Synthesis and Photocyclization of Macrocyclic Stilbene Derivatives[☆]

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The stereoselectivity of the formation of macrocyclic stilbenes as well as the regioselectivity of their photocyclization are strongly influenced by the length of the connecting alkanediyl chain. The stereoisomers of the macrocyclic stilbenes and the corresponding diols are identified by chemical and spectroscopic means.

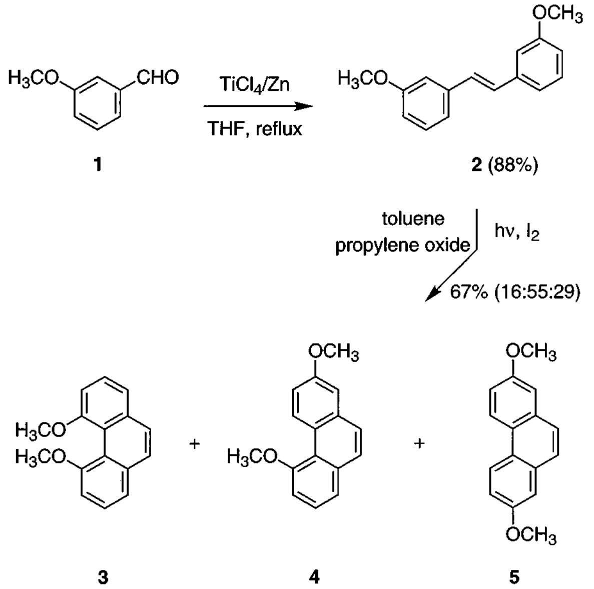
We became interested in the synthesis of macrocyclic stilbene derivatives with a tether between the 3- and 3′-positions in connection with our approach to configurationally stable 1,1′-bis(isoquinolines) as chiral ligands[1]. Simple *trans*-stilbenes are easily obtained by a McMurry reaction[2] with aryl aldehydes, as exemplified by the synthesis of 3,3′-dimethoxystilbene (**2**, Scheme 1). Oxidative photocyclization[3] of **2** leads to the formation of a mixture of the isomeric dimethoxyphenanthrenes **3**, **4** and **5**. Clearly, steric hindrance limits the proportion of the 4,5-disubstituted product **3**[4]: a 16:55:29 ratio is found, rather than the statistically expected ratio of 25:50:25. An electronic influence of the methoxy groups on the regioselectivity is less likely, since the photocyclization of the corresponding 3,3′-dimethylstilbene results in almost the same product ratio[5]. Based on a single example, Castedo and coworkers[6] demonstrated that a short tether connecting the 3- and 3′-positions[7] of the stilbene leads to the exclusive formation of 4,5-substituted phenanthrenes. We have studied the influence of the length of the tether on both the stereoselectivity of the McMurry reaction and on the regioselectivity of the subsequent photocyclization[8].

The starting materials for the intramolecular McMurry reactions, the bis(carbaldehydes) **8** (Scheme 2), were efficiently obtained from 3-hydroxybenzaldehyde (**7**) either by nucleophilic substitution at the bis(tosylate) **9b**[9] or by reaction with the alkanediols **6** under Mitsunobu conditions[10].

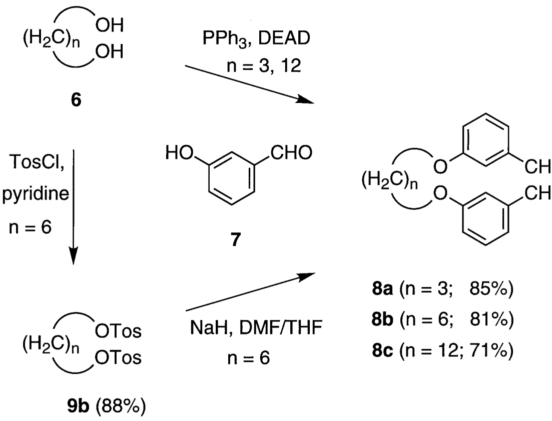
The stereochemical outcome of the intramolecular McMurry reaction is strongly influenced by the length of the tether. In the case of substrate **8a** with the dioxapentanediyl tether, the *cis* isomer of stilbene **11a** is isolated as the main product. Clearly, the rather short tether prevents the formation of the stereoisomer *trans*-**11a**. Instead, the 26-membered macrocycle **10a**, with two *trans*-configured stilbene units, is obtained in low yield as a virtually insoluble by-product.

The dioxaoctanediyl chain of substrate **8b** is sufficiently long to bring about a dramatic change in selectivity: a ratio of 90:10 in favour of the *trans* isomer of **11b** is observed. With the even longer tether of **8c**, the proportion of the *trans* isomer increases to 95%.

Scheme 1. Preparation and photocyclization of 3,3′-dimethoxystilbene (**2**)



