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Dibenzo[18]annulenes Incorporating Two Diphenylhexatriene Units

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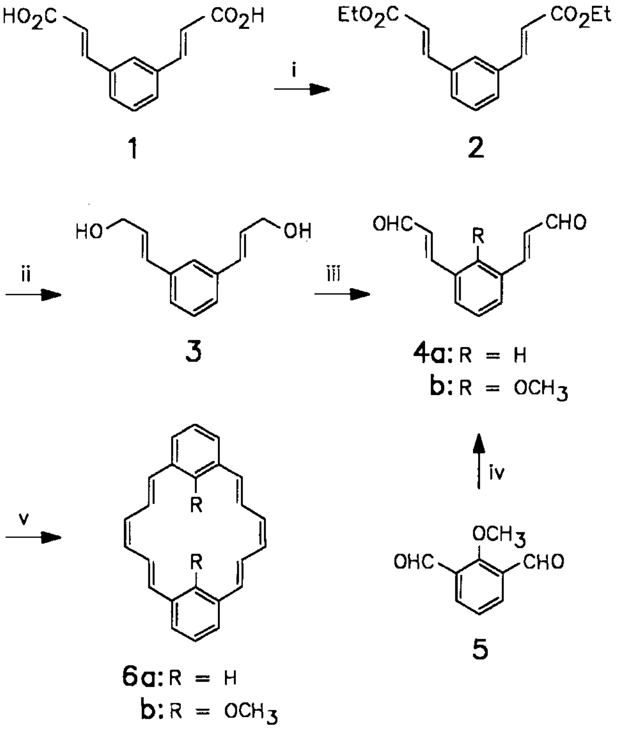
Received January 27, 1994

Key Words: Annulenes / Chromophores / Hexatrienes / Hydrocarbons / Macrocyclic compounds

The [6.6]cyclophanehexaene hydrocarbon **6a** and the dimethoxy[6.6]cyclophanehexaene **6b** are prepared starting with the unsaturated diacid **1**. An X-ray analysis of **6a** exhibits a planar molecular skeleton. NMR and optical data prove a not fully conjugated macrocyclic π system and its division into two largely separate chromophores.

Noncyclic and cyclic polyenes have been the subject of intensive research in organic chemistry during the past years[1]. 1,6-Diphenyl-1,3,5-hexatriene (DPH), for example, is a commonly used fluorescence indicator in investigations concerning the arrangement of molecules in vesicle and cell membranes, in liquid crystal phases, and in polymer films. Studies directed to the development of new organic materials with specific porperties by incorporating classical structural building blocks (like DPH) into macrocyclic systems[2] led us to the preparation of [6.6](1,3)cyclophane-1,3,5,13,15,17-hexaene (**6a**) and its dimethoxy derivative **6b** (Scheme 1).

Scheme 1. Reagents and conditions: i, ethanol, H_2SO_4 (96%); ii, $LiAlH_4$/aluminium chloride (3:1), tetrahydrofuran, room temp. (68%); iii, oxalyl chloride, dimethyl sulfoxide, triethylamine, dichloromethane, −60°C (95%); iv, 1. (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide, lithium methanolate, dimethylformamide, 90°C, 2. 10% HCl, tetrahydrofuran, room temp., chromatography (49%); v, $TiCl_4$, Zn, 1,4-dioxane, reflux, filter column chromatography (yields 11 and 18%, resp.)



