Preparation and Properties of New Methano-Bridged Dibenzo[*c,g*]phenanthrenes☆

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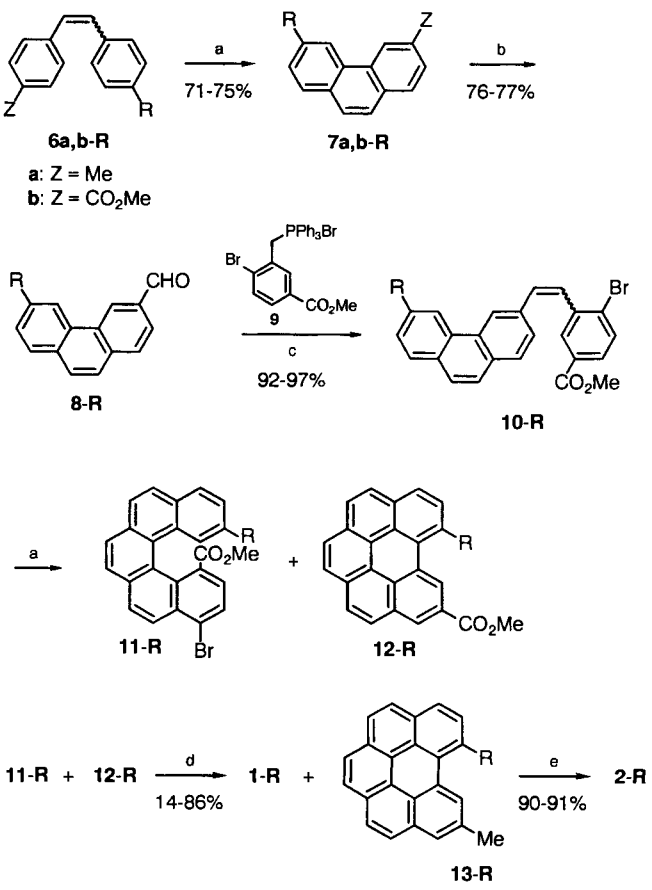
Intramolecular Friedel-Crafts alkylation of 1-(hydroxymethyl)[5]helicenes **1-R** and **15-Me** leads to 10,11-methano-bridged dibenzo[*c,g*]phenanthrenes **2-R** and **16-Me**, respectively. These molecules are shaped like the back of a turtle as shown by X-ray crystal structure analysis. Their nonplanarity, however, is not rigid, as revealed by the temperature dependence of their ^{1}H-NMR spectra. With inversion barriers of about 62.4 and 67.1 kJ mol^{-1} **2-H** and **2-Me** are surprisingly flexible. A remarkable diastereoselectivity is observed in the addition of methyl- and phenylmagnesium bromide to 1-formyl[5]helicenes **14-Me** leading to secondary alcohols **15a,b-Me**, which cyclize to bridged hydrocarbons **16a,b-Me**, in which the substituents R = Me, Ph are in the thermodynamically less favorable *endo*-position. Upon heating, *endo*-**16a,b-Me** isomerize to *exo*-**16a,b-Me** irreversibly.

Due to their theoretically interesting structures, the chiroptical and spectral properties of C_2-symmetric [*n*]helicenes have been investigated extensively[1]. These studies have revealed that a benzene ring is much more flexible than previously thought. In helicenes this flexibility comes to light in their unexpectedly facile racemization. Among several conceivable mechanisms for the thermal racemization of [5]- up to [9]helicenes the one proposed by R. H. Martin[2] calls for direct inversion with the terminal rings passing each other with considerable molecular deformations. In the transition state the terminal rings of a [6]helicene have to be parallel, while the racemization of a [5]helicene can proceed via a transition state with a coplanar arrangement of all five rings[3]. In an endeavor to utilize appropriately substituted enantiomerically pure [5]helicenes as chiral auxiliaries in asymmetric syntheses[4], we have observed the easy formation of the methano-bridged hydrocarbon **2-Me** by an intramolecular electrophilic alkylation. Comparable cyclizations of helicene skeletons have been reported previously. The parent hydrocarbon **2-H** has been mentioned by R. H. Martin[5] in a review as arising from 1-(hydroxymethyl)[5]-helicene **1-H**[6] upon treatment with acid. The same bridging of terminal rings has also been observed for hetero[5]- and carbo[6]helicene derivatives[7] while the unsubstituted 1-(hydroxymethyl)[6]helicene **3** eventually yields the spiro compound **5** after rearrangement fo the initial cyclization product **4**[8]. No experimental details and properties of the bridged [5]helicene **2-H** have been reported. Since compounds of type **2-R** constitute a new example of a nonplanar polycyclic aromatic hydrocarbon skeleton, we present in this

Scheme 1



a) hν, I_2. - b) R = H: i) NBS, CCl_4; ii) NaOMe, ^{i}PrNO$_2$; R = CH_3; i) $LiAlH_4$, THF; ii) PDC, CH_2Cl_2. - c) NaOMe, benzene. - d) $LiAlH_4$, THF, see text. - e) R = H: $MeSO_2Cl$, Et_3N, CH_2Cl_2; R = CH_3: PBr_3, benzene.

