), 2.15 (m, 2H), 2.18 (s, 2H), 2.67 (m, 2H), 3.75 (m, 2H), 3.90 (dd, *J* = 10.8, 5.4 Hz, 2H), 4.09 (m, 2H), 4.61 (br s, 2H), 5.86 (dd, *J* = 4.4, 3.3 Hz, 2H), 6.07 (dd, *J* = 4.4, 3.3 Hz, 2H), 6.43 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 21.09 (q), 38.19 (d), 38.66 (d), 42.26 (d), 42.82 (d), 64.02 (t), 112.8 (d), 131.4 (d), 133.4 (s), 133.5 (d), 143.0 (s), 170.9 (s); MS (EI) *m/z* (rel. intensity) 410 (M^+), 290 (5), 160 (100), 131 (10), 78 (11); HRMS calad for $C_{24}H_{26}O_6$ (M^+) 410.1725, Found: 410.1729. Anal. Calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found: C, 70.19; H, 6.49.

(1α,2α,3α,4α,5α,6α,7α,8α,9α,10α,13α,14α)-4,5-Di(acetoxymethyl)-10,13-dihydroxypentacyclo[6.6.2.2^{3,6}.0^{2,7}.0^{9,14}]octadeca-11,15,17-triene (22).

A solution of endione **21** (5.24 g, 12.78 mmol) in dry methanol (200 mL) was treated with cerium (III) chloride heptahydrate (12.40 g, 33.28 mmol) and stirred at 0 °C. Sodium borohydride (1.24 g, 32.7 mmol) was added in small portions and the temperature of reaction mixture was kept below 30 °C. After stirring for 3 h at room temperature, the reaction was quenched with cold water (200 mL) and the mixture was extracted with dichloromethane (150 mL x 3). The combined organic layers were washed with water (100 mL), brine (100 mL), and dried over magnesium sulfate. Purification by flash column chromatography (silica gel, 20% ethyl acetate-hexane as eluent) yielded endiol **22** as a white solid (4.86 g, 92%): mp 198-200 °C (dec.) (ethyl acetate-hexane); R_f: 0.34 (3:1, EtOAc /Hexane); IR (KBr) 3330 (br), 1728, 1250, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.00 (s, 6H), 2.01 (s, 2H), 2.05 (s, 2H), 2.16 (m, 2H), 2.51~2.54 (m, 6H), 3.68 (dd, *J* = 8.7, 10.8 Hz, 2H), 3.85 (dd, *J* = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, *J* = 3.0, 4.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 21.03 (q), 38.16 (d), 39.17 (d), 42.26 (d), 43.99 (d), 47.24 (d), 64.13 (t), 65.24 (d), 130.8 (d), 131.6 (d), 136.4 (d), 171.0 (s); MS (EI) *m/z* (rel. intensity) 414 (M^+, 8), 396 (M^+-H_2O, 16), 294 (M^+-2HOAc, 100), 276 (98), 227 (68), 209 (24); HRMS calad for $C_{24}H_{30}O_6$ (M^+) 414.2047, Found: 414.2043. Anal. Calcd for $C_{24}H_{30}O_6$: C, 69.54; H, 7.30. Found: C, 69.23; H, 7.32.

(1α,2α,3α,4α,5α,6α,7α,8α)-4,5-Di(acetoxymethyl)-9,10-benzotetracyclo[6.2.2.2^{3,6}.-0^{2,7}]tetradeca-9,11,13-triene (23).

To a solution of endiol **22** (3.25 g, 7.85 mmol) in dry pyridine (80 mL) was added dropwise a solution of phosphoryl chloride (4.88 g, 31.8 mmol) in pyridine (80 mL) at 0 °C, and the resulting yellow solution was stirred at room temperature for 72 h and then heated at 110 °C for another 1 h.