Scheme 2. Preparation of bis(carbaldehydes) **8**



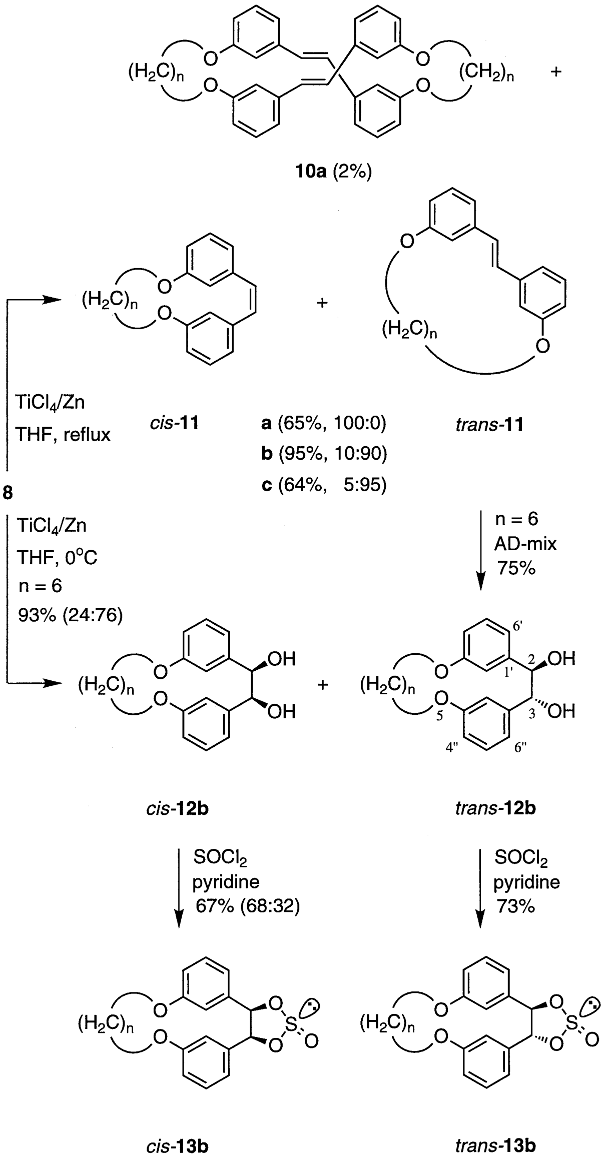
1434−193X/98/0101−0149 $ 17.50+.50/0

The chemoselectivity of the titanium-induced macrocyclization of the bis(carbaldehydes) **8** can be influenced by the reaction temperature[2b]: the McMurry reaction is favoured at reflux temperature in THF. In contrast, at 0 °C a pinacol coupling reaction[11][12] takes place: in the case of the bis(carbaldehyde) **8b** a 1:3 mixture of the macrocyclic *cis*- and *trans*-diols **12b** is obtained in excellent yield. In the ^{1}H-NMR spectra of the C_s-symmetrical *cis*-**12b** and the C_2-symmetrical *trans*-**12b**, the signals of the benzylic hydrogen atoms are seen as singlets at $\delta = 4.95$ and $\delta = 4.42$, respectively. The complex signal of the OCH_2 groups at $\delta = 3.90$ is simplified to an AB signal by homodecoupling experiments. The geminal coupling constant of the diastereotopic hydrogen atoms was determined to be 10.7 Hz for *cis*-**12b** and 10.3 Hz for *trans*-**12b**. Since the NMR spectra, including NOE experiments, did not allow a distinction to be made between the stereoisomers, we proved each configuration by derivatizing the diols **12b** with thionyl chloride. The *cis*-diol, *cis*-**12b**, leads to a mixture of two isomeric cyclic sulfites[13] *cis*-**13b**, one with the free electron pair of the sulfur atom on the same side as the benzylic hydrogen atoms, and the other with the free electron pair on the opposite side. C_s symmetry is maintained and in the ^{1}H-NMR spectrum of the mixture, the benzylic hydrogen atoms give rise to two distinct 1 H singlets at $\delta = 5.83$ and $\delta = 6.14$ in the ratio 32:68. In contrast, upon derivatizing the *trans*-diol, *trans*-**12b**, its C_2 symmetry is lost and the resulting *trans*-fused cyclic sulfite, *trans*-**13b**, consists of a single diastereoisomer, the benzylic hydrogen atoms of which are seen as an AB signal ($\delta_A = 4.89$, $\delta_B = 5.41$, $J = 9.7$ Hz).

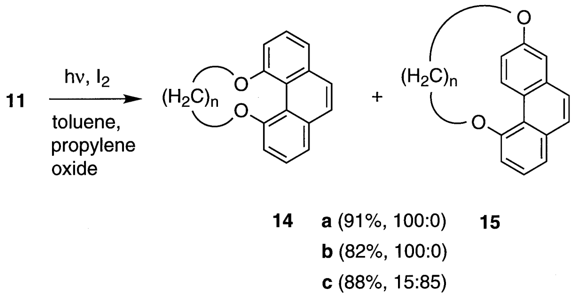
This unequivocal identification of the stereoisomeric diols **12b** is necessary in order to allow the *cis*- and the *trans*-stilbenes **11b** to be distinguished by chemical means. *trans*-**11b** is clearly identified by the transformation to the diol *trans*-**12b** by an osmium-catalyzed *cis*-dihydroxylation with AD-mix-β[14] (an enantiomeric excess of 77% was achieved).

Photocyclization of the macrocyclic stilbene derivatives **11** proceeds in the presence of iodine and affords good to excellent yields (82−91%) of the regioisomeric phenanthrenes **14** and **15** if the concentration of the starting material is kept low (10 mmol/l). Due to the preceeding photochemical equilibrium between the *cis* and *trans* isomers of the stilbenes **11**, a mixture of the stereoisomers can be employed. Depending on the length of the bridging chain, a change in the substitution pattern is observed. With the relatively short tethers of **11a** and **11b**, exclusively 4,5-substituted phenanthrenes **14** are obtained. The dioxatetradecanediyl tether of **11c** permits the formation of the 2,5-substituted phenanthrene **15c** as the main product, easily identified by the diagnostic signal of the bay region proton at $\delta = 9.74$. In principle, the length of this tether should be sufficient even for a (2,7)phenanthrenacyclophane, according to semiempirical calculations and in view of the results of Bodwell et al.[15], who succeeded in synthesizing the corresponding (2,7)pyrenacyclophane with the much shorter dioxaoctanediyl chain. Clearly, the roughly linear conformation of the alkanediyl chain that has to be adopted in the transition state leading to the (2,7)phenanthrenacyclophane is not feasible.

Scheme 3. McMurry reaction and pinacol coupling of **8**; preparation of the dioxathiolanes **13b**



Scheme 4. Photocyclization of stilbenes **11**



In conclusion, we have shown that the stereoselectivity of the formation of macrocyclic stilbenes as well as the regioselectivity of their photocyclization are strongly influenced by the length of the tether. We are currently investigating the efficiently accessible macrocyclic diols **12** as starting materials for syntheses of atropchiral bis(isoquinolines).

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Experimental Section

General: Melting points (uncorrected): Reichert Thermovar. − IR: Perkin-Elmer 983. − UV: Perkin-Elmer 554. − NMR: Bruker DRX 500, Bruker AM 400, Bruker WM 300; ^{1}H-NMR spectra were recorded in $CDCl_3$ with TMS as internal standard. ^{13}C-NMR spectra were measured using $CDCl_3$ as the solvent and the internal standard. − MS: MAT 311A (70 eV); GC-MS coupling: AMD 604 (column: Hewlett Packard 30 m × 0.32 mm × 0.25 µm HP5). − Polarimeter: Perkin-Elmer 241 polarimeter. − HPLC: Merck Hitachi L-6200 Intelligent Pump; Merck Hitachi D-7500 Chromato-Integrator; Merck Hitachi L-4000A UV Detector; Serva CHIRAL DNBPG-C=Si 100 Polyol column. − AD-mix-β[14] was purchased from Aldrich.

The basis for the nomenclature of the macrocycles is the appropriate IUPAC outline: *Phane Nomenclature*, International Union of Pure and Applied Chemistry, Organic Chemistry Division, Commission on Nomenclature of Organic Chemistry (Ed.: E. W. Godley), New Malden, Surrey, U.K., **1993**.

Synthesis of Bis(benzaldehydes) **8a** *and* **8c** *− General Procedure:* 3.66 g (30.0 mmol) of 3-hydroxybenzaldehyde (**7**) and 7.86 g (30.0 mmol) of triphenylphosphane were dissolved in 80 ml of dry THF. 10 mmol of diol **6** followed by 4.2 g (3.8 ml, 24 mmol) of diethyl azodicarboxylate (DEAD) were added and the resulting mixture was stirred at room temp. for 5 h. The solvent was then evaporated in vacuo and the residue was taken up in diethyl ether and washed three times with 50 ml of 15% NaOH. The organic phase was dried by filtration through silica gel and the solvent was evaporated.