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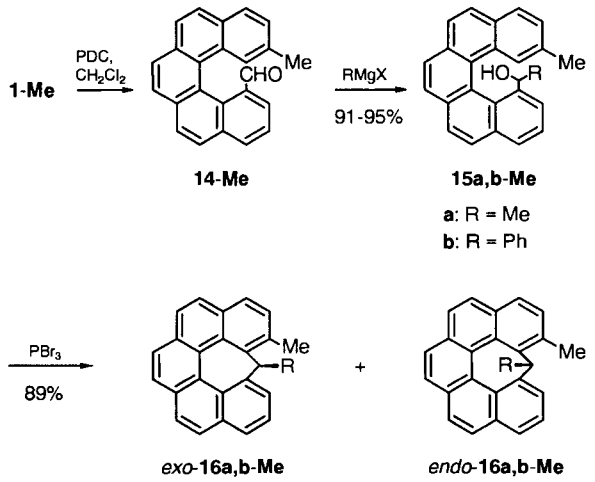
paper the physical properties and structural details of **2-Me** as well as some derivatives.

Synthesis of Methano-Bridged [5]Helicenes 2-R

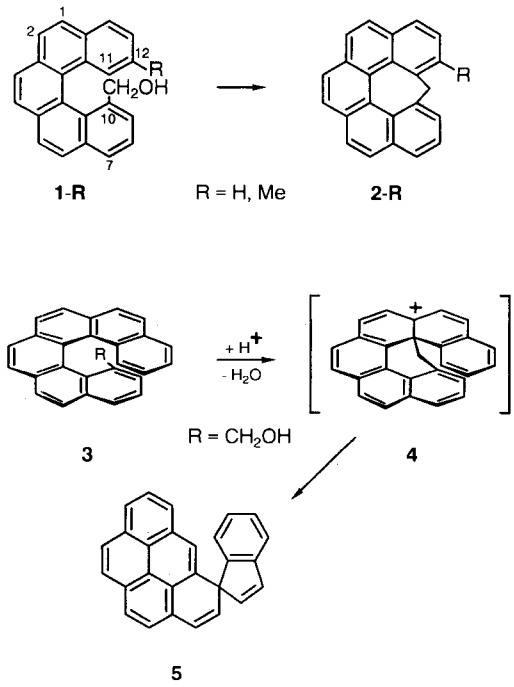
The preparation of [5]helicenes **2-R** has been achieved along a route which involves the photoinduced cyclization with subsequent dehydration of an appropriately substituted 1,2-diarylethene as the key step. According to the literature[1,5], this method, based on the photoconversion of stilbene to phenanthrene[9], is the most efficient for the preparation of *ortho*-anellated arenes[10]. As starting material for the new 1-substituted 13-methyl[5]helicenes **11-R** 2,7-dimethylphenanthrene **7a-Me** and methyl 7-methylphenanthrene-2-carboxylate **7b-R** (Scheme 1), prepared by oxidative photoconversion of the corresponding stilbene derivatives **6a,b-Me**[11], have been used.

Wittig reaction of **8-Me**[12] with the phosphonium ylide derived from **9** leads to diarylethene **10-Me**, which upon irradiation in cyclohexane in the presence of iodine is converted to the desired [5]helicene as the major product (32% yield). In addition, some benzoperylene **12-Me** (23%) is obtained in spite of the fact that the *ortho*-bromo substituent in **10-Me** normally prevents this type of cyclization. The ester **11-Me** upon reduction with lithium aluminum hydride (LAH) loses the bromine at the same time to provide the alcohol **1-Me**, which is transformed with phosphorus tribromide within 30 min into the methano-bridged dibenzo[*c*,*g*]phenanthrene **2-Me** in 91% yield.

Scheme 2



A similar sequence has been used to prepare the unsubstituted [5]helicene **1-H** from **6a-H**[11]. The isolation of the photocyclized product **11-H** is somewhat difficult. Eventually, **11-H** is obtained in 80% purity after column chromatography and several recrystallizations. It has been used for the subsequent reaction without further purification as a mixture with **12a-H** and reduced with lithium aluminum hydride to yield **1-H**, while the reaction of **12-H** leads to 8-methylbenzo[*g*,*h*,*i*]perylene **13**. Upon treatment with methanesulfonyl chloride and triethylamine **1-H** gives the bridged [5]helicenes **2-H** in good yield (90%).



Bridge-substituted derivatives **15a,b-Me** of **2-Me** are obtained by cyclization of secondary alcohols **15a,b-Me** prepared by addition of methyl- and phenylmagnesium bromide (PhMgBr), respectively, to the aldehyde **14-Me**, which in turn is obtained by oxidation of the primary alcohol **1-Me** with pyridinium dichromate in dichloromethane (Scheme 2). The overall yields for **16a-Me** and **16b-Me** are 72%.

The addition of PhMgBr to **14-Me** leads to only one of the two possible diastereomers of **15b-Me** which cyclizes to *endo*-**16b-Me** only, as corroborated by its ^{1}H-NMR spectrum with a significant high-field shift of the AA′BB′C pattern of the phenyl protons. Cyclization of the methyl-substituted alcohol **15a-Me** provided a mixture of *endo*- and *exo*-**16a-Me** in a ratio of 5:1.

Structure Analysis of 2-Me

The interesting topology of the molecules **2-H,Me**, which is evident upon inspection of a molecular model, has been confirmed by X-ray structure determination[13] of the pale yellow crystals of **2-Me** grown from a solution in *n*-hexane/dichloromethane. The end-on view (see Figure 1) shows that the molecule has the shape of a turtle back with the C^{18} methylene bridge sticking up and holding the adjacent two benzene rings in an upward bent conformation.