1. Preparation and NMR Results

For the synthesis of **6a** (Scheme 1) **1**[3] was treated with ethanol and H_2SO_4 whereby the propenoic ethyl ester **2** was obtained in 96% yield. The β-aryl α,β-unsaturated ester **2** was reduced with $LiAlH_4$/aluminium chloride (3:1) in dry tetrahydrofuran at room temperature and gave **3** (68% yield after kugelrohr distillation to separate **3** from the saturated compounds). Subsequent oxidation with dimethyl sulfoxide, oxalyl chloride, and triethylamine in anhydrous dichloromethane at −60°C furnished **4a** in 95% yield. 2-Methoxyisophthalaldehyde (**5**) served as starting material for the synthesis of **6b**. In contrast to the preparation of **5** reported in ref.[4], this compound was easily available in 94% yield by oxidation of 2,6-bis(hydroxymethyl)anisol with activated dimethyl sulfoxide. Contrary to the preparation of **4a**, the vinylogous dialdehyde **4b** can be prepared by treatment of **5** with 3 equiv. of (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide and a base followed by hydrolysis with diluted HCl in 49% yield (after separation from the monovinylogous dialdehyde by column chromatography). The bispropenals **4a** and **4b** were cyclodimerized in one step by carbonyl coupling using low-valent titanium[5]. In this reaction **4a/b** were given to a suspension of $TiCl_4$ and zinc in refluxing 1,4-dioxane under moderate dilution conditions, and the desired macrocycles **6a** and **6b** were obtained as single nonpolymeric compounds in 11 and 18% yields, respectively, after separation by filter column chromatography. Recrystallization from trichloromethane yielded yellow crystals of **6a** which carbonized above 350°C. The **IR** spectrum shows only two strong bands with significant absorptions for double bonds and aromatic rings. Remarkable in the ^{1}H-NMR spectrum are the downfield shifts of the olefinic (CH-8,11a; δ = 7.93, for numbering see Figure 1) and aromatic (CH-1; δ = 8.37) protons oriented to the centre of the molecule as has also been observed for hexa-*m*-phenylene[6a] and kekulene[6b]. This significant chemical shift shows that the *meta*-connected benzene rings suppress a macrocyclic (annulenoid) conjugation in favor of benzoid aromaticity. The coupling constants of the olefinic protons are consistent with an *E,Z,E* configuration. The ^{13}C-NMR spectrum shows as expected only seven signals. Compound **6b** also carbonizes above 350°C and shows only one strong band in the IR spectrum with significant absorption for the methoxy groups. In contrast to the NMR spectra of **6a**, the methoxy-substituted **6b** shows paired signals. The olefinic protons oriented to the centre of the molecule appear at δ = 8.40 and 8.73 and exhibit larger downfield shifts compared to **6a** and hexa-*m*-phenylene[6a]. The coupling constants for the olefinic protons also prove the *E,Z,E* configuration; in the ^{13}C-NMR spectrum eight signal pairs appear. This doubling of signals is due to additional steric effects in the hydrocarbon framework caused by introduction of methoxy groups, resulting in the disapperarance of the symmetry centre of the molecule[7] (see below).

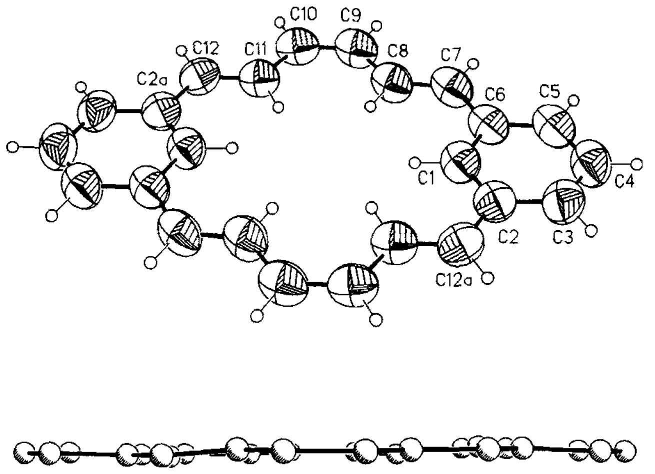


Figure 1. Above: Crystal structure of **6a**. Selected distances [pm] and angles [°]: C(1)–C(2) 138.3(3), C(2)–C(3) 139.9(3), C(3)–C(4) 137.2(4), C(6)–C(7) 146.1(4), C(7)–C(8) 133.6(4), C(8)–C(9) 143.2(4), C(9)–C(10) 134.7(4), C(10)–C(11) 145.9(3), C(11)–C(12) 133.3(3), C(12)–C(2a) 145.9(3); C(1)–C(6)–C(7) 121.5(2), C(6)–C(7)–C(8) 124.8(2), C(7)–C(8)–C(9) 128.6(2), C(8)–C(9)–C(10) 123.9(2), C(9)–C(10)–C(11) 125.0(2), C(10)–C(11)–C(12) 129.4(2), C(11)–C(12)–C(2a) 125.1(2). Below: Side-view of hydrocarbon **6a**