3,3'-[1,3-Propanediylbis(oxy)]bis(benzaldehyde) (**8a**)[16]: The crude product obtained from 0.76 g (10 mmol) of **6a** as outlined in the General Procedure was purified by flash chromatography on silica gel [TLC: silica gel, petroleum ether/diethyl ether (1:1), R_f = 0.80, 0.37, 0.03]. The fraction with R_f = 0.37 was dried in vacuo to afford 2.42 g (85%) of **8a**, colourless crystals, m.p. 56−58 °C.

3,3'-[1,12-Dodecanediylbis(oxy)]bis(benzaldehyde) (**8c**): The crude product obtained from 2.02 g (10 mmol) of **6c** as outlined in the General Procedure was purified by flash chromatography on silica gel [TLC: silica gel, petroleum ether/diethyl ether (2:1), R_f = 0.69, 0.35, 0.18, 0.01]. The fraction with R_f = 0.35 was dried in vacuo: 2.91 g (71%) of **8c**, colourless crystals, m.p. 73−74 °C. − IR (KBr): $\tilde{\nu}$ = 3085 cm^{-1} (w), 2943 (m), 2925 (m), 2852 (m), 1680 (s), 1600 (m), 1448 (w), 1395 (m), 1261 (s), 1168 (m), 1144 (m), 1041 (m), 791 (w), 761 (m). − UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.36, sh), 221 (4.67), 252 (4.30), 311 (3.82). − ^{1}H NMR (500 MHz): δ = 1.30−1.36 (m, 12 H), 1.46 ("t", "*J*" = 7.7 Hz, 4 H), 1.80 (m, 4 H), 4.01 (t, *J* = 6.5 Hz, 4 H, O−C*H*$_2$), 7.17 (m, 2 H), 7.38 ("d", "*J*" = 2.2 Hz), 7.42−7.44 (m, 4 H), 9.97 (s, 2 H, C*H*O). − ^{13}C NMR (125 MHz): δ = 25.99, 29.12, 29.34, 29.54, 68.28 (all t, partially overlapped), 112.72 (d), 121.95 (d), 123.30 (d), 129.98 (d), 137.76 (s), 159.71 (s), 192,21 (d). − MS (EI, 70 eV); *m/z* (%): 411 (17) [M$^+$ + 1], 410 (56) [M$^+$], 123 (31), 122 (33), 121 (28), 98 (40), 95 (33), 83 (49), 81 (29), 69 (78), 55 (100), 43 (33), 41 (50). − $C_{26}H_{34}O_4$ (410.56): calcd. C 76.06, H 8.35; found C 76.12, H 8.35.

3,3'-[1,6-Hexanediylbis(oxy)]bis(benzaldehyde) (**8b**): To a solution of 1.0 g (8.2 mmol) of 3-hydroxybenzaldehyde (**7**) in 5 ml of dry DMF and 5 ml of dry THF, 0.30 g (8.2 mmol) of NaH (60%, in mineral oil) was added in portions under argon. After stirring for 10 min at room temp., a solution of 1.71 g (4.00 mmol) of **9b** in 10 ml dry DMF/THF (1:1) was added. The reaction mixture was stirred for 9 h at 80 °C (bath temperature), hydrolyzed with 25 ml of aqueous sodium carbonate (10%), and extracted three times with 50 ml diethyl ether. The combined ethereal extracts were washed four times with 30 ml aqueous sodium carbonate (10%). The organic phase was dried with sodium sulfate, the solvent was evaporated, and the residue was purified by flash chromatography on silica gel with petroleum ether/diethyl ether (1:1; TLC: R_f = 0.44) to obtain 1.06 g (81%) of **8b** as colourless crystals with m.p. 74−77 °C (ref.[11] 78−80 °C).

General Procedure for the Synthesis of Stilbenes by the McMurry Reaction: To a stirred suspension of 6.0 g (92 mmol) zinc powder in 50 ml dry THF, 4.3 ml (7.4 g, 39 mmol) $TiCl_4$ was added slowly at −10 °C. Then, a solution of 7 mmol bis(benzaldehyde) **8** (14 mmol of **1**, respectively) in 250 ml of dry THF was added dropwise at reflux temperature and the mixture was stirred for 5 h. The reaction mixture was then hydrolyzed with 200 ml of aqueous (10%) $NaHCO_3$, and extracted with diethyl ether. The organic phase was dried by filtration through silica gel and concentrated.

trans-3,3'-Dimethoxystilbene (**2**): The crude product obtained from 1.91 g (14 mmol) of **1** as outlined in the General Procedure was purified by sublimation to yield 1.48 g (88%) of **2** as colourless crystals with m.p. 96−97 °C (ref.[2c] 101−102 °C).

McMurry Reaction with **8a**: The crude product obtained from 2.0 g (7 mmol) of **8a** as outlined in the General Procedure was purified by flash chromatography on silica gel [TLC: silica gel, petroleum ether/diethyl ether (5:1), R_f = 0.41] and dried in vacuo to give 1.2 g (65%) of *cis*-1,4(1,3)-dibenzena-5,9-dioxacyclononaphane-2-ene (*cis*-**11a**), colourless crystals, m.p. 52−54 °C. − IR (KBr): $\tilde{\nu}$ = 3431 cm^{-1} (w), 3057 (w), 2974 (m), 2928 (w), 2876 (w), 1597 (s), 1576 (m), 1474 (s), 1438 (m), 1245 (m), 1226 (w), 1212 (m), 1150 (w), 1131 (w), 1019 (m), 910 (w), 892 (w), 807 (s), 692 (m). − UV (CH_3CN): λ_{max} (lg ε) = 209 nm (4.43), 235 (4.25, sh), 293 (3.95, br.). − ^{1}H NMR (500 MHz): δ = 1.98 (quint, *J* = 6.3 Hz, 2 H, 7-H), 3.98 (t, *J* = 6.3 Hz, 4 H, 6-H/8-H), 6.63 (s, 2 H, 2-H/3-H), 6.83 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 2 H), 6.90 ("dt", "*J*" = 7.5, 1.3 Hz, 2 H), 7.18 (dd, *J* = 2.5, 1.6 Hz, 2 H, 2'-H/2''-H), 7.26 (t, *J* = 7.8 Hz, 2 H, 5'-H/5''-H). − ^{13}C NMR (125 MHz): δ = 30.25 (t), 67.49 (t), 119.14, 119.45, 123.60, 130.11, 130.27 (all d), 137.81 (s), 157.44 (s). − MS (EI, 70 eV); *m/z* (%): 253 (19) [M$^+$ + 1], 252 (100) [M$^+$], 210 (46), 194 (55), 16 (22), 165 (62), 93 (25), 91 (81), 71 (20), 55 (53). − $C_{17}H_{16}O_2$ (252.31): calcd. C 80.93, H 6.39; found C 81.06, H 6.44.