The bond angles in the seven-membered ring totally surrounded by aromatic rings increase from 110° for C^{19}–C^{18}–C^{21} to 126.1 and 126.7° for C^{20}–C^{21}–C^{22} and C^{21}–C^{22}–C^{23}, respectively. In line with this angle widening the anellated aromatic rings are distorted significantly, with values of 115.8 and 117.5° for C^7–C^{21}–C^{20} and C^{10}–C^{22}–C^{23} as the smallest. The bond angle at the sp^3-hybridized methano bridge C^{18} is slightly larger (110.0°) than the normal tetrahedral angle of 109.5°, whereas the C–H bonds at this

carbon enclose an angle of 107.2°. The bond lengths in the seven-membered ring vary between 151 for C^{18}–C^{19} and 147 pm for C^{21}–C^{22}; they are all longer than those in benzene (139 pm). On the other hand, several C–C distances in the aromatic rings, namely C^2–C^3, C^5–C^6, C^8–C^9, C^{11}–C^{12}, C^{14}–C^{15} are significantly shortened to an average of 135 pm. The remarkable distortion of the polycyclic aromatic ring skeleton is apparent in the torsional angles (see Figure 1).

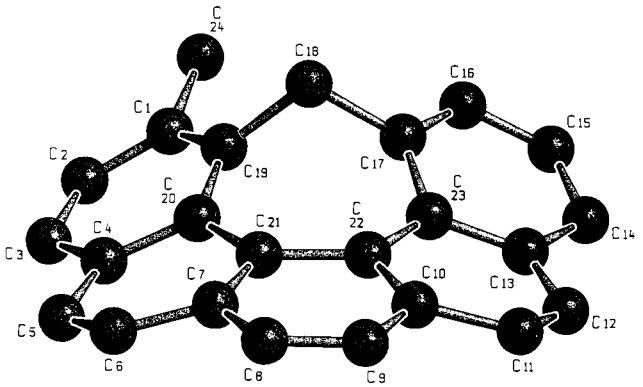
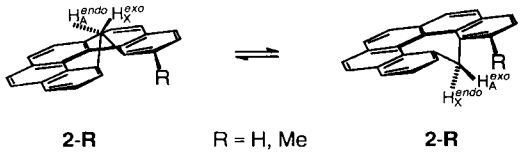


Figure 1. Molecular structure of **2-Me** in the crystal; bond distances [pm]: C(17)–C(18) 149, C(18)–C(19) 151, C(18)–C(17) 149, C(17)–C(23) 141, C(23)–C(22) 146, C(22)–C(21) 147, C(21)–C(20) 147; bond angles [°]: C(17)–C(18)–C(19) 110.0, C(18)–C(17)–C(23) 119.2, C(17)–C(23)–C(22) 123.6, C(23)–C(22)–C(21) 126.7, C(22)–C(21)–C(20) 126.1; torsional angles [°]: C(19)–C(20)–C(21)–C(22) 28.6, C(06)–C(07)–C(21)–C(22) 15.5, C(11)–C(10)–C(22)–C(21) 15.9, C(03)–C(04)–C(19)–C(20) 12.5, C(14)–C(13)–C(17)–C(23) 10.0, C(10)–C(22)–C(21)–C(20) 11.2, C(03)–C(02)–C(01)–C(24) 6.7, C(20)–C(19)–C(01)–C(24) 3.5

Dynamic Properties of 2-R

In view of the extraordinary shape of the molecule **2-Me** one can imagine an inversion process of the central ring which would convert the *exo*-oriented proton on the methano bridge to an *endo*-positioned one by rotation around the aryl to bridge C–C bonds.



2-R R = H, Me **2-R**

Figure 2. Inversion of the seven-membered ring in **2-R**

This exchange of protons H^{endo} and H^{exo} in **2-H,Me** can be analyzed by dynamic ^{1}H-NMR spectroscopy[14] because the signal of H^{endo} is drastically shifted upfield when the inversion process is slow on the NMR time scale. Around ambient temperature (294 K) there is only one singlet in the ^{1}H-NMR spectrum of **2-H**, at lower temperature (273 K) one observes an AB line pattern at $\delta = 4.38$. For **2-Me**, the spectrum shows two doublets for an AX spin system at $\delta = 3.60$ and 4.37 with $^2J = 12.7$ Hz around ambient temperature (298 K). The coalescence temperature for **2-Me** has been found to be 350 K, from which the free enthalpy of activation for the inversion process can be estimated as $\Delta G \approx 67.1$ kJ mol^{-1} according to the well-known formula[14]. Without the methyl group in close vicinity to the methano bridge, i.e. on going from **2-Me** to **2-H**, this inversion barrier is decreased to 62.4 kJ mol^{-1}.

The effect of a substitution on the methano bridge itself as in **16a,b-Me** is far more pronounced. We have not been able to determine the inversion barriers of the substituted compounds **15a,b-Me** by heating solutions of *endo*-**16a-Me** and *endo*-**16b-Me**, the thermodynamically more stable *exo* isomers are formed irreversibly.

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Experimental

General: ^{1}H NMR: Bruker WM 270 (270 MHz), WM 400 (400 MHz); internal standard tetramethylsilane (TMS). – ^{13}C NMR: Bruker WM 270 (67.93 MHz), WM 400 (100.62 MHz); internal standard TMS, the multiplicity of the ^{13}C-NMR signals was determined by the DEPT recording technique (DEPT: distortionless enhancement by polarization transfer) and characterized as follows: (+) primary or tertiary, (–) secondary, (Φ) quaternary C atoms. – IR: Beckman Acculab 4. – MS: Varian Mat CH-7 with Varian Aerograph 1740, Varian Mat 311 A (high resolution). – Melting points were obtained by using a Wagner & Munz melting point apparatus and are uncorrected. – Thin-layer chromatography was performed on aluminum-backed silica gel Merck Kieselgel 60 F_{254}. – Purifications by column chromatography were carried out with Merck Kieselgel 60 (70–230 mesh), flash chromatography was performed on silica gel chromatography medium 60, 20–45 μm (Amicon). – All reactions with water- and oxygen-sensitive compounds were carried out in an inert gas atmosphere (nitrogen or argon) in flame-dried glassware.