2. X-Ray Structure Analysis of Dibenzoannulene 6a

The geometry of **6a** was established by a single-crystal X-ray structural analysis[8] (Figure 1). As expected from the simplicity of the NMR spectra the X-ray analysis exhibits a planar macrocyclic skeleton with an inversion centre. The conjugated double bond systems of the two bridges are each *E,Z,E* configurated. The single bond lengths decrease from C(6)–C(7) to C(8)–C(9), the double bond lengths increase from C(7)–C(8) to C(9)–C(10) as expected in conjugated systems. Compared to the ideal sp^2 bond angle of 120° expanded angles up to 129.4° are found. Compound **6a** may be regarded as a dibenzo[18]annulene and for that reason these angles are increased by intramolecular repulsion and are, therefore, similarly strained as in [18]annulene (128.1°)[9]. The macrocycle **6a** contains two diphenylhexatriene units in which the double bonds are 1*E*,3*Z*,5*E*-configurated, and the free rotation of the benzene rings is suppressed. The diarylhexatriene **6a** allows the consequences of configurational and conformational fixation of the chromophore on the electronic excitation to be investigated by UV/Vis spectroscopy.

3. Optical Properties of Hexatrienes 6a and 6b

In contrast to (3*Z*)-DPH the longest wavelength absorption maximum of **6a** exhibits solely a hint of fine structures (Figure 2). It is located at 332 nm (in CH_2Cl_2) and as compared with the noncyclic and pronouncedly fine-structured (3*Z*)-DPH (350 nm in hexane)[10] it shows a hypsochromic shift of 18 nm. This shift to shorter wavelengths is due to the increase of the bond angles, causing a reduction of the conjugation. The expected hypsochromic shift of the longest wavelength absorption maximum of the methoxy-substituted **6b** is compensated by the additional chromophores of the methoxy groups (**6b**: 334 nm in CH_2Cl_2). The absence of an absorption band at even longer wavelengths in the UV/Vis spectrum of **6a/b** confirms the assumption that the macrocycle contains two isolated diphenylhexatriene systems instead of a single chromophore extending over the whole ring[11]. A further proof for a division of the molecule into two separate chromophores is the absorption band at 270 nm. From a theoretical viewpoint this is due to the absence of a symmetry centre[12] and has proven to be characteristic of the presence of a (*Z*)-double bond within a polyene chain. This "*cis*-peak" of the macrocycle **6a** is striking by the sole fact of its occurrence, since **6a** shows an inversion centre in the X-ray structure. As expected from the NMR spectra **6b** shows an intensive "*cis*-peak" and a moderately intense longest wavelength absorption maximum, due to deviation from the central symmetry. Whereas the emission maximum of (*E,Z,E*)-DPH is located at 450 nm (in *n*-heptane)[13], a pronounced bathochromic shift of 40 nm characterizes the transition to the macrocycle **6a** (490 nm in CH_2Cl_2), and in the case of **6b** (385 nm in CH_2Cl_2) a distinct hypsochromic shift of 65 nm is observed. The difference between absorption and emission maxima is significantly larger in hydrocarbon **6a** than in the methoxy analog **6b**.