After cooling, crushed ice (150 g) was added to the reaction mixture and the product was extracted into ether (50 mL x 3). The combined extracts were washed with water (50 mL x 3), 10% HCl (50 mL x 3), saturated $NaHCO_3$ (50 mL x 2) and brine (50 mL). The organic phase was dried ($MgSO_4$), filtered and evaporated in vacuum. The product was purified by flash column chromatography (silica gel, 3% EtOAc/Hexane as eluent) to give pure **23** (2.23 g, 75%) as a white solid: mp 113-115 °C (Et_2O/Hexane); R_f: 0.42 (1:9, EtOAc /Hexane); IR (KBr) 3030, 1724, 1245, 1035, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (s, 6H), 2.06 (s, 2H), 2.07 (s, 2H), 2.14 (m, 2H), 3.75 (m, 4H), 3.90 (dd, J = 5.4, 10.5 Hz, 2H), 5.86 (dd, J = 3.3, 4.7 Hz, 2H), 6.05 (dd, J = 3.1, 4.4 Hz, 2H), 7.03 (m, 2H), 7.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 20.98 (q), 38.13 (d), 42.19 (d), 43.45 (d), 45.50 (d), 64.01 (t), 122.3 (d), 124.9 (d), 131.4 (d), 133.4 (d), 145.9 (s), 170.9 (s); MS (EI) *m/z* (rel. intensity) 378 (M^+, 2), 318 (M^+-HOAc, 3), 258 (M^+-2HOAc, 100), 243 (22), 128 (99); HRMS calad for $C_{24}H_{26}O_4$ (M^+) 378.1843, Found: 378.1832. Anal. Calcd for $C_{24}H_{26}O_4$: C, 76.16; H, 6.92. Found: C, 76.17; H, 6.83.

(1α,2α,3α,4α,5α,6α,7α,8α)-4,5-Di(hydroxymethyl)-9,10-benzotetracyclo[6.2.2.2^{3,6}.-0^{2,7}]tetradeca-9,11,13-triene (24).

To a suspension of $LiAlH_4$ (0.54 g, 14.21 mmol) in anhydrous THF (100 mL) was slowly added under an atmosphere of N_2 a solution of diacetate **23** (2.34 g, 6.43 mmol) in anhydrous THF (50 mL). The mixture was stirred at room temperature for 6 h and then at 50 °C for another 1 h. The reaction was quenched by sequential addition of H_2O (0.5 mL), 15% aqueous NaOH (0.5 mL), and H_2O (1.5 mL). After the mixture was stirred for 1 h, the milky solution was filtered, and the solids was washed with THF (30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The solid was purified by chromatography (silica gel, 30% EtOAc/Hexane as eluent) to give diol **24** (1.78 g, 93%) as a white solids: mp 179-180 °C (methanol/benzene); R_f: 0.34 (2:1, EtOAc /Hexane); IR (KBr) 3240 (br), 1475, 1065, 1030, 750, 700 cm^{-1}; ^1H NMR (pyridine-d_5, 300 MHz) δ 2.03 (s, 2H), 2.35 (m, 2H), 2.82 (m, 2H), 3.65 (m, 4H), 3.97 (m, 2H), 5.81 (dd, J = 3.9, 4.2 Hz, 2H,), 5.99 (dd, J = 3.9, 4.5 Hz, 2H,), 6.22 (m, 2H), 7.12 (m, 2H), 7.22 (m, 2H); ^{13}C NMR (pyridine-d_5, 75.43 MHz) δ 38.51 (d), 43.45 (d), 45.16 (d), 46.99 (d), 61.72 (t), 121.8 (d), 124.2 (d), 130.8 (d), 132.8 (d), 145.9 (s); MS (EI) *m/z* (rel. intensity) 294 (M^+, 28), 276 (M^+-H_2O, 14), 246 (32), 128 (100); HRMS calad for $C_{20}H_{22}O_2$ (M^+) 294.1620, Found: 294.1616. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.34; H, 7.50.

(1α,2α,3α,6α,7α,8α)-4,5-Dimethylidene-9,10-benzotetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradeca-9,11,13-triene (10).

To a solution of diol **24** (1.6 g, 5.44 mmol) in dry pyridine (50 mL) was added a solution of *p*-toluenesulfonyl chloride (12.44 g, 65.30 mmol) in dry pyridine (15 mL) at 0 °C under N_2. After stirring at 0 °C for 6 h, the mixture was slowly poured into cold water (150 mL) and extracted with dichloromethane (60 mL x 3). The combine extracts were washed with 10% HCl (30 mL), water (60 mL), brine(60 mL), and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the resulting light yellow solids were immediately used in the next reaction. The prepared ditosylate (3.11 g, 5.17 mmol) was dissolved in dry DMSO (40 mL) under N_2 at room temperature, and a solution of potassium *t*-butoxide (3.47 g, 30.98 mmol) in DMSO (15 mL) was