[2-Bromo-5-(methoxycarbonyl)benzyl]triphenylphosphonium Bromide (**9**): To a solution of 24.4 g (0.11 mol) of methyl 4-bromo-3-methylbenzoate in 100 ml of dry CCl_4 were added 19.0 g (0.11 mol) of *N*-bromosuccinimide and 200 mg of azoisobutyronitrile (AIBN). The reaction mixture was heated at reflux for 3 h, filtered, the residue washed with 50 ml of CCl_4 and the solvent evaporated. Recrystallisation of the residue from hexane/dichloromethane (60:1) gave 23.2 g (71%) of methyl 4-bromo-3-(bromomethyl)benzoate. – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 3.94$ (s, 3H, CO_2CH_3), 4.63 (s, 2H, CH_2Br), ABX system [$\delta_A = 7.67$, $\delta_B = 7.83$, $\delta_X = 8.14$, $^3J_{AB} = 8.1$, $^4J_{AX} = 2.0$ Hz, 3H, 6(5,2)-H].

A solution of 20.0 g (65.0 mmol) of methyl 4-bromo-3-(bromomethyl)benzoate and 25.0 g (95.4 mmol) of triphenylphosphane in 200 ml of toluene was heated to reflux for 3 h. The precipitate was collected on a filter, washed with petroleum ether and dried in vacuo to give 31.5 g (85%) of **9**. – ^{1}H NMR (270 MHz, $CDCl_3$): 2.79 (s, 3H, CO_2CH_3), 5.88 (d, $^3J = 16.2$ Hz, 2H, CH_2P), 7.48–8.00 (m, 18H, aromatic H).

3-Phenanthrenecarbaldehyde (**8-H**)[12]: 3.8 g (21 mmol) of *N*-bromosuccinimide and 200 mg of dibenzoyl peroxide were added to a solution of 4.08 g (21 mmol) of **7a-H**[12] in 20 ml of CCl_4 and then refluxed for 4 h. After filtration the solvent was evaporated from the filtrate and the crude product recrystallized from hexane/dichloromethane (4:1) to yield 4.3 g (76%) of 3-(bromomethyl)phenanthrene as colorless crystals, m.p. 107–108°C. – IR (KBr):

$\tilde{\nu}$ = 3060 cm^{-1}, 2920, 1685, 1450, 1400, 1295, 1145, 1085, 1040, 960, 840, 800, 745, 690. – ^1H NMR (270 MHz, $CDCl_3$): δ = 4.78 (s, 2H, CH_2Br), 7.59–7.94 (m, 7H, aromatic H), 8.69 (d, 1H, 5-H), 8.70 (s, 1H, 4-H). – MS (70 eV): *m/z* (%) = 272 (14) [M^+ ^{81}Br], 270 (14) [M^+ ^{79}Br], 191 (100) [M^+ – Br].

To a solution of 564 mg (26 mmol) of sodium in 30 ml of dry methanol was added 2.3 ml (26 mmol) of 2-nitropropane in 3.7 ml of methanol followed by the addition of a suspension of 5.0 g (18.5 mmol) of 3-(bromomethyl)phenanthrene[12] in 200 ml of methanol. The mixture was kept in the darkness at 22 °C for 14 h with stirring, then the solvent was removed in vacuo, and 100 ml of water and 75 ml of diethyl ether were added to the residue. The yellow organic layer was washed three times with 20 ml each of a 10% sodium hydroxide solution and subsequently with 25 ml of a satd. sodium chloride solution. Filtration of the residue over silica gel (dichloromethane, R_f = 0.44) afforded 3.9 g (100%) of **8-H**, m.p. 221 °C (hexane/dichloromethane, 4:1). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 2840, 2750, 1700, 1620, 1570, 1510, 1300, 1240, 1205, 1185, 850, 760. – ^1H NMR (270 MHz, $CDCl_3$): δ = 7.65–8.11 (m, 7H, aromatic H), 8.77 (d, 1H, aromatic H), 9.18 (s, 1H, aromatic H), 10.26 (s, 1H, CHO). – MS (70 eV): *m/z* (%) = 206 (100) [M^+], 177 (55) [M^+ – CHO].

6-Methyl-3-phenanthrenecarbaldehyde (**8-Me**)[11]: To a suspension of 1.95 g (48.8 mmol) of lithium aluminum hydride and 400 ml of tetrahydrofuran (THF) was added 12.2 g (48.8 mmol) of **7b-Me** in 200 ml of THF and the reaction mixture refluxed for 14 h, hydrolyzed by sequential addition of 0.5 ml of water, 0.5 ml of a 15% NaOH solution, and 15 ml of water. After filtration, repeated washing of the precipitate with ether (50 ml each) and evaporation of the solvents, the residue was taken up in diethyl ether (400 ml) and extracted three times with water (100 ml each) and a satd. NaCl solution, dried ($MgSO_4$) and concentrated. Recrystallization from ethanol gave 10.0 g (93%) 3-(hydroxymethyl)-6-methylphenanthrene, m.p. 200–202 °C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1}, 3000, 2900, 2850, 1500, 1410, 990, 965, 815, 800. – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.63 (s, 3H, Ar-CH_3), 4.98 (s, 2H, Ar-CH_2OH), AB system [δ_A = 7.66, δ_B = 7.71, $^3J_{AB}$ = 8.9 Hz, 2H, 9(10)-H], AB system [δ_A = 7.44, δ_B = 7.87, $^3J_{AB}$ = 8.0 Hz, 2H, 1(2)-H], AB system [δ_A = 7.92, δ_B = 8.12, $^3J_{AB}$ = 8.2 Hz, 2H, 7(8)-H], 8.50 (s, 1H, 5-H), 8.66 (s, 1H, 4-H).