In the course of the extraction, a colourless precipitate was collected by filtration and was purified by recrystallization from ethyl acetate. 35 mg (2%) of *trans,trans*-1,4,10,13(1,3)-tetrabenzena-5,9,14,18-tetraoxacyclooctadecaphane-2,11-diene (**10a**) was obtained as colourless crystals, m.p. 203−205 °C. − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} (w), 2913 (w), 1593 (s), 1489 (m), 1459 (m), 1443 (m), 1411 (w), 1320 (w), 1295 (w), 1249 (s), 1170 (s), 1162 (s), 1054 (w), 1020 (m), 994 (w), 958 (m), 845 (w), 790 (m), 691 (m). − UV (CH_3CN): λ_{max} (lg ε) = 202 nm (4.64), 286 (4.10, br.), 305 (4.09, sh), 315 (4.04, sh). − ^{1}H NMR (500 MHz): δ = 2.28 (quint, *J* = 6.2 Hz, 4 H, 7-H/16-H), 4.27 (t, *J* = 6.3 Hz, 8 H, 6-H/8-H/15-H/17-H), 6.84 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 4 H), 7.07 (s, 4 H, 2-H/3-H/11-H/12-H), 7.10 ("ddd", "*J*" = 7.7, 1.4, 0.9 Hz, 4 H), 7.16 ("dd", "*J*" = 2.3, 1.6 Hz, 4 H), 7.26 (t, *J* = 7.9 Hz, 4 H). − ^{13}C

NMR (125 MHz): δ = 29.04 (t), 65.17 (t), 112.85 (d), 114.63 (d), 119.49 (d), 129.03 (d), 129.74 (d), 138.80 (s), 159.18 (s). − MS (EI, 70 eV); *m/z* (%): 505 (38) [M$^+$ + 1], 504 (100) [M$^+$], 252 (10), 165 (17), 147 (10). − $C_{34}H_{32}O_4$ (504.61): calcd. C 80.93, H 6.39; found C 80.89, H 6.39.

McMurry Reaction with **8b**: The crude product obtained from 2.3 g (7 mmol) of **8b** as outlined in the General Procedure was purified by flash chromatography on silica gel with petroleum ether/diethyl ether (5:1) [TLC: silica gel, petroleum ether/diethyl ether (1:1), R_f = 0.73, 0.66, 0.31, 0.16].

First Fraction (R_f = 0.73): 0.21 g (10%) of *cis*-1,4(1,3)-dibenzena-5,12-dioxacyclododecaphane-2-ene (*cis*-**11b**), slightly contaminated with a small amount of the *trans* isomer, *trans*-**11b**, identified by its NMR data: − ^{1}H NMR (300 MHz): δ = 1.40−1.44 (m, 4 H, 8-H/9-H), 1.64 ("t", "*J*" = 6.0 Hz, 4 H, 7-H/10-H), 3.95 (t, *J* = 5.7 Hz, 4 H, 6-H/11-H), 6.55 (s, 2 H, 2-H/3-H), 6.76 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 2 H), 6.81 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 2 H), 6.98 (dd, *J* = 2.4, 1.7 Hz, 2 H, 2′-H/2′′-H), 7.23 (t, *J* = 7.9 Hz, 2 H, 5′-H/5′′-H). − ^{13}C NMR (75 MHz): δ = 23.43 (t, C-8/C-9), 27.21 (t, C-7/C-10), 66.72 (t, C-6/C-11), 113.92 (d), 116.02 (d), 122.17 (d), 129.53 (d), 130.07 (d), 138.18 (s, C-1′/C-1′′), 158.13 (s, C-3′/C-3′′).

Second Fraction (R_f = 0.66): 1.8 g (86%) of *trans*-1,4(1,3)-dibenzena-5,12-dioxacyclododecaphane-2-ene (*trans*-**11b**), colourless crystals, m.p. 118−120 °C. − IR (KBr): ṽ = 3026 cm^{-1} (w), 2958 (m), 2935 (m), 2859 (m), 1600 (s), 1584 (m), 1491 (m), 1476 (m), 1430 (w), 1321 (w), 1304 (w), 1293 (w), 1245 (s), 1169 (m), 1040 (m), 1029 (m), 1001 (m), 989 (m), 981 (m), 956 (w), 871 (w), 860 (m), 784 (s), 694 (m). − UV (CH_3CN): λ_{max} (lg ε) = 203 nm (4.36), 220 (3.92, sh), 275 (3.23), 282 (3.19). − ^{1}H NMR (300 MHz): δ = 1.57 (m, 4 H, 8-H/9-H), 1.88 (m, 4 H, 7-H/10-H), 4.20 (t, *J* = 7.0 Hz, 4 H, 6-H/11-H), 6.75 (d, *J* = 1.3 Hz, 2 H, 2′-H/2′′-H), 6.79 (ddd, *J* = 8.1, 2.8, 0.8 Hz, 2 H), 6.95 (s, 2 H, 2-H/3-H), 7.03 (dt, *J* = 7.6, 1.1 Hz, 2 H), 7.24 (t, *J* = 7.8 Hz, 2 H, 5′-H/5′′-H). − ^{13}C NMR (75 MHz): δ = 27.51 (t, C-8/C-9), 28.07 (t, C-7/C-10), 68.73 (t, C-6/C-11), 115.19 (d), 116.05 (d), 116.89 (d), 130.15 (d), 134.09 (d), 140.94 (s, C-1′/C-1′′), 157.86 (s, C-3′/C-3′′). − MS (EI, 70 eV); *m/z* (%): 295 (22) [M$^+$ + 1], 294 (100) [M$^+$], 213 (12), 212 (73), 211 (36), 210 (15), 195 (28), 194 (19), 183 (15), 165 (30), 83 (14), 55 (51), 41 (21). − $C_{20}H_{22}O_2$ (294.40): calcd C 81.60, H 7.53; found C 81.60, H 7.57.

McMurry Reaction with **8c**: The crude product obtained from 2.87 g (7 mmol) of **8c** as outlined in the General Procedure was purified by flash chromatography on silica gel with petroleum ether/diethyl ether (9:1) [TLC: silica gel, petroleum ether/diethyl ether (9:1), R_f = 0.62, 0.54, 0.46].

First Fraction (R_f = 0.62): 79.7 mg (3%) of *cis*-1,4(1,3)-dibenzena-5,18-dioxacyclooctadecaphane-2-ene (*cis*-**11c**), slightly contaminated with a small amount of the *trans* isomer, *trans*-**11c**, identified by its NMR data: ^{1}H NMR (500 MHz): δ = 1.25−1.42 (m, 16 H), 1.68 ("t", "*J*" = 6.7 Hz, 4 H), 3.73 (t, *J* = 6.5, 4 H, 6-H, 17-H), 6.58 (s, 2 H, 2-H/3-H), 6.75 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 2 H), 6.79 (dd, *J* = 2.5, 1.5 Hz, 2 H, 2′-H/2′′-H), 6.81 (ddd, *J* = 7.3, 2.6, 1.0 Hz, 2 H), 7.16 ("t", "*J*" = 7.9 Hz, 2 H, 5′-H/5′′-H). − ^{13}C NMR (125 MHz): δ = 24.87, 26.89, 27.26, 27.57, 28.41, 67.32 (all t), 113.52, 114.61, 121.73, 129.26, 130.39 (all d), 138.53 (s, C-3′/C-3′′), 158.95 (s, C-1′/C-1′′).