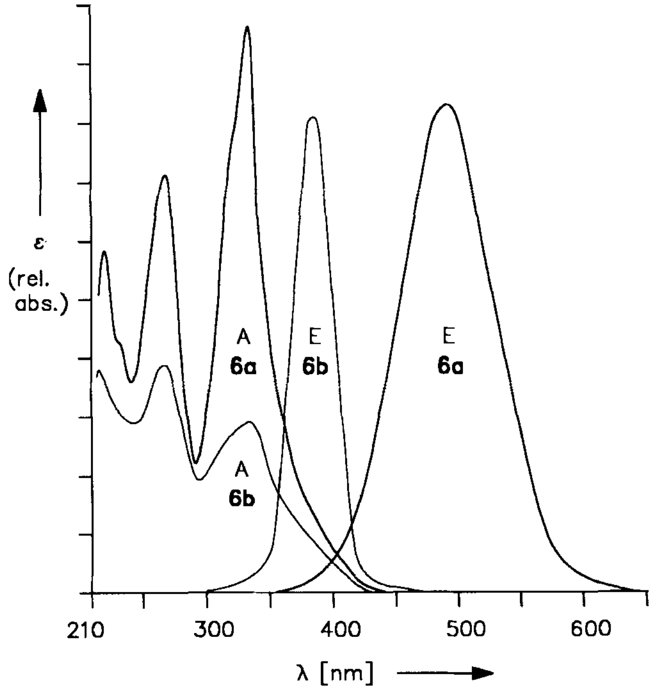


Figure 2. Electronic absorption (A) and emission (E) spectra (in CH_2Cl_2, T = 293 K, excitation at 390 and 385 nm) of hydrocarbon **6a** and **6b**. ε in relative units

Experimental

Melting points: Kofler-Mikroskop-Heiztisch, uncorrected. – ^{1}H and ^{13}C NMR: Bruker WM-250 (250 MHz/62.9 MHz), AC-200 (200 MHz/50.3 MHz), AC-400 (400 MHz/100.6 MHz). – MS: A.E.I. MS-50 (70 eV). – UV/Vis: J 720 JASCO International Co., LTD. – Column chromatography: Merck silica gel 60 (40–63 μm). – TLC: Merck silica gel plates 60 F$_{254}$. – IR: Pye Unicam, SP-1100. – On account of the nonstoichiometric adhesion of solvent molecules and the high proportion of carbon atoms in the [18]annulenes the elemental analyses are not in accordance with the hydrocarbon formulae and therefore are not mentioned. – Organic solvents were purified by standard procedures.

Diethyl 1,3-Benzenebispropenoate (**2**): 13.0 g (59 mmol) of **1**[3], 40 g (8.6 mol) of dry ethanol, and 4.9 g (54 mmol) of concd. H$_2$SO$_4$ were heated at reflux for 4 h, and after the removal of ethanol under reduced pressure the residue was suspended in water, and the reaction was carefully quenched with K$_2$CO$_3$. The aqueous solution was extracted with CH$_2$Cl$_2$. The organic phase was washed with a satd. aqueous NaCl solution, dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure. Yield of **2** 15.7 g (96%), m.p. 49°C. – ^{1}H NMR (250 MHz, CDCl$_3$, *J* values in Hz): δ 1.33 (t, ^3J 7.1, 6H, CH$_3$), 4.26 (q, ^3J 7.1, 4H, CH$_2$), 6.44 (d, ^3J 16.1, 2H, H$_{olefin}$), 7.38 (dd, ^3J 6.7, ^3J 6.7, 1H, H$_{arom}$), 7.51 (d, ^3J 7.1, 2H, H$_{arom}$), 7.62 (s, 1H, H$_{arom}$), 7.66 (d, ^3J 16.1, 2H, H$_{olefin}$). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 14.26 (CH$_3$), 60.56 (CH$_2$), 119.25 (CH$_{olefin}$), 127.55 (CH$_{arom}$), 129.37 (2 CH$_{arom}$), 135.13 (Cq$_{arom}$), 143.56 (CH$_{olefin}$), 166.62 (CO$_2$R). – MS, *m/z* (%): 274 [M$^+$] (75), 245 [M$^+$ – C$_2$H$_5$] (100), 229 [M$^+$ – C$_2$H$_5$O] (40), 199 [245 – C$_2$H$_6$O] (50), 183 (25), 155 (20). – IR (KBr): $\tilde{\nu}_{max}$ = 2986 cm^{-1} w, 1722 s (C=O), 1636 s (C=C), 1175 vs (C–O), 1033 m, 985 m, 855 w, 791 m. – C$_{16}$H$_{18}$O$_4$: calcd. 274.1200, found 274.1210 (MS).

