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Synthesis, Reactions and Thermal Properties of endo-5,12:endo-6,11-Dietheno-5,5a,6,11,11a,12-hexahydronaphthacene¹

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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-dimethylidenediethenoanthracene 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 bisepoxide 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 topology² 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 space⁴ was demonstrated for endo,endo-dimethanonaphthalene skeletal systems (e.g. 1) by rate enhancements in solvolytic reactions⁵ 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 1⁸ and bromination of 2⁹, while only the adduct of N-type was found in the bromination of 3¹⁰ 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 bonds¹³ 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.



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.





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 pyridine¹⁷ (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



The synthesis of 6 was then decided to be approached by the Diels-Alder reaction of tetracyclic bis-butadiene 813d 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 In our hand, bis-butadiene 8 reacted with dimethyl acetylenedicarboxylate documented.19 (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 tetramethoxycarbonylsubstituted diethenonaphthacene 17 in 82% yield. However, the desired bis-adduct 18 of bisbutadiene 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.



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 1913d 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 pbenzoquinone 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 ¹H 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-It is worth noting that endione 21, when purified cyclohexadienes with maleic anhydride.^{13d,21} 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 equivalent²³), 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



formation of **25** in 48% yield (Scheme 3). The bis-sulfonate **25** was smoothly reduced with 10% sodium amalgam in methanol according to literature procedures²⁴ 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 ¹H 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 Prinzbach²⁷ 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



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 ¹H 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.



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).



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 ethanobridges 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**



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 bisepoxide **34** in 88% yield. The ¹H-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 ¹H NMR spectrum and a ¹³C 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





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 endostereochemistry. When treatment with zinc in acetic acid, dibromide 35b underwent 1,4debromination to regenerate hydrocarbon 6 in good yield (78%). The second isomeric dibromide, obtained in yield of 11%, exhibited a less complex ¹H NMR spectrum and a ¹³C NMR spectrum of 12 lines for 22 carbon atoms, indicating the presence of a plane symmetry element in the Among three possible dibrominated products of U-type, only exo, exo and endo, endo molecule. 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 An oxygen-containing product, isolated in small amounts and choice of the two (Scheme 4). various yields (~6%), showed a ¹H NMR spectrum having six groups of signals due to nonaromatic hydrogens and a ¹³C 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 field³³ 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 $^{\circ}C^{13b}$ or perchlorobutadiene/160 $^{\circ}C^{25}$), tetracyclic tetraene 27 underwent [4+2] cycloreversion cleanly to benzene and barrelene. Higher temperature (210 $^{\circ}C \pm 5 ^{\circ}C$) 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 $^{\circ}C \pm 5 ^{\circ}C$, 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 $^{\circ}C$ 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 CDCl₃ as solvent (unless otherwise indicated) and tetramethylsilane (for ¹H NMR), CDCl₃ (for ¹³C NMR) as internal references (0 δ , 77.0 δ). The multiplicity of ¹³C NMR signals taken from DEPT analysis refers to the number of attached H's (i.e., s = C, d = CH, t = CH₂, q = CH₃). 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.

$(1\alpha, 2\alpha, 3\beta, 6\beta, 7\alpha, 8\alpha, 9\alpha, 10\alpha, 13\alpha, 14\alpha)$ -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 CeCl₃·7H₂O (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 CH₂Cl₂ (20 mL). After stirring for 10 min., the aqueous layer was separated and further extracted with CH₂Cl₂ (20 mL x 3). The combined organic layers were washed with brine (20 mL x 3), dried (Na₂SO₄), and filtered. The filtrate was evaporated under reduced pressure leaving a off-white solid which was recrystallized from CHCl₃-cyclohexane to give enediol **14** as colorless crystals (0.9 g, 90%): mp 175-176 °C; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₁₉H₂₀Cl₄O₄: C, 50.22; H, 4.44. Found: C, 50.23; H, 4.43.

$(1\alpha, 2\alpha, 3\beta, 6\beta, 7\alpha, 8\alpha)$ -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).