Second Fraction (R_f = 0.54): 1.62 g (61%) of *trans*-1,4(1,3)-dibenzena-5,18-dioxacyclooctadecaphane-2-ene (*trans*-**11c**), colourless crystals, m.p. 84−86.5 °C. − IR (KBr): ṽ = 2925 cm^{-1} (s), 2852 (m), 1603 (w), 1592 (m), 1584 (m), 1492 (w), 1446 (w), 1286 (w), 1252 (w), 1242 (m), 1162 (s), 964 (w), 694 (w). − UV (CH_3CN): λ_{max} (lg ε) = 203 nm (4.34), 213 (4.33), 220 (4.33), 305 (4.29, br.), 319 (427), 333 (4.12, sh). − ^{1}H NMR (500 MHz): δ = 1.39 ("s", br., 8 H), 1.48 ("d", "*J*" = 3.4 Hz, 8 H), 1.83 ("t", "*J*" = 7.1 Hz, 4 H), 4.13 (t, *J* = 7.3 Hz, 4 H, 6-H/17-H), 6.82 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 2 H), 7.04 ("t", "*J*" = 1.9 Hz, 2 H, 2′-H/2′′-H), 7.06 (s, 2 H, 2-H/3-H), 7.11 ("dt", "*J*" = 7.6, 1.2 Hz, 2 H), 7.26 ("t", "*J*" = 7.9 Hz, 2 H, 5′-H/5′′-H). − ^{13}C NMR (125 MHz): δ = 25.80, 27.64, 28.83, 29.62, 29.80, 68.41 (all t), 111.74, 116.30, 118.87, 128.73, 129.87 (all d), 138.37 (s), 159.13 (s). − MS (EI, 70 eV); *m/z* (%): 379 (29) [M$^+$ + 1], 378 (100) [M$^+$], 212 (40), 211 (16), 195 (12), 183 (11), 165 (14), 69 (10), 55 (22). − $C_{26}H_{34}O_2$ (378.56): calcd C 82.49, H 9.05; found C 82.25, H 9.03.

Synthesis of 1,4(1,3)-Dibenzena-5,12-dioxacyclododecaphane-2,3-diol (**12b**). − (a) *Pinacol Coupling:* To a suspension of 6.3 g (0.10 mol) of zinc powder in 50 ml of dry THF, 3.0 ml (5.2 g, 27 mmol) of $TiCl_4$ was added slowly at −10 °C under argon. A solution of 1.5 g (4.6 mmol) of **8b** in 250 ml of dry THF was added dropwise at −10 °C and the mixture was stirred for 3 h. The reaction mixture was then hydrolyzed with 200 ml of aqueous (10%) $NaHCO_3$ and extracted with diethyl ether. The organic phase was dried by filtration through silica gel, concentrated, and the residue was purified by flash chromatography on silica gel [TLC: silica gel, petroleum ether/diethyl ether (1:1), R_f = 0.27, 0.16].

First Fraction (R_f = 0.27): 1.06 g (71%) of 2*R**,3*R**-1,4(1,3)-dibenzena-5,12-dioxacyclododecaphane-2,3-diol (*trans*-**12b**) as colourless crystals with m.p. 112.5−115.5 °C. − IR (KBr): ṽ = 3432 cm^{-1} (s), 2934 (m), 1609 (m), 1487 (m), 1449 (m), 1399 (w), 1318 (m), 1268 (s), 1168 (m), 1030 (s), 936 (w), 869 (m), 789 (m), 702 (m), 631 (w), 584 (w), 475 (w). − ^{1}H NMR (500 MHz): δ = 1.40 (m, 4 H, 8-H/9-H), 1.62 (m, 4 H, 7-H/10-H), 3.17 (s, 2 H, 2-OH/3-OH), 3.83 (m, 2 H, 6-H$_a$/11-H$_a$), 3.96 (m, 2 H, 6-H$_b$/11-H$_b$), 4.42 (s, 2 H, 2-H/3-H), 5.88 (dd, *J* = 2.4, 1.7 Hz, 2 H, 2′-H/2′′-H), 6.74 (ddd, *J* = 7.3, 2.5, 0.9 Hz, 2 H, 4′-H/4″-H), 7.11 (dt, *J* = 7.7, 1.2 Hz, 2 H, 6′-H/6′′-H), 7.25 (t, *J* = 8.0 Hz, 2 H, 5′-H/ 5″-H). The multiplet at δ = 1.40 is simplified to a singlet by spin saturation at δ = 1.62. The multiplets at δ = 3.83 and δ = 3.96 are reduced to two doublets with a coupling constant of ^2J = 10.3 Hz by spin saturation at δ = 1.62. − ^{1}H-NOE difference spectra (400 MHz): (a) Spin saturation at δ = 3.17 (2-OH/3-OH): δ = 4.42 (+14%, 2-H/3-H), 7.11 (+5%, 6′-H/6″-H); (b) spin saturation at δ = 4.42 (2-H/3-H): δ = 3.17 (+13%, 2-OH/3-OH), 5.89 (+14%, 2′-H/2″-H), 7.11 (+10%, 6′-H/6″-H). − ^{13}C NMR (125 MHz): δ = 22.61 (t, C-8/C-9), 26.70 (t, C-7/C-10), 65.76 (t, C-6/C-11), 79.31 (d, C-2/C-3), 113.25, 116.06, 118.03 (d), 129.33 (d, C-5′/C-5″), 140.98 (s, C-1′/C-1″), 157.37 (s, C-3′/C-3″). − MS (EI, 70 eV); *m/z* (%): 329 (29) [M$^+$ + 1], 328 (100) [M$^+$], 205 (13), 124 (71), 123 (54), 107 (20), 106 (20), 105 (19), 95 (46), 83 (65), 82 (22), 77 (24), 55 (61), 41 (19). − $C_{20}H_{24}O_4$ (328.41); calcd C 73.15, H 7.37; found C 73.11, H 7.29.