1,3-Benzenebis-2-propenol (**3**): 11.78 g (88 mmol) of aluminium chloride was added carefully in small portions with stirring under Ar to a cooled suspension of 10.3 g (271 mmol) of LiAlH$_4$ in 250 ml of dry THF. After warming to room temp. a solution of 10.0 g (36 mmol) of **2** in 100 ml of dry THF was added dropwise within 45 min, and the reaction was allowed to proceed at room temp. for 30 min. The mixture was then hydrolyzed with 100 ml of wet THF, 100 ml of water, and 100 ml of dilute H$_2$SO$_4$. The solvent was evaporated under reduced pressure, and the aqueous phase was extracted during 1 d with CH$_2$Cl$_2$. The organic phase was washed with water, dried with Na$_2$SO$_4$ and the solvent removed. Kugelrohr distillation at 250°C/1.33322 Pa yielded 4.7 g (68%) of a white solid, m.p. 56–58°C, b.p. 250°C/1.33322 Pa. – ^{1}H NMR (200 MHz, CDCl$_3$, *J* values in Hz): δ 2.54 (s, 2H, OH), 4.27 (d, ^3J 6.7, 4H, CH$_2$), 6.31 (m, 3H, H$_{arom}$), 6.54 (d, ^3J 16, 2H, H$_{olefin}$), 7.23 (s, 1H, H$_{arom}$), 7.26 (d, ^3J 16, 2H, H$_{olefin}$). – ^{13}C NMR (62.9 MHz, [D$_6$]acetone): δ 63.79 (CH$_2$), 125.83 (CH$_{arom}$), 126.57 (CH$_{olefin}$), 130.22, 130.53 (CH$_{arom}$), 131.75 (CH$_{olefin}$), 139.02 (Cq$_{arom}$). – MS, *m/z* (%): 190 [M$^+$] (93), 143 (30), 128 [M$^+$ – CH$_3$O] (90), 117 (100), 115 (70), 105 (40), 91 (50). – IR (KBr): $\tilde{\nu}_{max}$ = 3370 cm^{-1} s (OH), 1441 m, 1100 m, 1110 s, 966 vs, 766 m. – C$_{12}$H$_{14}$O$_2$: calcd. 190.0990, found 190.0995 (MS).

1,3-Benzenebispropenal (**4a**): To a cooled (–60°C) solution of 3.36 g (26 mmol) of oxalyl chloride in 25 ml of dry CH$_2$Cl$_2$ was added a solution of 4.14 g (53 mmol) of DMSO in 10 ml of CH$_2$Cl$_2$ with stirring under Ar. The reaction mixture was stirred for 30 min, then a solution of 2.19 g (11.5 mmol) of **3** dissolved in 25 ml of CH$_2$Cl$_2$ and 5 ml of DMSO was added at –40°C within 45 min; stirring was continued for an additional 1 h. Subsequently 14.56 g (1.44 mol) of triethylamine was added, and the reaction mixture was stirred for 5 min and then allowed to warm to room temp. Then 150 ml of water was added, and the aqueous layer was reextracted with additional CH$_2$Cl$_2$. The combined organic layers were washed successively with dilute HCl, water, a satd. aqueous NaHCO$_3$ solution, water, and a satd. aqueous NaCl solution, then dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure to yield 2.00 g (94%) of **4a** as a yellow solid, m.p. 112–115°C. – ^{1}H NMR (200 MHz, CDCl$_3$, *J* values in Hz): δ 6.75 (dd, ^3J 16, ^3J 6.7, 2H, H$_{olefin}$), 7.5 (d, ^3J 16, 2H, H$_{olefin}$), 7.6 (m, 4H, H$_{arom}$), 9.73 (d, ^3J 6.7, 2H, CHO). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 128.53, 129.67, 130.01 (CH$_{arom}$), 130.61 (CH$_{olefin}$), 135.06 (Cq$_{arom}$), 151.21 (CH$_{olefin}$), 193.39 (CHO). – MS, *m/z* (%): 186 [M$^+$] (85), 169 [M$^+$ – OH] (20), 157 [M$^+$ – CHO] (100), 128 [M$^+$ – 2 CHO] (80), 115 (50), 77 (70). – IR (KBr): $\tilde{\nu}_{max}$ = 2126 cm^{-1} w, 1663 vs (C=O), 1620 m (C=C), 1124 s, 975 m, 786 w, 684 w. – C$_{12}$H$_{10}$O$_2$: calcd. 186.0678, found 186.0678 (MS).