A mixture of 1114 (345 mg, 1 mmol) and benzenediazonium-2-carboxylate Method 1. 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 CH₂Cl₂ (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 MgSO₄, 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 CH₂Cl₂ (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 (Na₂SO₄), 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). ¹H NMR spectral data is consistent with the reported one.¹⁶

$(1\alpha, 2\alpha, 3\alpha, 10\alpha, 11\alpha, 12\alpha)$ -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 acetylenedicarboxylate (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 (Et₂O); R_f 0.75 (3:2 ethyl acetate/hexane); IR (KBr) 2953, 1734, 1647, 1436, 1325, 1255, 1062, 696 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₃₀H₃₀O₈ (M⁺) 518.1941, Found: 518.1936; Anal. Calcd for C₃₀H₃₀O₈: C, 69.49; H, 5.83. Found: C, 69.22; H, 5.93.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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 N₂ 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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₃₀H₂₆O₈ (M⁺) 514.1628; Found: 514.1627.

$(1\alpha, 2\alpha, 3\beta, 6\beta, 7\alpha, 8\alpha, 9\alpha, 10\alpha)$ -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 N2 to a stirring solution of the diol 1913d (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 NaHCO3 (20 mL x 3), and brine (30 mL), and then dried over anhydrous MgSO4. 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); Rf: 0.43 (3:2, ether/hexane); IR (KBr) 1752, 1725, 1235, 705 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₁₉H₂₂O₅: C, 69.07; H, 6.72. Found: C, 69.06; H. 6.66.

$(1\alpha, 2\alpha, 3\alpha, 4\alpha, 5\alpha, 6\alpha, 7\alpha, 8\alpha, 9\alpha, 14\alpha)$ -4,5-Dl(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 N₂ 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 N₂. 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); Rf: 0.43 (1:1, EtOAc/hexane); IR (KBr) 3010, 1724, 1702, 1604, 1240, 710 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₄H₂₆O₆ (M⁺) 410.1715, Found: 410.1729. Anal. Calcd for C24H26O6: 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 CH₂Cl₂/hexane as a white solid: mp 195-197 °C (CH₂Cl₂/hexane); Rf: 0.43 (1:1, EtOAc/hexane); IR (KBr) 3404, 1718, 1495, 1270 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₄H₂₆O₆ (M⁺) 410.1725, Found: 410.1729. Anal. Calcd for C₂₄H₂₆O₆: C, 70.23; H, 6.38. Found: C, 70.19; H, 6.49.

$(1\alpha, 2\alpha, 3\alpha, 4\alpha, 5\alpha, 6\alpha, 7\alpha, 8\alpha, 9\alpha, 10\alpha, 13\alpha, 14\alpha)$ -4,5-Di(acetoxymethyl)-10,13-dihydroxy-pentacyclo[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 \times 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 acetatehexane); Rf: 0.34 (3:1, EtOAc /Hexane); IR (KBr) 3330 (br), 1728, 1250, 1235 cm⁻¹; ¹H NMR (CDCl₃, 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 = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 4.09 (m, 2H), 5.77 (m, 4H), 6.31 (dd, J = 5.4, 10.8 Hz, 2H), 5.77 (m, 4H), 5.77 (m, 5H), 5.77 (3.0, 4.2 Hz, 2H); ¹³C NMR (CDCl₃, 75.43 MHz) & 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+-H₂O, 16), 294 (M+-2HOAc, 100), 276 (98), 227 (68), 209 (24); HRMS calad for C24H30O6 (M+) 414.2047, Found: 414.2043. Anal. Calcd for C24H30O6: C. 69.54; H, 7.30. Found: C, 69.23; H, 7.32.

$(1\alpha, 2\alpha, 3\alpha, 4\alpha, 5\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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% HCI (50 mL x 3), saturated NaHCO₃ (50 mL x 2) and brine (50 mL). The organic phase was dried (MgSO₄), 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 (Et₂O/Hexane); R_f: 0.42 (1:9, EtOAc /Hexane); IR (KBr) 3030, 1724, 1245, 1035, 715 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₄H₂₆O₄ (M⁺) 378.1843, Found: 378.1832. Anal. Calcd for C₂₄H₂₆O₄: C, 76.16; H, 6.92. Found: C, 76.17; H, 6.83.