Second Fraction (R_f = 0.16): 0.34 g (22%) of 2*R**,3*S**-1,4(1,3)-dibenzena-5,12-dioxacyclododecaphane-2,3-diol (*cis*-**12b**) as colourless crystals with m.p. 107−109 °C. − IR (KBr): ṽ = 3459 cm^{-1} (m), 3035 (w), 2938 (m), 1607 (m), 1583 (m), 1485 (w), 1478 (w), 1449 (s), 1261 (s), 1160 (w), 1147 (w), 1026 (s), 787 (w), 770 (m), 717 (m). − UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.42), 218 (4.15, sh), 271 (3.52), 280 (3.48, sh). − ^{1}H NMR (300 MHz): δ = 1.41 (m, 4 H, 8-H/9-H), 1.64 (m, 4 H, 7-H/10-H), 2.61 (s, 2 H, 2-OH/3-OH), 3.90 (m, 4 H, 6-H/11-H), 4.95 (s, 2 H, 2-H/3-H), 6.03 (dd, *J* = 2.4, 1.8 Hz, 2 H, 2′-H/2″-H), 6.76 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 2 H, 4′-H/4″-H), 6.94 ("d", "*J*" = 7.6 Hz, 2 H, 6′-H/6″-H), 7.24 ("t", "*J*" = 7.9 Hz, 2 H, 5′-H/5″-H). The multiplet at δ = 1.41 is simplified to a singlet by spin saturation at δ = 1.64. The multiplet at δ = 3.90 becomes two doublets with resonances at δ =

3.89 and 3.90 and with a coupling constant $^2J = 10.7$ Hz by spin saturation at δ = 1.64. − ^{1}H-NOE difference spectra [500 MHz (a), 300 MHz (b)]: (a) Spin saturation at δ = 2.61 (2-OH/3-OH): δ = 4.95 (+3.0%, 2-H/3-H), 6.03 (+2.2%, 2′-H/2″-H), 6.94 (+3.8%, 6′-H/6″-H); (b) spin saturation at δ = 4.95 (2-H/3-H): δ = 2.61 (+1.8%, 2-OH/3-OH), 6.03 (+7.6%, 2′-H/2″-H), 6.94 (+9.3%, 6′-H/6″-H). − ^{13}C NMR (75 MHz): δ = 22.59 (t, C-8/C-9), 26.79 (t, C-7/C-10), 65.70 (t, C-6/C-11), 77.74 (d, C-2/C-3), 113.09 (d), 115.06 (d), 118.84 (d), 128.84 (d, C-5′/C-5″), 140.13 (s, C-1′/C-1″), 157.81 (s, C-3′/C-3″). − MS (EI, 70 eV); *m/z* (%): 329 (22) [M$^+$ + 1], 328 (100) [M$^+$], 205 (10), 124 (65), 123 (45), 107 (16), 106 (16), 105 (15), 95 (36), 83 (59), 82 (18), 77 (19), 55 (55), 41 (14). − $C_{20}H_{24}O_4$ (328.41); calcd. C 73.15, H 7.37; found C 72.96, H 7.42.

(b) *trans*-**12b** *from Stilbene trans*-**11b** *with AD-mix-β:* To a solution of 1.4 g of AD-mix-β[14] and 95 mg of methanesulfonamide in 5 ml water and 5 ml of *tert*-butyl alcohol, 0.19 g (0.65 mmol) *trans*-**11b** was added at 0 °C and the mixture was stirred vigorously for 8 h at 0 °C and then for 22 h at room temp. Solid sodium sulfite (1.5 g) was added, the suspension was stirred for 45 min and then extracted four times with 20 ml of dichloromethane. The combined organic extracts were washed with 20 ml of aqueous 2 M KOH, dried by filtration through silica gel and concentrated to dryness. Purification by flash chromatography on silica gel with petroleum ether/diethyl ether (1:1) furnished 158 mg (75%) of *trans*-**12b** with an enantiomeric ratio of 88.7:11.3 determined by HPLC; $[\alpha]_D^{25}$ = 21.703 (c = 6.4, CH_2Cl_2)].

Synthesis of the Cyclic Sulfite **13b**. − *General Procedure:* To a mixture of 0.66 g (2.0 mmol) of one diastereoisomer of diol **12b** and 0.33 ml (0.32 g, 4.0 mmol) of pyridine in 10 ml of dry dichloromethane, 0.22 ml (0.36 g, 3.0 mmol) of thionyl chloride was added. The reaction mixture was stirred under argon for 5 min and then filtered through a short silica gel column. The solvent was evaporated and the residue was recrystallized from dichloromethane/pentane.

trans-1,3(1,3)-Dibenzena-2(4,5)-[(1,3,2)-dioxathiolana]-4,11-dioxacycloundecaphane S-Oxide (*trans*-**13b**): 0.55 g (73%) from *trans*-**12b**, colourless crystals [R_f = 0.60; silica gel, hexane/diethyl ether (1:1)], m.p. 129−136 °C. − IR (KBr): ṽ = 2931 cm^{-1} (m), 1609 (m), 1584 (m), 1488 (m), 1448 (m), 1321 (w), 1270 (s), 1216 (s), 1173 (m), 1158 (m), 1093 (w), 1043 (m), 986 (s), 929 (m), 875 (w), 833 (w), 785 (m), 759 (m), 711 (s), 688 (m). − UV (CH_3CN): λ_{max} (lg ε) = 205 nm (4.54), 220 (4.21, sh), 276 (3.66), 280 (3.63, sh). − ^{1}H NMR (500 MHz): δ = 1.35−1.44 (m, 2 H, 7-H$_a$/8-H$_a$), 1.46−1.54 (m, 2 H, 7-H$_b$/8-H$_b$), 1.59−1.68 (m, 2 H, 6-H$_a$/9-H$_a$), 1.70−1.78 (m, 2 H, 6-H$_b$/9-H$_b$), 3.87−3.98 (m, 2 H, 5-H$_a$/10-H$_a$), 4.02−4.11 (m, 2 H, 5-H$_b$/10-H$_b$), 4.89 (d, J = 9.7 Hz, 2 H), 5.41 (d, J = 9.7 Hz, 2 H), 6.13 (t, J = 2.1 Hz, 2 H, 2′-H/2′′-H), 6.90 (dd, J = 8.1, 2.4 Hz, 2 H), 7.18 Hz (d, J = 7.8 Hz, 1 H), 7.35 (d, J = 7.8 Hz, 1 H), 7.39 (t, J = 7.9 Hz, 1 H), 7.42 (t, J = 7.9 Hz, 1 H). − ^{13}C NMR (125 MHz): δ = 23.85, 23.89, 28.10, 28.12, 67.13, 67.19 (all t), 85.55, 91.42, 114.54, 114.87, 116.21, 116.27, 116.65, 117.83, 130.50, 130.68 (all d), 133.29, 134.26, 158.43, 158.56 (all s). − MS (EI, 70 eV); *m/z* (%): 375 (18) [M$^+$ + 1], 374 (78) [M$^+$], 326 (43), 226 (12), 205 (12), 123 (27), 122 (19), 121 (22), 107 (19), 105 (13), 91 (15), 83 (85), 82 (36), 55 (100), 41 (25). − $C_{20}H_{22}O_5S$ (374.45): calcd. C 64.15, H 5.92; found C 64.19, H 6.02.