then added. After the reaction mixture was heated at 40 °C with stirring for 8 h, cold hexane (50 mL) was added, and the mixture was stirred for another 10 min. followed by separation of both layers. The bottomed layer (DMSO solution) was mixed with ice-water (150 g) and extracted with diethyl ether (50 mL x 3). The diethyl ether extracts were combined with upper layer (hexane solution) and washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$. Evaporation of solvent left crude product which was purified by flash column chromatography (silioca gel, hexane as eluent) and recrystallization to give pure hydrocarbon **10** (0.69 g, 49% from diol **24**) as a white solid; mp 151-152 °C (Hexane); R_f: 0.23 (Hexane); IR (KBr) 3010, 2904, 1456, 1342, 893, 884, 754, 728, 673 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 2H), 3.26 (m, 2H), 3.83 (m, 2H), 4.80 (s, 2H), 5.12 (s, 2H), 5.92 (dd, J = 3.5, 4.5 Hz, 2H), 6.12 (dd, J = 3.4, 4.3 Hz, 2H), 7.04 (m, 2H), 7.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 43.39 (d), 45.24 (d), 47.13 (d), 102.5 (t), 122.2 (d), 124.8 (d), 130.3 (d), 133.3 (d), 145.9 (s), 147.3 (s); MS (EI) *m/z* (rel. intensity) 255 (M^+, 100), 243 (11), 153 (10), 128 (26), 115 (13); HRMS calad for $C_{20}H_{18}$ (M^+) 258.1398, Found: 258.1409. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.93; H, 7.09.

(1α,2α,3α,6α,7α,8α,11β,12α)-11,12-Di(phenylsulfonyl)-4,5-benzopentacyclo[6.6.2.-$2^{3,6}.0^{2,7}.0^{9,14}$]octadeca-4,9(14),15,17-tetraene (25).

To a suspension of **10** (0.42 g, 1.63 mmol) and zinc chloride (0.50 g, 3.67 mmol) in anhydrous toluene (15 mL) was added *trans*-1, 2-bis(phenylsulfonyl)ethylene (1.13 g, 3.67 mmol) under N_2. The reaction mixture was stirred at 85 °C for 6 h and then the solution was filtered and concentrated to give a white residue. Chromatography on silica gel (50% CH_2Cl_2/hexane as eluent) gave the cycloadduct **25** as a white solid (0.44 g, 48%): mp 147-148 °C (CH_2Cl_2/Hexane); R_f: 0.27 (3:1. CH_2Cl_2/Hexane); IR (KBr) 3048, 2935, 1608, 1585, 1469, 1446, 1304, 1142, 1080, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45 (m, 1H), 1.81 (m, 1H), 2.53~2.62 (m, 4H), 2.85 (m, 2H), 3.41 (m, 1H), 3.47 (m, 1H), 3.84 (d, J = 6.9 Hz, 1H), 3.95 (d, J = 6.3 Hz, 1H), 5.81 (m, 2H), 5.98 (m, 2H), 7.03~7.73 (m, 14H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 22.33 (t), 22.37 (t), 44.84 (d), 44.97 (d), 45.19 (d), 45.28 (d), 45.40 (d), 45.43 (d), 57.51 (d), 57.99 (d), 122.3 (d), 122.4 (d), 124.7 (d), 124.8 (d), 128.6 (d), 128.7 (d), 129.0 (d), 129.3 (d), 132.0 (d), 132.1 (d), 132.6 (d), 132.9 (d), 133.9 (d), 134.2 (d), 135.3 (s), 135.5 (s), 136.9 (s), 137.0 (s), 146.6 (s), 146.7 (s); MS (EI) *m/z* (rel. intensity) 566 (M^+, 2.6), 424 (17), 361 (70), 283 (34), 233 (35), 143 (87), 129 (76); HRMS calad for $C_{34}H_{30}S_2O_4$ (M^+-$C_6H_5SO_2$) 424.1500, Found: 424.1498. Anal. Calcd for $C_{34}H_{30}S_2O_4 \cdot 0.5$ CH_2Cl_2: C, 68.02; H, 5.13. Found: C, 67.94; H, 5.14.

(1α,2α,3α,6α,7α,8α)-4,5-Benzopentacyclo-[6.6.2.$2^{3,6}.0^{2,7}.0^{9,14}$]octadeca-4,9(14),-11,15,17-pentaene (26).