$(1\alpha,2\alpha,3\alpha,4\alpha,5\alpha,6\alpha,7\alpha,8\alpha)$ -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 LiAlH₄ (0.54 g, 14.21 mmol) in anhydrous THF (100 mL) was slowly added under an atmosphere of N2 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 guenched by sequential addition of H₂O (0.5 mL), 15% agueous NaOH (0.5 mL), After the mixture was stirred for 1 h, the milky solution was filtered, and the and H₂O (1.5 mL). solids was washed with THF (30 mL). The combined organic layers were dried over MgSO4 and The solid was purified by chromatography (silica gel, 30% EtOAc/Hexane as concentrated. eluent) to give diol 24 (1.78 g, 93%) as a white solids: mp 179-180 °C (methanol/benzene); Rf: 0.34 (2:1, EtOAc /Hexane); IR (KBr) 3240 (br), 1475, 1065, 1030, 750, 700 cm⁻¹; ¹H NMR (pyridined₅, 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); ¹³C NMR (pyridine-d₅, 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+-H₂O, 14), 246 (32), 128 (100); HRMS calad for C₂₀H₂₂O₂ (M⁺) 294.1620, Found: 294.1616. Anal. Calcd for C₂₀H₂₂O₂: C, 81.60; H, 7.53. Found: C, 81.34; H, 7.50.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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 N₂. 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% HCI (30 mL), water (60 mL), brine(60 mL), and dried over anhydrous MgSO₄. 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 N₂ 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 MgSO₄. 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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₀H₁₈ (M⁺) 258.1398, Found: 258.1409. Anal. Calcd for C₂₀H₁₈: C, 92.98; H, 7.02. Found: C, 92.93; H, 7.09.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha, 11\beta, 12\alpha)$ -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 N₂. 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% CH₂Cl₂/hexane as eluent) gave the cycloadduct **25** as a white solid (0.44 g, 48%): mp 147-148 °C (CH₂Cl₂/Hexane); R_f: 0.27 (3:1. CH₂Cl₂/Hexane); IR (KBr) 3048, 2935, 1608, 1585, 1469, 1446, 1304, 1142, 1080, 694 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₃₄H₃₀S₂O₄ (M⁺-C₆H₅SO₂) 424.1500, Found: 424.1498. Anal. Calcd for C₃₄H₃₀S₂O₄ · 0.5 CH₂Cl₂: C, 68.02; H, 5.13. Found: C, 67.94; H, 5.14.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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 N₂ 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 MgSO₄. 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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₂H₂₀ (M⁺) 284.1566, Found: 284.1566. Anal. Calcd for C₂₂H₂₀: C, 92.91; H, 7.09. Found: C, 92.89; H, 6.83.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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-5,6dicyanoquinone (0.12 g, 0.53 mmol) in dry benzene (20 mL) was refluxed under N₂ 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 Et₂O and hexane was added dropwise till the appearance of turbidness. Drop(s) of dry Et₂O 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/Et₂O as colorless crystallines: mp 204-205 °C; Rf: 0.42 (hexane); IR (KBr) 3062, 1466, 1360, 741, 695 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₂H₁₈ (M+) Anal. Calcd for C₂₂H₁₈: C, 93.58; H, 6.42. Found: C, 93.42; H, 6.42. 282.1409, Found: 282.1409.