cis-1,3(1,3)-Dibenzena-2(4,5)-[(1,3,2)-dioxathiolana]-5,11-dioxacycloundecaphane S-Oxide (*cis*-**13b**): 0.50 g (67%) of a diastereomeric mixture (0.48:1) was obtained from *cis*-**12b**. The diastereomers [R_f = 0.48 and R_f = 0.59; silica gel, hexane/diethyl ether (2:1)] were not separated. The ^{1}H-NMR signals were assigned to the diastereoisomers by their integrals, the ^{13}C-NMR signals by their intensities. − ^{1}H NMR (500 MHz): First diastereoisomer of *cis*-**13b**: δ = 1.41−1.49 (m, 4 H, 7-H/8-H), 1.64 (m, 4 H, 6-H/9-H), 3.89 (t, J = 6.6 Hz, 4 H, 5-H/10-H), 5.83 (s, 2 H, 4′′′-H/5′′′-H), 6.63 (ddd, J = 7.5, 1.5, 0.9 Hz, 2 H), 6.67 (ddd, J = 8.4, 2.6, 0.9 Hz, 2 H), 6.83 (dd, J = 2.5, 1.7 Hz, 2 H, 2′-H/2′′-H), 7.01 (“t”, “J” = 7.9 Hz, 2 H, 5′-H/5′′-H); second diastereoisomer of *cis*-**13b**: δ = 1.41−1.49 (m, 4 H, 7-H/8-H), 1.64 (m, 4 H, 6-H/9-H), 3.90 (t, J = 6.1 Hz, 4 H, 5-H/10-H), 6.14 (s, 2 H, 4′′′-H/5′′′-H), 6.44 (dd, J = 2.5, 1.6 Hz, 2 H, 2′-H/2′′-H), 6.55 (ddd, J = 7.6, 1.6, 1.0 Hz, 2 H), 6.69 (ddd, J = 8.3, 1.6, 0.9 Hz, 2 H), 7.04 (“t”, J = 8.0 Hz, 2 H, 5′-H/5′′-H). − ^{13}C NMR (75 MHz): First diastereoisomer of *cis*-**13b**: δ = 23.11 (t, C-7/C-10), 26.60 (t, C-6/C-9), 66.54 (t, C-5/C-10), 87.37 (d, C-4′′′/C-5′′′), 113.92 (d), 115.50 (d), 119.67 (d), 128.95 (d), 135.01 (s, C-1′/C-1′′), 158.31 (s, C-3′/C-3′′); second diastereoisomer of *cis*-**13b**: δ = 23.17 (t, C-7/C-8), 26.39 (t, C-6/C-9), 66.47 (t, C-5/C-10), 84.44 (d, C-4′′′/C-5′′′), 113.33 (d), 115.07 (d), 119.13 (d), 129.14 (d), 134.31 (s, C-1′/C-1′′), 158.22 (s, C-3′/C-3′′). − GC-MS coupling: First diastereoisomer with retention time ca. 25 min (temperature of capillary column 230 °C): MS; *m/z* (%): 375 (9) [M$^+$ + 1], 374 (39) [M$^+$], 326 (22) [M$^+$ − SO], 310 (22) [M$^+$ − SO_2], 281 (25), 203 (18), 122 (21), 121 (46), 107 (18), 83 (61), 82 (28), 77 (20), 55 (100), 44 (23); second diastereoisomer with retention time ca. 30 min (temperature of capillary column 230 °C): MS; *m/z* (%): 375 (8) [M$^+$ + 1], 374 (32) [M$^+$], 326 (20) [M$^+$ − SO], 310 (22) [M$^+$ − SO_2], 281 (20), 203 (19), 122 (18), 121 (44), 107 (16), 83 (57), 82 (30), 77 (22), 55 (100), 44 (24). − $C_{20}H_{22}O_5S$ (374.45, diastereomeric mixture): calcd. C 64.15, H 5.92; found C 64.21, H 6.02.

General Procedure for the Photocyclization: Argon was bubbled through a solution of 1 mmol of stilbene **11** and 1.3 mmol of iodine in 90 ml of toluene for 30 min. Then, 10 ml of propylene oxide[3a] was added and the mixture was irradiated with light from a Philips HPK 125 lamp. The reaction was monitored by NMR and further iodine was added every 2 h in 0.25-mmol portions until the stilbene derivative was no longer detectable. The solvent was then evaporated from the reaction mixture.

Photocyclization of **2**: The crude product (quantitative conversion) obtained from 0.24 g (1.0 mmol) of **2** after 8 h of exposure as outlined in the General Procedure was directly analyzed by ^{1}H-NMR spectroscopy. By flash chromatography [silica gel, petroleum ether/MTBE (5:1)], enriched fractions of the isomers were obtained, allowing their identification by NMR spectroscopy: **3** (16%), **4** (55%), **5** (29%).

4,5-Dimethoxyphenanthrene (**3**): The ^{1}H-NMR spectrum is in accord with reported data[17].

2,5-Dimethoxyphenanthrene (**4**)[4]: ^{1}H NMR (500 MHz): δ = 3.91 (s, 3 H), 4.05 (s, 3 H), 7.07 (dd, J = 7.4, 1.6 Hz, 1 H), 7.23 (d, J = 2.8 Hz, 1 H, 1-H), 7.25 (dd, J = 9.3, 2.9 Hz, 1 H, 3-H), 7.43 (“t”, “J” = 7.7 Hz, 1 H, 7-H), 7.46 (dd, J = 7.9, 1.4 Hz, 1 H), 7.63 (d, J = 8.8 Hz, 1 H), 7.66 (d, J = 8.8 Hz, 1 H), 9.57 (d, J = 9.4 Hz, 1 H, 4-H).

2,7-Dimethoxyphenanthrene (**5**): The ^{1}H-NMR spectrum is in accord with reported data[4][18].

Photocyclization of cis-**11a**: The crude product obtained from 252 mg (1 mmol) of *cis*-**11a** after 4 h of exposure as outlined in the General Procedure was purified by flash chromatography [TLC: silica gel, petroleum ether/diethyl ether (5:1), R_f = 0.25] and dried in vacuo to give 228 mg (91%) of 2,6-dioxa-1(4,5)-phenanthrenacyclohexaphane (**14a**) as colourless crystals with m.p. 112−114 °C. − IR (KBr): ṽ = 2948 cm^{-1} (m), 2885 (w), 1565 (w), 1517 (m), 1442 (s), 1428 (w), 1319 (s), 1260 (s), 1246 (s), 1217 (w), 1054 (s), 1033 (m), 827 (s), 720 (w). − UV (CH_3CN): λ_{max} (lg ε) = 218 nm (4.60), 258 (4.62), 286 (4.52), 316 (4.11), 340 (2.95, sh, br.). − ^{1}H NMR (500 MHz): δ = 2.38 (quint, *J* = 5.9 Hz, 4 H, 4-H), 4.68 (t, *J* = 5.9 Hz, 4 H, 3-H/5-H), 7.20−7.24 (m, 4 H), 7.44−7.50 (m, 4 H), 7.51 (s, 2 H, 9′-H/10′-H). − ^{13}C NMR (125 MHz): δ = 30.17 (t, C-4), 69.48 (t, C-3/C-5), 115.34 (d), 121.40 (d), 122.28 (s), 126.56 (d), 126.63 (d), 134.76 (s), 158.82 (s, C-4′/C-5′). − MS (EI, 70 eV); *m/z* (%): 251 (17) [M^+ + 1], 250 (100) [M^+], 222 (37), 221 (12), 209 (10), 192 (18), 165 (16), 164 (11), 163 (21), 152 (15). − $C_{17}H_{14}O_2$ (250.30): calcd. C 81.58, H 5.64; found C 81.33, H 5.65.