10.2 g (45.9 mmol) of 3-(hydroxymethyl)-6-methylphenanthrene in 220 ml of dichloromethane was stirred at 22 °C with 43.0 g (115 mmol) of pyridinium dichromate (PDC) for 24 h (the reaction time can be shortened to 6 h by adding 1 g of molecular sieves, 3 Å). To the suspension was added 50 g of silica gel, the solvent was evaporated and the residue filtered over 200 g of silica gel (dichloromethane) to give 8.3 g (82%) of **8-Me**, m.p. 114–116 °C (diethyl ether). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1}, 1675, 1600, 1545, 1495, 1410, 1365, 1285, 1230, 1195, 1170, 830, 800, 740, 725. – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.69 (s, 3H, Ar-CH_3), AB system [δ_A = 7.51, δ_B = 7.82, $^3J_{AB}$ = 8.0 Hz, 2H, 9(10)-H], AB system [δ_A = 7.71, δ_B = 7.86, $^3J_{AB}$ = 8.6 Hz, 2H, 1(2)-H], AB system [δ_A = 7.96, δ_B = 8.06, $^3J_{AB}$ = 8.4 Hz, 2H, 7(8)-H], 8.57 (s, 1H, 5-H), 9.16 (s, 1H, 4-H), 10.26 (s, 1H, Ar-CHO).

$C_{16}H_{12}O$ (220.3) Calcd. C 87.24 H 5.50
Found C 87.30 H 5.70

General Procedure for the Preparation of 1,2-Disubstituted Diarylethenes **10-H** *and* **10-Me** *by Wittig Reaction:* A suspension of 11 mmol of substituted benzyltriphenylphosphonium bromide **9** and 10 mmol of aldehyde in 125 ml of dry benzene was treated for 30 min with stirring with a solution of sodium methoxide (from 72 mmol of sodium) in 50 ml of dry methanol. Stirring was continued for an additional 2 h, 2.5 ml of water was added, subsequently 25 g of silica gel. Then the solvents were removed. Filtration of the residue over 100 g of silica gel gave analytically pure diarylethenes **10-H** and **10-Me**, respectively.

Methyl 4-Bromo-3-[2-(3-phenanthrenyl)ethenyl]benzoate (**10-H**): According to the above procedure, 5.00 g (24.3 mmol) of **8-H** was converted to 9.03 g (92%) of (*E,Z*)-**10-H**, R_f = 0.33/0.27 (dichloromethane/petroleum ether), *E*:*Z* = 5:4 (^1H NMR). After recrystallization of a small amount from ethanol/dichloromethane (10:1) only the (*E*)-isomer was obtained as yellow crystals, m.p. 147 °C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3010, 2950, 1750, 1590, 1440, 1300, 1250, 1110, 1030, 850, 835, 760. – ^1H NMR (270 MHz, $CDCl_3$): (*E*)-**10-H**: δ = 3.99 (s, 3H, CO_2CH_3), AB system [δ_A = 7.48, δ_B = 7.65, $^3J_{AB}$ = 16 Hz, 2H, 1″(2″)-H], 7.60–7.90 (m, 10H, aromatic H), 8.75 (d, 1H, aromatic H), 8.78 (s, 1H, aromatic H). – (*Z*)-**10-H**: ^1H NMR (270 MHz, $CDCl_3$): δ = 3.7 (s, 3H, CO_2CH_3), AB system [δ_A = 6.7, δ_B = 7.1, $^3J_{AB}$ = 12 Hz, 2H, 1″(2″)-H], 7.50–7.90 (m, 12H, aromatic H). – MS (70 eV): *m/z* (%) = 418 (64) [M^+ ^{81}Br], 416 (68) [M^+ ^{79}Br], 337 (4.1) [M^+ – Br], 278 (100) [M^+ – CO_2CH_3 – Br].

$C_{24}H_{17}BrO_2$ (417.3) Calcd. C 69.08 H 4.11 Br 19.15
Found C 68.92 H 4.08 Br 19.43

Methyl 4-Bromo-3-[2-(6-methyl-3-phenanthrenyl)ethenyl]benzoate (**10-Me**): The reaction of 4.5 g (20.5 mmol) of **8-Me** with 12.0 g (21.9 mmol) of **9** gave 8.1 g (97%) of (*E/Z*)-**10-Me**, R_f = 0.37/0.33 (dichloromethane/petroleum ether). Recrystallization from ethanol/dichloromethane (10:1) led only to the (*E*)-isomer, yellow crystals, m.p. 135–138 °C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2940, 1700, 1435, 1290, 1240, 1100, 1015, 955, 830, 745. – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.67 (s, 3H, Ar-CH_3), 4.00 (s, 3H, Ar-CO_2CH_3), 7.46–7.90 (m, 6H, aromatic H), AB system [δ_A = 7.46, δ_B = 7.64, $^3J_{AB}$ = 16.1 Hz, 2H, 1″(2″)-H], ABC system [δ_A = 7.67, δ_B = 7.78, δ_C = 8.45, $^3J_{AB}$ = 8.4, $^4J_{BC}$ = 2.0 Hz, 3H, 2(5,6)-H], 8.54 (s, 1H, 5″-H), 8.76 (s, 1H, 4″-H). – MS (70 eV): *m/z* (%) = 432 (99) [M^+ ^{81}Br], 430 (100) [M^+ ^{79}Br].