To a mechanically stirred solution of *trans*-1,2-bis- (phenylsulfonyl) ethylene cycloadduct **25** (0.22 g, 0.39 mmol) and disodium hydrogen phosphate (0.42 g, 2.96 mmol) in anhydrous methanol (30 mL) was added, at room temperature and under N_2 10% of sodium amalgam (1.34 g, 5.83 mmol of sodium) in portions within a period of 1 h. The reaction mixture was stirred for additional 10 h, filtered, and the filtrate was poured into cold water (60 mL) and extracted with dichloromethane (30 mL x 3). The combined extracts were washed with brine (30 mL) and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure to leave a white residue

which was chromatographed on silica gel (hexane as eluent) to yield compound **26** (0.10 g, 90%) as a white solid: mp 147-148 °C (hexane); R_f: 0.48 (hexane); IR (KBr) 3063, 2893, 1466, 748, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.19 (s, 2H), 2.71 (s, 4H), 3.03 (m, 2H), 3.57 (m, 2H), 5.59 (s, 2H), 6.06 (m, 4H), 6.99 (dd, J = 3.3, 5.4 Hz, 2H), 7.09 (dd, J = 3.3, 5.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 27.94 (t), 45.25 (d), 45.41 (d), 46.60 (d), 124.7 (d, two peaks), 132.7 (d), 132.8 (d), 137.7 (s), 146.9 (s); MS (EI) *m/z* (rel. intens.) 284 (M^+, 100), 154 (26), 128 (12), 115 (5); HRMS calad for $C_{22}H_{20}$ (M^+) 284.1566, Found: 284.1566. Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.89; H, 6.83.

(1α,2α,3α,6α,7α,8α)-4,5:9,10-Bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,-13-tetraene (6).

A mixture of pentacyclic pentaene **26** (0.10 g, 0.35 mmol) and 2,3-dichloro-5,6-dicyanoquinone (0.12 g, 0.53 mmol) in dry benzene (20 mL) was refluxed under N_2 for 3 h. Evaporation of the solvent gave a residue which was chromatographed on silica gel (hexane as eluent) to give bis-benzo **6** (0.09 g, 91%) as a white solid. The bis-benzo **6** thus obtained was dissolved in a small amount of dry Et_2O and hexane was added dropwise till the appearance of turbidness. Drop(s) of dry Et_2O was added and the resulting clear solution was then placed in a crystallization chamber under a saturated hexane atmosphere at room temperature to afford single crystals suitable for the X-ray analysis. Pure sample of bis-benzo **6** was obtained by recrystallization from hexane/Et_2O as colorless crystallines: mp 204-205 °C; R_f: 0.42 (hexane); IR (KBr) 3062, 1466, 1360, 741, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.19 (s, 2H), 3.77 (m, 4H), 6.16 (dd, J = 3.3, 4.5 Hz, 4H), 6.95 (dd, J = 3.3, 4.5 Hz, 4H), 7.07 (dd, J = 3.3, 4.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 45.45 (d), 45.95 (d), 122.4 (d), 124.8 (d), 133.2 (d), 146.5 (s); MS (EI) *m/z* (rel. intensity) 282 (M^+,100), 154 (M^+-naphthalene), 141 (15), 128 (14); HRMS cald for $C_{22}H_{18}$ (M^+) 282.1409, Found: 282.1409. Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.42; H, 6.42.

5,6-Benzo-11,12-di(hydroxymethyl)hexacyclo[8.3.1.0^{2,7}.0^{3,14}.0^{4,9}.0^{8,13}]tetradec-5-ene (30). Irradiation of 24.

A degassed solution of diol **24** (0.60 g, 2.04 mmol) in acetone/ benzene (1:1, 150 mL) was irradiated under N_2 with a 450 W medium-pressure mercury lamp, shielded with a Pyrex glass filter for 6 h. After evaporation of the solvent, the product was purified by recrystallization from methanol/ benzene to give pure **30** (0.58 g, 96%) as a white crystalline solid: mp 255-256 °C (methanol/ hexane); IR (KBr) 3249, 1029, 760 cm^{-1}; ^1H NMR (C_5D_5N, 300 MHz) δ 1.78 (s, 2H), 1.92 (s, 2H), 2.33 (s, 2H), 2.63 (br, 4H), 2.85 (s, 2H), 3.79 (m, 2H), 4.27 (m, 2H), 6.47 (m, 2H, OH), 7.30 (m, 4H); ^{13}C NMR (C_5D_5N, 75.43 MHz) δ 34.31 (d), 36.69 (d), 37.82 (d), 41.88 (d), 43.48 (d), 43.56 (d), 63.61 (t), 125.3 (d), 126.2 (d), 140.7 (s); MS (EI) *m/z* (rel. intensity) 294 (M^+, 61), 276 (M^+-H_2O, 20), 246 (M^+, 17), 179 (14), 167 (13), 155 (13), 128 (100); HRMS calad for $C_{20}H_{22}O_2$ (M^+) 294.1602, Found 294.1613. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.50; H, 7.46.