Photocyclization of **11b**: The crude product obtained from 294 mg (1 mmol) of **11b** after 6 h of exposure as outlined in the General Procedure was purified by flash chromatography [TLC: silica gel, petroleum ether/diethyl ether (5:1), R_f = 0.51, 0.31, 0.22]. The fraction with R_f = 0.51 was dried in vacuo furnishing 240 mg (82%) of 2,9-dioxa-1(4,5)-phenanthrenacyclononaphane (**14b**) as colourless crystals with m.p. 136−138 °C. − IR (KBr): ṽ = 2926 cm^{-1} (m), 2877 (w), 1563 (w), 1519 (m), 1441 (s), 1326 (s), 1252 (s), 1103 (w), 1066 (m), 1048 (s), 1031 (m), 818 (s), 761 (w), 716 (m). − UV (CH_3CN): λ_{max} (lg ε) = 202 nm (4.27, sh), 218 (4.52), 254 (4.55), 292 (4.48), 320 (3.95, sh), 350 (2.93). − ^{1}H NMR (500 MHz): δ = 1.82 (m, 4 H, 5-H/6-H), 1.94 (m, 4 H, 4-H/7-H), 4.24 (t, *J* = 5.2 Hz, 4 H, 3-H/8-H), 7.06 (dd, *J* = 7.9, 1.1 Hz, 2 H), 7.40 (dd, *J* = 7.7, 1.2 Hz, 2 H), 7.49 (t, *J* = 7.8 Hz, 2 H, 2′-H/7′-H), 7.57 (s, 2 H, 9′-H/10′-H). − ^{13}C NMR (125 MHz): δ = 24.52 (t, C-5/C-6), 27.58 (t, C-4/C-7), 66.92 (t, C-3/C-8), 107.48 (d), 118.95 (d), 119.18 (s), 126.54 (d), 126.81 (d), 134.70 (s), 156.72 (s, C-4′/C-5′). − MS (EI, 70 eV); *m/z* (%): 293 (15) [M^+ + 1], 292 (79) [M^+], 211 (15), 210 (100), 182 (20), 152 (12), 55 (24). − $C_{20}H_{20}O_2$ (292.38): calcd. C 82.16, H 6.89; found C 82.16, H 6.90.

Photocyclization of **11c**: The crude product obtained from 379 mg (1 mmol) of **11c** after 6 h of exposure as outlined in the General Procedure was purified by flash chromatography [TLC: silica gel, petroleum ether/diethyl ether (9:1), R_f = 0.61, 0.51, 0.41, 0.29].

First Fraction (R_f = 0.61): 49 mg (13%) of 2,15-dioxa-1(4,5)-phenanthrenacyclopentadecaphane (**14c**), slightly contaminated with a small amount of the isomer **15c**, identified by its NMR data: − ^{1}H NMR (500 MHz): δ = 1.39 ("s", br., 8 H), 1.48 ("d", "*J*" = 3.4 Hz, 8 H), 1.83 ("t", "*J*" = 7.1 Hz, 4 H), 3.98 (t, *J* = 7.7 Hz, 4 H, 3-H/14-H), 7.09 (dd, *J* = 7.9, 1.2 Hz, 2 H), 7.41 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.49 ("t", "*J*" = 7.8 Hz, 2 H, 2′-H/7′-H), 7.57 (s, 2 H, 9′-H/10′-H). − ^{13}C NMR (125 MHz): δ = 23.54, 25.50, 26.15, 26.80, 28.59, 69.11 (all t), 109.53 (d), 119.30 (d), 119.44 (s), 126.60 (d), 126.74 (d), 134.52 (s), 157.59 (s).

Second Fraction (R_f = 0.51): 282 mg (75%) of 2,15-dioxa-1(2,5)-phenanthrenacyclopentadecaphane (**15c**), colourless crystals with m.p. 118−120 °C. − IR (KBr): ṽ = 2927 cm^{-1} (s), 2854 (m), 1614 (m), 1566 (w), 1526 (m), 1453 (m), 1327 (w), 1297 (w), 1266 (s), 1230 (s), 1154 (m), 1142 (m), 1071 (m), 1043 (w), 871 (w), 825 (m). − UV (CH_3CN): λ_{max} (lg ε) = 204 (4.38), 263 (4.72), 281 (4.29), 295 (4.06, sh), 305 (3.82, sh), 329 (3.00), 344 (3.23), 362 (3.26). − ^{1}H NMR (500 MHz): δ = 1.32 (m, 6 H), 1.41 (m, 4 H), 1.44−1.51 (m, 4 H), 1.71 (m, 2 H), 1.80 (m, 2 H), 2.00 (m, 2 H), 4.26 (t, *J* = 5.1 Hz, 2 H), 4.32 (t, *J* = 7.1 Hz, 2 H), 7.10 (dd, *J* = 7.1, 1.9 Hz, 1 H), 7.28 (dd, *J* = 9.4, 3.3 Hz, 1 H, 3′-H), 7.33 (d, *J* = 2.8 Hz, 1 H, 1′-H), 7.43−7.48 (m, 2 H), 7.62 (d, *J* = 8.8 Hz, 1 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 9.74 (d, *J* = 9.4 Hz, 1 H, 4′-H). − ^{13}C NMR (125 MHz): δ = 24.62, 26.20, 26.98, 27.39, 28.35, 28.59, 29.00, 29.14, 29.77, 68.03, 69.48 (all t, partially overlapped), 108.97 (d), 113.21 (d), 114.21 (d), 120.98 (s), 121.23 (d), 124.56 (s), 125.58 (d), 127.25 (d), 127.71 (d), 130.39 (d), 133.58 (s), 134.59 (s), 156.11 (s), 157.76 (s). − MS (EI, 70 eV); *m/z* (%): 377 (28) [M^+ + 1], 376 (100) [M^+], 306 (10), 277 (11), 211 (17), 210 (97), 182 (10), 181 (15), 55 (12), 41 (10). − $C_{26}H_{32}O_2$ (376.54): calcd. C 82.94, H 8.57; found C 82.84, H 8.52.

☆ Dedicated to Prof. Dr. *Richard P. Kreher* on the occasion of his 65th birthday.

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