5,6-Benzo-11,12-di(hydroxymethyl)hexacyclo[8.3.1.0^{2,7}.0^{3,14}.0^{4,9}.0^{8,13}]tetradec-5ene (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 N₂ 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 (C₅D₅N, 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); ¹³C NMR (C₅D₅N, 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⁺-H₂O, 20), 246 (M⁺, 17), 179 (14), 167 (13), 155 (13), 128 (100); HRMS calad for C₂₀H₂₂O₂ (M⁺) 294.1602, Found 294.1613. Anal. Calcd for C₂₀H₂₂O₂: 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 MgSO₄, and then concentrated to leave a white residue. Chromatography (silica gel, hexane as eluent) gave **29** (0.11 g, 46%): mp 145-146 °C (Et₂O/hexane); R_f: 0.63 (hexane); IR (KBr) 3075, 2955, 1601, 1485, 1315, 1246 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₀H₁₈ (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 \times 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 (CDCl₃) δ 1.94 (s, 2H), 2.66 (s, 4H), 3.27 (s, 4H), 3.91 (s, 12H), 7.63 (s, 4H); ¹³C NMR (CDCl₃, 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 C₃₀H₂₆O₈ (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 N₂ 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 (CDCl₃, 300 MHz) δ 1.95 (s, 2H), 2.62 (s, 4H), 3.17 (s, 4H), 7.20~7.28 (m, 8H); ¹³C NMR (CDCl₃, 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 C₂₂H₁₈ (M⁺) 282.1395, Found: 282.1408. Anal. Calcd for C₂₂H₁₈: C, 93.58; H, 6.42. Found: C, 93.38; H, 6.47.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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/cm² pressurizationdepressurization cycles of hydrogen. The reactor was then pressurized to 6 Kg/cm² 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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₂H₂₂ (M⁺) 286.1723, Found: 286.1729. Anal. Calcd for C₂₂H₂₂: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.81.

$(1\alpha, 2\alpha, 3\alpha, 6\alpha, 7\alpha, 8\alpha)$ -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 (MgSO₄), 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 oC (dec.) (CH₂Cl₂-hexane); R_f: 0.74 (EtOAc); IR (KBr) 3026, 2925, 1478, 1461, 1323, 1183, 946, 825, 734, 612, 528 cm⁻¹; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C22H18O2 (M+) 314.1300; Found: 314.1307. Anal. Calcd for C22H18O2: 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-dlbromo-5:6,11:12-bisbenzopentacyclo[8.4.0.0^{2,7}.0^{4,9}.0^{8,13}]-tetrade-ca-5,11-diene (35b) (137 mg, 62%) as a white solid. An analytical sample was obtained by recrystallization from CH₂Cl₂-Et₂O: mp 170-171 °C; R_f: 0.31 (1:4, CH₂Cl₂/hexane); IR (KBr) 3020, 2961, 1476, 1236, 749 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) \delta 1.58 (m, 2H), 2.62 (m, 1H), 2.76 (m, 1H), 3.39 (d, <i>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); ¹³C NMR (CDCl₃, 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 C₂₂H₁₈Br₂: 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, CH₂Cl₂/ hexane); IR (KBr) 3032, 2952, 1478, 1460, 1224,754, 686 537, 472 cm^{-1; 1}H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₂H₁₈Br₂ (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, CH₂Cl₂/hexane); IR (KBr) 3020, 2926, 1483, 1462, 1072, 1049 744 cm⁻¹: ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₂H₁₈O (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 $^{\circ}C \pm 3 \,^{\circ}C$ for 12h (or 250 $^{\circ}C$ for 3h). After cooling to 0 $^{\circ}C$, the glass tube was opened and the reaction mixture was then dissolved in CDCl₃. 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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 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) Å³, empirical formula: $C_{22}H_{18}$. Cell dimensions were obtained from 14 reflections with 20 angle in the range $8.36^{\circ} - 28.11^{\circ}$. Crystal dimensions: $0.80 \times 0.78 \times 10^{\circ}$

0.54 mm, Fw = 282.4, Z = 4, F(000) = 600, D_{calc} = 1.287 g/cm³, $\lambda = 0.71073$ Å, 20 (max) = 50.0°. The intensity data were collected on a Siemens R3m/V diffractometer using the θ /2 θ 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 I₀ > 3.0 σ (I₀). 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) Å³, empirical formula: $C_{44}H_{36}Br_4$ (two molecules of **35b**). Cell dimensions were obtained from 18 reflections with 20 angle in the range $11.06^{\circ} - 23.81^{\circ}$. 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/cm³, $\lambda = 0.71073$ Å, 20 (max) = 50.0°. The intensity data were collected on a Siemens R3m/V diffractometer using the 0/20 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 $I_0 > 3.0 \sigma$ (I_0). 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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REFERENCES