5,6-Benzo-11,12-dimethylenehexacyclo[8.3.1.$0^{2,7}$.$0^{3,14}$.$0^{4,9}$.$0^{8,13}$]tetradec-5-ene (29).

This substance was prepared from diol **30** (0.27 g, 0.92 mmol) and toluenesulfonyl chloride (2.10 g, 11.0 mmol) in dry pyridine (15 mL) as described for preparation of **10**. The resulting tosylate was used immediately by treatment with potassium *t*-butoxide (1.23 g, 11.0 mmol) in DMSO (30 mL) at room temperature. After the completion of reaction (ca. 8h), hexane (60 mL) and ice-water (60 g) were added. The aqueous layer was extracted with ethyl ether (30 mL x 2). The combined extracts were washed with water (50 mL), brine (50 mL), dried over $MgSO_4$, and then concentrated to leave a white residue. Chromatography (silica gel, hexane as eluent) gave **29** (0.11 g, 46%): mp 145-146 °C (Et_2O/hexane); R_f: 0.63 (hexane); IR (KBr) 3075, 2955, 1601, 1485, 1315, 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.08 (m, 2H), 2.53 (m, 4H), 2.77 (m, 2H), 3.05 (m, 2H), 4.86 (s, 2H), 5.41 (d, J = 0.9 Hz, 2H), 7.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 39.44 (d), 41.19 (d), 43.62 (d), 43.67 (d), 45.27 (d), 105.30 (t), 124.80 (d), 125.80 (d), 139.70 (s), 144.30 (s); MS (EI) *m/z* (rel. intensity) 258 (M^+, 100), 243 (13), 229 (8), 215 (8), 141 (11), 128 (28), 115 (12); HRMS calad for $C_{20}H_{18}$ (M^+) 258.1399, Found: 258.1409.

5,6;11,12-Bis(3,4-dimethoxycarbonylbenzo)hexacyclo[8.3.1.$0^{2,7}$.$0^{3,14}$.$0^{4,9}$.$0^{8,13}$]-tetradeca-5,11-diene (31).

A solution of **17** (86.0 mg, 0.101 mmol) in benzene (7 mL) was placed in a quartz tube (10 mm OD × 200 mm length). A stream of nitrogen was bubbled through the solution. The solution was photolyzed for 8 h using a 450 W medium pressure Hanovia mercury lamp in a borosilicate immersion well. The solvent was then evaporated in vacuo to leave crude product which was recrystallized from dichloromethane-hexane to give pure **31** (85.5 mg, 100%) as a white solid: mp 135-137 °C; IR (KBr) 2951, 1732, 1616, 1435, 1292, 1122, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (s, 2H), 2.66 (s, 4H), 3.27 (s, 4H), 3.91 (s, 12H), 7.63 (s, 4H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 39.8 (d), 42.9 (d), 43.9 (d), 52.5 (q), 125.6 (d), 129.7 (s), 143.3 (s), 168.4 (s); MS (EI, 70 eV) *m/z* 514 (M^+, 100), 483 (48), 270 (41), 226 (34), 213 (25); HRMS calad for $C_{30}H_{26}O_8$ (M^+) 514.1628; Found: 514.1619.

5,6:12,13-bisbenzohexacyclo[8.3.1.$0^{2,7}$.$0^{3,14}$.$0^{4,9}$.$0^{8,13}$]-tetradeca-5,11-diene (32).