$C_{25}H_{19}BrO_2$ (431.3) Calcd. C 69.62 H 4.44 Br 18.53
Found C 69.52 H 4.52 Br 18.51
C 69.34 H 4.52 Br 18.32

General Procedure for the Photocyclization of 1,2-Disubstituted Diarylethenes: A solution of 7.4 mmol of diarylethene and 600 mg (2.4 mmol) of iodine in 6 l of anhydrous cyclohexane was irradiated in a "falling-film photolysis apparatus"[11]. The progress of the reaction was monitored by analytical TLC (silica gel). After complete consumption of the diarylethene the solvent was evaporated and the residue purified by chromatography.

3-Methylphenanthrene (**7a-H**): According to the above procedure a total of 10.0 g (52 mmol) of **6a-H** gave after column chromatography (R_f = 0.29, petroleum ether/dichloromethane, 2:1) 6.9 g (71%) of **7a-H**. – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.64 (s, 3H, Ar-CH_3), 7.42–7.93 (m, 7H, aromatic H), 8.49 (s, 1H, 4-H), 8.70 (d, ^3J = 8.0 Hz, 1H, 5-H).

Methyl 6-Methyl-3-phenanthrenecarboxylate (**7b-Me**): The above procedure was applied by using 9.4 g (37.2 mmol) of **6b-Me**. Chromatography (R_f = 0.29, dichloromethane/petroleum ether, 1:1) gave 7.0 g (75%) of **7b-Me**, m.p. 125–126 °C (benzene) as colorless prisms. – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2950, 1710, 1610, 1500, 1435, 1300, 1280, 1260, 1240, 1120, 850, 830, 745. – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.66 (s, 3H, Ar-CH_3), 4.04 (s, 3H, CO_2CH_3), AB system [δ_A = 7.45, δ_B = 7.78, $^3J_{AB}$ = 8.0 Hz, 2H, 7(8)-H] AB system [δ_A = 7.64, δ_B = 7.87, $^3J_{AB}$ = 9.0 Hz, 2H, 9(10)-H], AB system

[$\delta_A = 7.87$, $\delta_B = 8.18$, $^3J_{AB} = 8.2$ Hz, 2H, 1(2)-H], 8.55 (s, 1H, 5-H), 9.37 (s, 1H, 4-H). – MS (70 eV): *m/z* (%) = 250 (100) [M^+].

$C_{17}H_{14}O_2$ (250.3) Calcd. C 81.58 H 5.64
Found C 81.39 H 5.64
C 81.27 H 5.65

Methyl 7-Bromodibenzo[c,g]phenanthrene-10-carboxylate (**11-H**): Irradiation of 2.95 g (7.1 mmol) of **10-H** gave after flash chromatography ($R_f = 0.14$, petroleum ether/ethyl acetate, 10:1) 1.85 g of a fraction containing three products in a ratio 7:5:1, as determined by ^{1}H-NMR spectroscopy. This crude material was directly used for the subsequent transformations. A small sample was recrystallized from diethyl ether/petroleum ether to yield **11-H** with 80% purity contaminated with methyl benzo[g,h,i]perylene-6-carboxylate **12-H** (^{1}H NMR). – **11-H**: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.75$ (s, 3H, CO_2CH_3), 7.53 (dd, 1H, aromatic H), 7.83–7.98 (m, 8H, aromatic H), AB system [$\delta_A = 8.01$, $\delta_B = 8.40$, $^3J_{AB} = 8.8$ Hz, 2H, 3(4)-H]. – MS (70 eV): *m/z* (%) = 416/414 (5.7/3.8) [M^+], 357/355 (13/31) [$M^+ - CO_2CH_3$], 335 (100) [M^+ – Br], 276 (79) [M^+ – Br – CO_2CH_3]. – **12-H**: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 3.04$ (s, 3H, CO_2CH_3), 7.64–7.87 (m, 5H, aromatic H), 8.19 (dd, 2H, aromatic H), 8.34 (m, 1H, aromatic H), 8.63 (d, 1H, aromatic H), 9.19 (br. s, 2H, aromatic H).