- (1α, 2α, 3α, 6α, 7α, 8α)-4, 5:9,10-bisbenzotetracyclo[6. 2. 2. 2^{3, 6}. 0^{2, 7}]tetradeca-4, 9, 11,13tetraene.
- 2. (a) Goldstein, M. J.; Hoffmann, R. J. Am. Chem. Soc. 1971, 93, 6193.
- (a) Gleiter, R.; Schäfer, W. Acc. Chem. Res. 1990, 23, 369. (b) Paddon-Row, M. N.; Jordan, K. D. In Modern Models of Bonding and Delocalization; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; Chapter 3; pp 115-194. (c) Klein, G.; Paquette, L. A. Tetrahedron Lett. 1976, 2419.
- 4. Hoffmann, R. Acc. Chem. Res. 1971, 4, 1.
- (a) Allred, E. L.; Hinshaw, J. C. *Tetrahedron Lett.* **1968**, 1293. (b) Allred, E. L.; Lyon, G. D.; Stroebel, G. *J. Am. Chem. Soc.* **1979**, *101*, 3415.

- (a) Martin, H.-D.; Schwesinger, R. *Chem. Ber.* 1974, *107*, 3143. (b) Prinzbach, H.;
 Sedelmeier, G.; Martin, H.-D. *Angew. Chem. Int. Ed. Engl.* 1977, *16*, 103. (c) Martin, H.-D.
 Mayer, B. *ibid.* 1983, *22*, 283.
- (a) Jones II, G.; Becker, W. G.; Chiang, S. H. *J. Am. Chem. Soc.* 1983, *105*, 1269.
 (b) Smith, E. C.; Barborak, J. C. *J. Org. Chem.* 1976, *41*, 1433.
 (c) Marchand, A. P.; Chou, T.-C.; Ekstrand, J. D.; van der Helm, D. *ibid.* 1976, *41*, 1438.
 (d) Eaton, P. E.; Cassar, L.; Hudson, R. A.; Hwang, D. R. *ibid.* 1976, *41*, 1445.
 (e) Metha, G.; Padma, S.; Ösawa, E.; Barbiric, D. A.; Mochizuki, Y. *Tetrahedron Lett.* 1987, *28*, 1295.
 (f) Ösawa, E.; Aigami, K.; Inamoto, Y. *J. Org. Chem.* 1977, *42*, 2621.
- Soloway, S. B.; Damiana, A. M.; Sim, J. W.; Bluestone, H.; Lidov, R. E. J. Am. Chem. Soc. 1960, 82, 5377.
- Lee, C.-H.; Liang, S.; Haumann, T.; Boese, R.; de Meijere, A. Angew. Chem. Int. Ed. Engl. 1993, 32, 559.
- 10. Underwood, G. R.; Ramamoorthy, B. Tetrahedron Lett. 1970, 4125.
- (a) Sasaki, T.; Kanematsu, K.; Kondo, A. *J. Org. Chem.* **1974**, *39*, 2246. (b) Sasaki, T.; Kanematsu, K.; Kondo, A. *Tetrahedron* **1975**, *31*, 2215. (c) Sasaki, T.; Kanematsu, K.; Kondo, A. *J. Chem. Soc. Perkin I* **1976**, 2516.
- 12. LeGoff, E.; Oka, S. J. Am. Chem. Soc. 1969, 91, 5665.
- (a) Chou, T.-C.; Jiang, T.-S.; Hwang, J.-T.; Lin, C.-T. *Tetrahedron Lett.* **1994**, *35*, 4165. (b)
 Lin, C.-T.; Hwang, B.-P.; Chou, T.-C. *J. Chin. Chem. Soc.* **1993**, *40*, 159. (c) Chou, T.-C.;
 Hong, P.-C.; Lin, C.-T. *Tetrahedron Lett.* **1991**, *32*, 6351. (d) Lin, C.-T.; Chou, T.-C. *J. Org. Chem.* **1990**, *55*, 2252.
- 14. Chou, T.-C.; Chiou, J.-H. J. Chin. Chem. Soc. 1986, 33, 227.
- 15. *cis*-Dihydronaphthalene is not easy to make and would not survive long enough to be synthetically useful at a temperature above 90 °C at which most Diels-Alder reactions are performed. Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 2579.
- 16. Paquett, L. A.; Dunkin, I. R. J. Am. Chem. Soc. 1975, 97, 2243.
- 17. Schmid, G. H.; Rabai, J. Synthesis 1988, 332.
- Compound 9 is a formal Diels-Alder adduct of benzene and naphthalene. It was made from the corresponding iron tricarbonyl-diene complex by oxidation with ceric ammonium nitrate at -20 °C, but rapidly decomposed into its components at 0 °C. Grimme, W.; Köser, H. G. Angew. Chem. Int. Ed. Engl. 1980, 19, 307.
- (a) Vogel, P. In Stereochemistry and Reactivity of Systems Containing π Electrons, Watson,
 W. H., Ed., Verlag Chemie International: Deerfield Beach, FL, 1983; pp 147-194. (b) Vogel,
 P. In Advances in Theoretically Interresting Molecules, Thummel, R. P., Ed., JAI Press Inc.;
 London, 1989; pp 201-357.
- (a) For review see: Cossu, S.; De Lucchi, O.; Fabbri, D.; Licini, G.; Pasquato, L. Organic Prep.& Proc. 1991, 23, 571. (b) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. J. Org. Chem. 1984, 49, 596.
- 21. Chou, T.-C.; Chuang, K.-S.; Lin, C.-T. J. Org. Chem. 1988, 53, 5168.
- 22. Azzena, U.; Cossu, S.; De Lucchhi, O.; Melloni, G. Synth. Comm. 1988, 18, 351.