A degassed solution of **6** (50 mg, 0.18 mmol) in benzene (10 mL) was photolyzed under N_2 with a 450 W medium-pressure mercury lamp, shielded with a Pyrex glass filter for 6 h. Evaporation of the solvent gave a residue which was purified by chromatography over silica gel using hexane as eluent to yield compound **20** (45 mg, 90%) as a white solid: mp 237-238 °C; R_f: 0.6 (hexane); IR (KBr) 3034, 2969, 2902, 1583, 1482, 1309, 1243, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (s, 2H), 2.62 (s, 4H), 3.17 (s, 4H), 7.20~7.28 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 40.22 (d), 43.26 (d), 44.44 (d), 125.0 (d), 125.8 (d), 140.4 (s); MS (EI) *m/z* (rel. intensity) 282 (M^+, 100%), 154 (24), 141 (8); HRMS calad for $C_{22}H_{18}$ (M^+) 282.1395, Found: 282.1408. Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.38; H, 6.47.

(1α,2α,3α,6α,7α,8α)-4,5:9,10-Bisbenzotetracyclo[6.2.2.$2^{3,6}$.$0^{2,7}$]tetradeca-4,9-diene (33).

A mixture of **6** (98 mg, 0.35 mmol), 10% Pd/C (10.6 mg, 0.01 mmol), benzene (5 mL) and ethanol (30 mL) was placed in a 150-mL stainless steel autoclave equipped with a electric stirrer

(Parr apparatus). The unit was sealed and then purged five times with 5 Kg/cm^2 pressurization-depressurization cycles of hydrogen. The reactor was then pressurized to 6 Kg/cm^2 with hydrogen then heated to 60 °C with stirring and held at this temperature for 12 h. The reaction was terminated by discharged of hydrogen and the resulting mixture was filtered and concentrated to give white solids. Subsequent chromatography (Silica, hexane as eluent) gave **33** (90 mg, 92%) as a white solid: mp > 220 °C (sublimated); R_f: 0.66 (hexane); IR (KBr) 2988, 2920, 2277, 1489, 1451, 1123, 752, 728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43 (d, J = 7.8 Hz, 4H), 1.58 (s, 2H), 2.53 (d, J = 7.5Hz, 4H), 3.10 (s, 4H), 7.07 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 22.33 (t), 39.08 (d), 39.57 (d),122.7 (d), 125.8 (d), 146.2 (s); MS (EI) *m/z* (rel. intensity) 287 (M^++1, 24), 286 (M^+, 100), 258 (25), 157 (56), 129 (94), 115 (25); HRMS calad for $C_{22}H_{22}$ (M^+) 286.1723, Found: 286.1729. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.81.

(1α,2α,3α,6α,7α,8α)-11,12;13,14-Diepoxy-4,5:9,10-bisbenzotetracyclo[6.2.2.2^{3,6}.-0^{2,7}]tetradeca-4,9-diene (34).

To a solution of **6** (0.112 g, 0.397 mmol) in methylene chloride (5 mL) at 0 °C was added *m*-CPBA (0.143 g, 0.829 mmol). The reaction mixture was stirred at 0 °C for 24 h then allowed to reach room temperature and stirred for another 4 h. The reaction time was determined by the analysis of reaction mixture using thin layer chromatography. After the completion of reaction, the mixture was diluted with methylene chloride (35 mL), poured into 10% aqueous NaOH (20 mL), and extracted with methylene chloride (30 mL). The organic layer was successively washed with water (15 mL x 2) and brine(15 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product thereby obtained was purified by flash column chromatography (silica gel, 25% EtOAc-hexane as eluent) to give bis-epoxy **34** (0.11 g, 88%) as a white solid: mp 256-258 °C (dec.) (CH_2Cl_2-hexane); R_f: 0.74 (EtOAc); IR (KBr) 3026, 2925, 1478, 1461, 1323, 1183, 946, 825, 734, 612, 528 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (d, J = 0.9 Hz, 2H), 3.59 (m, 4H), 3.63 (s, 4H), 7.01 (dd, J = 5.3, 3 Hz, 4H), 7.14 (dd, J = 5.3, 3 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 41.36 (d), 42.04 (d), 48.70 (d), 123.6 (d), 126.9 (d), 138.5 (s); MS (EI) *m/z* (rel. intensity) 314 (M^+, 57), 298 (M^+-Oxygen, 4), 267 (9), 252 (10), 228 (13), 170 (24), 141 (78), 128 (58), 115 (100); HRMS calad for $C_{22}H_{18}O_2$ (M^+) 314.1300; Found: 314.1307. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.94; H, 5.82.