Methyl 7-Bromo-12-methyldibenzo[c,g]phenanthrene-10-carboxylate (**11-Me**): According to the above procedure, 3.0 g (7.0 mmol) of **10-Me** gave after flash chromatography ($R_f = 0.36$, petroleum ether/ethyl acetate, 10:1) 1.91 g of a fraction containing two compounds, which could be separated by recrystallization from dichloromethane/hexane (1:1). – **11-Me**: 852 mg (32%), m.p. 180–183°C (ethanol/dichloromethane, 10:1) as yellow crystals. – IR (KBr): $\tilde{\nu} = 3040$ cm^{-1}, 2940, 1700, 1440, 1265, 1250, 1195, 1180, 1160, 1140, 1075, 840, 830, 750, 735. – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.26$ (s, 3H, Ar-CH_3), 2.74 (s, 3H, CO_2CH_3), 7.72 (s, 1H, 11-H), AB system [$\delta_A = 7.36$, $\delta_B = 7.82$, $^3J_{AB} = 8.0$ Hz, 2H, 13(14)-H], AB system ($\delta_A = 7.57$, $\delta_B = 7.90$, $^3J_{AB} = 7.8$ Hz, 2H, aromatic H), 7.78–7.97 (m, 4H, aromatic H), AB system [$\delta_A = 7.99$, $\delta_B = 8.37$, $^3J_{AB} = 8.7$ Hz, 2H, 8(9)-H]. – ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 21.7$ (+) (Ar-CH_3), 51.2 (+) (OCH_3), 124.9 (+), 125.4 (+), 125.9 (+), 126.8 (Φ), 127.4 (+), 127.6 (+), 127.8 (+), 128.2 (+), 128.3 (+), 128.6 (+), 129.0 (+), 129.4 (+), 130.0 (Φ), 130.9 (Φ), 131.6 (Φ), 132.6 (Φ), 135.4 (Φ), 167.5 (Φ) (C=O). – MS (70 eV): *m/z* (%) = 430 (34) [M^+ ^{81}Br], 428 (33) [M^+ ^{79}Br], 290 (85) [M^+ – Br – CO_2CH_3].

$C_{25}H_{17}BrO_2$ (429.3) Calcd. C 69.94 H 3.99 Br 18.61
Found C 69.79 H 3.99 Br 18.36

12-Me: 548 mg (23%) by concentration of the mother liquor. – IR (KBr): $\tilde{\nu} = 2940$ cm^{-1}, 1730, 1420, 1310, 1280, 1255, 1230, 1190, 830. – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 3.28$ (s, 3H, Ar-CH_3), 4.15 (s, 3H, CO_2CH_3), AB system [$\delta_A = 7.88$, $\delta_B = 8.08$, $^3J_{AB} = 8.0$ Hz, 2H, 9(10)-H], 8.04–8.13 (m, 4H, aromatic H), AB system ($\delta_A = 8.29$, $\delta_B = 8.35$, $^3J_{AB} = 8.2$ Hz, 2H, aromatic H), 8.77 (s, 1H, 5-H), 9.47 (s, 1H, 7-H). – MS (70 eV): *m/z* (%) = 348 (100) [M^+].

General Procedure for the Reduction of Methoxycarbonyl-Substituted Dibenzo[c,g]phenanthrenes: To a solution of 4.0 mmol of lithium aluminum hydride (LAH) in 40 ml of dry THF was added 4.0 mmol of the aromatic ester, and the mixture was heated under reflux until TLC showed no more starting material. Hydrolysis by sequential addition of 0.5 ml of water, 0.5 ml of a 15% NaOH solution and 1.5 ml of water, filtration, repeated washing of the precipitate with diethyl ether (20 ml each), and evaporation of the solvents gave a crude material, which was dissolved in diethyl ether (20 ml). The organic layer was washed with water (5 ml), then with a satd. sodium chloride solution (5 ml), and dried with $MgSO_4$. Removal of the solvents and column chromatography of the residue gave the pure alcohols.

10-(Hydroxymethyl)dibenzo[c,g]phenanthrene (**1-H**): According to the above procedure 1.5 g (3.6 mmol) of **11-H** gave, after work-up and chromatography (petroleum ether/dichloromethane, 2:1):

Fraction I ($R_f = 0.98$): 147 mg (14%) of 6-methylbenzo[g,h,i]perylene (**13-H**) as a yellow solid (hexane/dichloromethane, 5:1) m.p. 165–167°C. – IR (KBr): $\tilde{\nu} = 3030$ cm^{-1}, 2950, 2905, 2850, 1610, 1590, 1445, 1330, 1260, 1160, 1140, 1090, 1020, 880, 855, 840, 820, 760, 720, 640. – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.82$ (s, 3H, CH_3), 7.97–8.22 (m, 7H, aromatic H), 8.34 (d, 2H, aromatic H), 8.82 (s, 1H, 7-H), 8.98 (dd, 1H, 8-H). – MS (70 eV): *m/z* (%) = 290 (100) [M^+], 289 (32) [M^+ – H], 287 (26) [M^+ – 3H], 276 (32) [M^+ – CH_2].

$C_{23}H_{14}$ (290.4) Calcd. C 95.14 H 4.85
Found C 94.83 H 4.89

II ($R_f = 0.38$): 184 mg (17%) of **1-H**, m.p. 116–119°C. – IR (KBr): $\tilde{\nu} = 3540$ cm^{-1}, 3350 (bs), 2940, 1435, 1160, 1035, 975, 850, 845, 790, 745. – ^{1}H NMR (270 MHz, $CDCl_3$): AB system ($\delta_A = 3.66$, $\delta_B = 3.94$, $^2J_{AB} = -13.6$ Hz, 2H, CH_2OH), 7.16 (ddd, 1H, aromatic H), 7.49 (ddd, 1H, aromatic H), 7.72 (d, 2H, aromatic H), 7.76 (d, 1H, aromatic H), 7.84 (d, 1H, aromatic H), 7.91 (s, 2H, aromatic H), 7.93–7.97 (m, 5H, aromatic H). – MS (70 eV): *m/z* (%) = 308 (8.0) [M^+], 290 (45) [$M^+ - H_2O$], 277 (100) [$M^+ - CH_2OH$].