- 23. Corey, E. J.; Ravindranathan, T.; Terashima, S. J. Am. Chem. Soc. 1971, 93, 4326.
- (a) Patney, H. K. J. Org. Chem. 1988, 53, 6106. (b) Chenier, P. J.; Stevens, B. J. Synth. Comm. 1988, 18, 1947.
- 25. The crystal packing in **6** has indicated that the structural deformation of **6** is not caused by intermolecular short contacts.
- (a) All calculations were performed on a Micro VAX II based Nicolet SHELXTL PLUS system. (b) ORTEP, Johnson, C.K., **1976**, developed, Oak Ridge National Laboratory, Tennessee, USA.
- 27. Melder, J. P.; Wahl, F.; Fritz, H.; Prinzbach, H. Chimia. 1987, 41, 426.
- The ring current of the fused benzene ring in benzobicyclo[2.2.2]octenes is known to shield syn (or exo in 33) protons and to deshield the corresponding anti (or endo in 33) protons. Tori, K.; Hata, Y.; Muneyuki, R.; Takano, Y.; Tsuji, T.; Tanida, H. Canad. J. Chem. 1964, 42, 926.
- (a) Marchand, A. P. Stereochemical Application of NMR Studies in Rigid Bicyclic Systems; Verlag Chemie International: Deerfield Beach, FL, 1982; pp 15-19. (b) Chou, T.-C.; Yang, M.-S.; Lin, C.-T. J. Org. Chem. 1994, 59, 661.
- 30. Ohwada, T.; Okamoto, I.; Haga, N.; Shudo, K. J. Org. Chem. **1994**, *59*, 3975.
- NMR Studies of epoxides of benzobicyclo[2.2.2]octenes: Tori, K.; Kitahonoki, K.; Takano,
 Y.; Tanida, H.; Tsuji, T. *Tetrahedron Lett.* **1964**, 559.
- 32. Ösawa, E.; Aigami, K.; Inamoto, Y. Tetrahedron 1978, 34, 509.
- Molecular mechanics calculation was carried out by using SYBYL force field^a within SPARTAN package^b. a. Clark, M; Cramer III, R.D.; and van Opensch, N. *J. Computational Chem.* **1989**, *10*, 982. b. Wavefunction, Inc., Irvine, CA 92715, USA.
- 34. The diference in calculated strain energies using MM3 force field amounts to only 1.28 kcal/mol with *N*-type skeleton being more stable.

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