Bromination of 6. To a stirred solution of **6** (0.140 g, 0.50 mmol) in chloroform (10 mL) at 0 °C was added dropwise a solution of bromine (0.13 g, 0.81 mmol) in chloroform (3 mL) under nitrogen. After the reaction mixture was stirred at 0 °C for 12 h., the solvent was evaporated under reduced pressure to leave a light yellow residue consisting of three observable products which was separated by flash chromatography (silica gel, 1:9 dichloromethane/hexane as eluent) to yield ***endo*-1,*exo*-2-dibromo-5:6,11:12-bisbenzopentacyclo[8.4.0.0^{2,7}.0^{4,9}.0^{8,13}]-tetradeca-5,11-diene (35b)** (137 mg, 62%) as a white solid. An analytical sample was obtained by recrystallization from CH_2Cl_2-Et_2O: mp 170-171 °C; R_f: 0.31 (1:4, CH_2Cl_2/hexane); IR (KBr) 3020, 2961, 1476, 1236, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (m, 2H), 2.62 (m, 1H), 2.76 (m, 1H), 3.39 (d, J = 6 Hz, 1H), 3.51 (d, J = 5.7 Hz,1H), 3.62 (m, 1H), 3.93 (d, J = 5.7 Hz, 1H), 4.15 (d, J = 5.7 Hz,1H), 5.07 (d, J = 5.4 Hz,1H), 7.23 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 35.50 (d), 36.66 (d),

38.81 (d), 39.56 (d), 40.11 (d), 41.56 (d), 45.59 (d), 46.13 (d), 54.59 (d), 55.90 (d), 122.90 (d), 124.3 (d), 124.6 (d), 125.8 (d), 126.1 (d), 126.7 (d), 127.2 (d), 127.3 (d), 139.4 (s), 139.5 (s), 141.5 (s), 143.1 (s); MS (EI) *m/z* (rel. intensity) 444 (M^+ + 4, 19), 442 (M^++ 2, 38), 440 (M^+, 20), 363 (68), 361 (68), 281 (100), 235 (30), 233 (30), 153 (78). Anal. Calcd for $C_{22}H_{18}Br_2$: C, 59.76; H, 4.10. Found:C, 59.72; H, 4.12.

***exo*-8,*exo*-14-Dibromo-5:6,12:13-bisbenzo-pentacyclo[8.3.1.$0^{2,7}$.$0^{3,11}$.$0^{4,9}$]-tetradeca-5,12-diene (36a)** (24 mg, 11%): mp 219-221 °C (hexane/ benzene); Rf 0.17 (1:4, CH_2Cl_2/ hexane); IR (KBr) 3032, 2952, 1478, 1460, 1224,754, 686 537, 472 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.75 (dm, *J* = 9.6 Hz, 1H), 2.20 (dt, *J* = 9.6, 3.3 Hz, 1H), 2.99 (m, 2H), 3.33 (m, 2H), 3.41 (dd, *J* = 5.5, 3.3 Hz, 2H), 5.43 (d, *J* = 5.4 Hz, 2H), 7.08~7.26 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 40.70 (d), 44.10 (d), 45.24 (d), 48.57 (d), 48.81 (d), 53.50 (d), 124.8 (d), 125.2 (d), 125.7 (d), 127.0 (d), 139.3 (s), 141.6 (s); MS (EI,70eV) *m/z* 444 (M^++ 4, 12), 442 (M^++ 2, 24), 440 (M^+, 12), 363 (22), 361 (23), 281 (34), 235 (32), 233 (33), 153 (100), 128 (90), 115 (22). HRMS calad for $C_{22}H_{18}Br_2$ (M^+) 439.9775, Found: 439.9782.

10-Oxa-5:6,13:14-bisbenzo-hexacyclo[9.3.1.$0^{2,7}$.$0^{3,12}$.$0^{4,9}$.$0^{8,15}$]pentadeca-5,13-diene (37) (8 mg, 6%): mp 258-261 °C (dec., ethyl ether); Rf 0.05 (1:4, CH_2Cl_2/hexane); IR (KBr) 3020, 2926, 1483, 1462, 1072, 1049 744 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.86 (dm,*J* = 9.9 Hz, 1H), 1.95 (dm, *J* = 9.9 Hz, 1H), 2.84 (m, 2H), 3.11 (m, 2H), 3.19 (m, 2H), 4.07 (m, 2H), 7.20-7.26 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 35.02 (d), 42.22 (d), 44.49 (d), 46.05 (d), 47.37 (d), 81.50 (d), 124.8 (d), 125.1 (d), 126.3 (d), 126.6 (d), 140.1 (s), 140.5 (s); MS (EI, 70 eV) *m/z* 298 (M^+, 90), 170 (100), 141 (81), 128 (59), 115 (28). HRMS calad for $C_{22}H_{18}O$ (M^+) 298.1358; Found: 298.1365.