2-Methoxy-1,3-benzenebispropenal (**4b**): A lithium methoxide solution prepared from 0.42 g (60 mmol) of lithium in 100 ml of dry methanol was added dropwise during 3 h under Ar to a stirred solution of 3.29 g (20 mmol) of **5** and 25.76 g (60 mmol) of (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide in 150 ml of dry DMF at 90°C. After stirring of the solution for a further 5 h at 90°C it was cooled to room temp., poured into water and the mixture extracted several times with ether. The combined extracts were washed with a satd. aqueous NaCl solution and dried with Na$_2$SO$_4$. After removal of the solvent the residue was dissolved in 70 ml of THF and the solution mixed with 60 ml of 10% hydrochloric acid. The mixture was stirred for 3 h at room temp., then poured into water and extracted several times with CH$_2$Cl$_2$. The combined organic layers were washed with an aqueous NaHCO$_3$ solution, several times with a satd. aqueous NaCl solution, and dried with Na$_2$SO$_4$. The residue obtained after removal of the solvent was chromatographed on silica gel (eluent: *n*-hexane/diethyl ether, 1:3, v/v, R_f 0.41) to give 100 mg (2%) of monovinylogous dialdehyde and 2.2 g (49%) of **4b** as a yellow solid, m.p. 159–161°C. – ^{1}H NMR (250 MHz, CDCl$_3$, *J* values in Hz): δ 3.83 (s, 3H, OCH$_3$), 6.78 (dd, ^3J 16.1, ^3J 7.8, 2H, H$_{olefin}$), 7.23 (t, ^3J 7.7, 1H, H$_{arom}$), 7.68 (d, ^3J 7.7, 2H, H$_{arom}$), 7.78 (d, ^3J 16.1, 2H, H$_{olefin}$), 9.77 (d, ^3J 7.8, 2H, CHO). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 63.66 (OCH$_3$), 125.32 (CH$_{arom}$) 128.75 (Cq$_{arom}$), 130.56 (CH$_{arom}$), 130.83, 146.01 (CH$_{olefin}$), 158.46 (CqOCH$_3$), 193.75 (CHO). – MS, *m/z* (%): 216 [M$^+$] (30), 185 [M$^+$ – CH$_3$O] (100), 157 [185 – CO] (20), 128 [157 – CHO] (30). – IR (KBr): $\tilde{\nu}_{max}$ = 2925 cm^{-1} w (OCH$_3$), 1672 vs (C=O), 1616 m (C=C), 1123 s (C–O), 968 m, 782 m, 597 m.

[6.6](1,3)Cyclophane-1,3,5,13,15,17-hexaene (**6a**): 6.6 ml (60 mmol) of titanium tetrachloride was added with stirring under Ar to 300 ml of dry 1,4-dioxane to give a yellow suspension. Then 4 ml of pyridine was added, and after stirring for 15 min 7.85 g (120 mmol) of zinc powder was given to the reaction mixture. The resultant at first green then black suspension was refluxed for 2.5 h before slow dropwise addition (during 5 h) of a solution of 1.86 g (10 mmol) of **4a** in 100 ml of dry 1,4-dioxane. The reaction mixture was held at reflux for 1 h and then allowed to cool to room temp. The reaction was quenched by careful addition of 100 ml of a satd. aqueous Na$_2$CO$_3$ solution. The grey suspension was extracted with CH$_2$Cl$_2$ during 2 d. The organic layer was washed with a satd. aqueous NaCl solution, dried with Na$_2$SO$_4$, and the solvent was evaporated. The yellow residue was chromatographed on a column of silica gel (eluent: CH$_2$Cl$_2$, R_f 0.94) to yield the titel compound **6a** as a yellow solid. Recrystallization from CHCl$_3$ yielded 168 mg (11%) of yellow crystals, m.p. >350°C. – ^{1}H NMR (400 MHz, CDCl$_3$, *J* values in Hz): δ 6.38 (d, ^3J 10.5, 4H, HC-9,10a), 6.62 (d, ^3J 15.5, 4H, HC-7,12a), 7.09 (d, ^3J 7.5, 4H, HC-3,5), 7.26 (dd, ^3J