Debromination of 35b. A solution of **35b** (44 mg, 0.10 mmol) in ethyl acetate (10 mL) containg fresh prepared zinc dust and acetic acid (0.1 mL) was stirred at 25 °C for 36 h. The reaction mixture was filtered and washed with water (3 mL). Removal of ethyl acetate gave a white residue which was then purified by chromatography (silica gel, hexane as eluent) to give **6** (23 mg, 78%).

Thermolysis of 6. A glass tube (5-mm OD×20 cm length) was filled with **6** (0.01 g, 0.035 mmol) and then sealed under high vacuum. The reaction tube was placed in an oven controlled at 210 °C ± 3 °C for 12h (or 250 °C for 3h). After cooling to 0 °C, the glass tube was opened and the reaction mixture was then dissolved in $CDCl_3$. The ^1H NMR spectrum indicated that the reaction mixture contained benzobicyclo[2. 2. 2]octatriene and naphthalene in a ca. 1:1 ratio, based on the integration of absorption peaks. ^1H NMR ($CDCl_3$, 300 MHz) for benzobicyclo[2.2.2]octatriene: δ 4.92 (m, 2H, bridge head protons), 6.88 (m, 6H, vinylic and aromatic protons) and 7.12 (dd, *J* = 3.3, 5.2 Hz, 2H, aromatic protons); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 49.12 (d), 122.2 (d), 123.4 (d), 139.7 (d), 147.5 (s).

Crystal structure of 6.

Space group and cell dimensions: orthorhombic P_{nma}, a = 11.090 (3) Å, b = 20.488 (4) Å, c = 6.412 (2) Å, and V=1456.9 (6) $Å^3$, empirical formula: $C_{22}H_{18}$. Cell dimensions were obtained from 14 reflections with 2θ angle in the range 8.36° - 28.11°. Crystal dimensions: 0.80 x 0.78 x

0.54 mm, F_W = 282.4, Z = 4, F(000) = 600, D_{calc} = 1.287 g/cm^3, λ = 0.71073 Å, $2\theta_{(max)}$ = 50.0°. The intensity data were collected on a Siemens R3m/V diffractometer using the $\theta/2\theta$ scan method. The hkl ranges were 0 < h < 13, 0 < k < 24, 0 < l <6. There were 1159 independent reflections collected above background measured at room temperature and 930 with $I_o > 3.0\ \sigma\ (I_o)$. The final R indices was 0.0314 with R_w = 0.0417. GoF = 1.36. In the last density map, the deepest hole was -0.12 eÅ^{-3}, and the highest peak 0.15 eÅ^{-3}. Tables of atomic co-ordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

Crystal structure of 35b.

Space group and cell dimensions: orthorhombic P_{bcm}, a = 10.176 (3) Å, b = 12.826 (5) Å, c = 26.717 (8) Å, and V = 3487 (2) Å^3, empirical formula: $C_{44}H_{36}Br_4$ (two molecules of **35b**). Cell dimensions were obtained from 18 reflections with 2θ angle in the range 11.06° - 23.81°. Crystal dimensions: 0.44 x 0.26 x 0.22 mm, F_W = 884.4, Z = 4, F(000) = 1760, D_{calc} = 1.684 g/cm^3, λ = 0.71073 Å, $2\theta_{(max)}$ = 50.0°. The intensity data were collected on a Siemens R3m/V diffractometer using the $\theta/2\theta$ scan method. The hkl ranges were 0 < h < 12, 0 < k < 15, 0 < l < 31. There were 3112 independent reflections collected above background measured at room temperature and 1364 with $I_o > 3.0\ \sigma\ (I_o)$. The final R indices was 0.0493 with R_w = 0.0470. GoF = 1.22. In the last density map, the deepest hole was -0.52 eÅ^{-3}, and the highest peak 0.58 eÅ^{-3}. Tables of atomic co-ordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

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