7.5, 2H, HC-4), 7.93 (dd, ^3J 15.5, ^3J 10.5, 4H, HC-8,11a) 8.37 (s, 2H, HC-1). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 118.86, 125.74 (CH_{arom}), 128.06 (CH_{olefin}), 129.23 (CH_{arom}), 129.39 (CH_{olefin}), 130.00 (CH_{olefin}), 137.92 (Cq_{arom}). – MS, *m/z* (%): 308 [M^+] (100). – IR (KBr): $\tilde{\nu}_{max}$ = 953 cm^{-1} vs (C=C–H), 746 s (ar). – UV (CH_2Cl_2): λ_{max} = 332 nm (ε 58110), 270 (43580). – $C_{24}H_{20}$: calcd. 308.1560, found 308.1569 (MS).

12,24-Dimethoxy[6.6](1,3)cyclophane-1,3,5,13,15,17-hexaene (**6b**): The procedure used for the synthesis of **6a** was applied to 2.16 g (10 mmol) of **4b**. The product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/petroleum 40–60°C, 1:4, v/v, R_f 0.36). Yield: 331 mg (18%), m.p. >350°C. – ^{1}H NMR (250 MHz, $CDCl_3$, *J* values in Hz): δ 3.6 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.35 (dd, ^3J 16.0, ^3J 8.7, 4H, CH_{olefin}), 6.41 (dd, ^3J 16.0, ^3J 8.7, 4H, CH_{olefin}), 6.98 (m, 6H, CH_{arom}), 8.40 (dd, ^3J 16.0, ^3J 8.7, 2H, CH_{olefin}), 8.73 (dd, ^3J 16.0, ^3J 8.7, 2H, CH_{olefin}). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 59.23, 60.11 (OCH_3), 123.30, 123.68 (Cq_{arom}), 126.81 (CH_{arom}), 128.67, 129.06, 130.36, 130.71, 132.71, 132.88 (CH_{olefin}), 133.37, 133.45 (CH_{arom}), 157.76, 158.06 ($CqCOH_3$). – MS, *m/z* (%): 368 [M^+] (100), 337 [$M^+ - CH_3O$] (15). – IR (KBr): $\tilde{\nu}_{max}$ = 2925 cm^{-1} vs (OCH_3), 1655 w (C=C), 971 m (C=C–H). – UV (CH_2Cl_2): λ_{max} = 334 nm (ε 17840), 270 (23590). – $C_{26}H_{24}O_2$: calcd. 368.1770, found 368.1778 (MS).

X-Ray Crystal Structure Analysis of **6a**[8]: Crystal data: $C_{24}H_{20}$, $M = 308.4$, monoclinic, space group $P2_1/c$, yellow blocks, dimensions 0.1 × 0.3 × 0.4 mm^3, $a = 10.724(1)$, $b = 4.767(1)$, $c = 16.919(1)$ Å, $\alpha = 90$, $\beta = 90.05(1)$, $\gamma = 90°$, $V = 864.9(1)$ Å^3, $Z = 4$, $d_c = 1.18$ Mg/m^3, $\lambda(\text{Cu-}K_\alpha) = 1.54178$ Å, $F(000) = 328$, $T = 293$ K. In the range $5° < 2\Theta < 120°$ a total of 1279 intensity data were measured on an Enraf-Nonius CAD4 diffractometer (graphite-monochromatized Cu-K_α radiation) by using the ω scan type. Data reduction ($R_{int} = 0.029$) yielded 918 symmetry-independent data with $F > 3\sigma(F)$. The structure was determined by direct methods and refinement (full-matrix least-squares, 111 parameters). Non-hydrogen atoms were refined anisotropically, hydrogen atoms localized by difference electron density determination and refined by using a riding model. $R = 0.051$ [$R_w = 0.055$, $w^{-1} = \sigma^2(F) + 0.0010F^2$]. An extinction correction was applied. The program SHELXTL Plus[14] was used.

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[7] We assume that **6b** adopts to a chiral conformation (NMR time scale), presumably with a slight helical twisting of the triene units.

[8] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58053, the names of the authors, and the journal citation.

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