10-(Hydroxymethyl)-12-methyldibenzo[c,g]phenanthrene (**1-Me**): According to the above procedure 500 mg (1.2 mmol) of **11-Me** was converted to 242 mg (86%) of **1-Me**, isolated by chromatography ($R_f = 0.30$, dichloromethane/petroleum ether, 2:1), m.p. 99–101°C (dichloromethane/hexane, 2:1) as yellow needles. – IR (KBr): $\tilde{\nu} = 3540$ cm^{-1}, 3040, 2900, 1590, 1365, 1290, 1025, 840, 820, 750. – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.21$ (s, 3H, Ar-CH_3), AB system ($\delta_A = 3.71$, $\delta_B = 3.99$, $^2J_{AB} = -13.5$ Hz, 2H, CH_2OH), 7.31 (d, 1H, aromatic H), 7.59 (s, 1H, 11-H), 7.68–7.75 (m, 2H, aromatic H), 7.82–8.01 (m, 8H, aromatic H). – MS (70 eV): *m/z* (%): = 322 (20) [M^+], 304 (22) [$M^+ - H_2O$].

$C_{24}H_{18}O$ (322.4) Calcd. C 89.41 H 5.62
Found C 89.19 H 5.75

12-Methyldibenzo[c,g]phenanthrene-10-carbaldehyde (**14-Me**): 230 mg (0.71 mmol) of **1-Me** and 664 mg (1.78 mmol) of pyridinium dichromate were stirred in 3.5 ml of dichloromethane for 24 h. Silica gel (2 g) was added, the solvent removed and the residue chromatographed ($R_f = 0.35$, dichloromethane) to give 205 mg (90%) of **14-Me**, yellow prisms, m.p. 193–195°C (hexane/dichloromethane, 10:1). – IR (KBr): $\tilde{\nu} = 3040$ cm^{-1}, 2950, 1670, 1600, 1365, 1295, 845, 795, 760, 690. – ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.22$ (s, 3H, Ar-CH_3), 7.65 (s, 1H, 14-H), 7.29–8.20 (m, 11H, aromatic H), 9.22 (s, 1H, Ar-CHO). – MS (70 eV): *m/z* (%) = 320 (29) [M^+], 291 (41) [M^+ – CHO], 276 (100) [M^+ – CHO – CH_3].

$C_{24}H_{16}O$ (320.4) Calcd. C 89.97 H 5.03
Found C 89.30 H 5.00

General Method for the Addition of Grignard Reagents to **14-Me**: To a solution of 0.28 mmol of **14-Me** in 10 ml of dry THF was added with stirring at 22°C within 5 min the corresponding Grignard reagent. The resulting mixture was stirred for an additional 1 h and then poured into 50 ml of ice-cold 2 N hydrochloric acid. The aqueous layer was extracted with two portions of diethyl ether (15 ml each), the combined organic layers were washed twice with water (8 ml each) and a satd. sodium chloride solution (8 ml). Evaporation of the solvent gave the pure alcohols. An analytically pure sample was obtained by recrystallization from hexane/dichloromethane (5:1).

10-(1'-Hydroxyethyl)-12-methyldibenzo[c,g]phenanthrene (**15a-Me**): The reaction of 30 mg (0.093 mmol) of **14-Me** with 0.1 ml of a 3 M methylmagnesium bromide solution in THF gave 30 mg (95%) of **15a-Me**, m.p. 161–162 °C (hexane/dichloromethane, 5:1). – IR (KBr): $\tilde{\nu}$ = 3550 cm^{-1}, 3040, 2960, 2910, 1360, 1260, 1130, 1095, 1065, 1030, 1000, 960, 870, 835, 815, 750, 705, 640. – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.61 (d, ^3J = 6.2 Hz, 3H, CHOH-CH_3), 2.28 (s, 3H, Ar-CH_3), 4.73 (q, ^3J = 6.2 Hz, 1H, CHOHCH$_3$), 7.32–7.95 (m, 12H, aromatic H).

$C_{25}H_{20}O$ (336.4) Calcd. 318.1408 ($M^+ - H_2O$)
Found 318.1407 (MS)

10-(1'-Hydroxy-1'-phenylmethyl)-12-methyldibenzo[c,g]phenanthrene (**15b-Me**): The reaction of 90 mg (0.28 mmol) of **14-Me** with 5 ml of a 0.3 M phenylmagnesium chloride solution gave 101 mg (91%) of **15b-Me**, yellow needles m.p. 158–159 °C (hexane/dichloromethane, 5:1). – IR (KBr): $\tilde{\nu}$ = 3540 cm^{-1}, 3020, 2890, 1475, 1430, 1350, 1170, 1150, 1130, 1030, 835, 750, 720, 705, 685, 640. – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.29 (s, 3H, Ar-CH_3), AX system (δ_A = 1.17, δ_X = 5.76, $^3J_{AX}$ = 2.5 Hz, 2H, Ar_2CH-OH), 6.22–6.32 (m, 2H, phenyl-H), 7.39–7.99 (m, 12H, aromatic H), 6.78–6.83 (m, 3H, phenyl-H). – MS (70 eV): *m/z* (%) = 398 (0.5) [M^+], 380 (32) [$M^+ - H_2O$], 365 (16) [$M^+ - H_2O - CH_3$], 276 (100) [$M^+ - H_2O - CH_3 - C_7H_5$].

$C_{30}H_{22}O$ (398.5) Calcd. C 90.42 H 5.56
Found C 90.42 H 5.60

General Procedure for the Bridging of 10-(hydroxymethyl)dibenzo[c,g]phenanthrenes **1-R** *and* **15-Me**. – *Method A:* A solution of 0.5 mmol of alcohol in 10 ml of dry benzene was treated with 0.1 ml of a 0.58 M solution of phosphorus tribromide in dry benzene. After 0.5 h the resulting mixture was poured into 5 ml of cold water, 20 ml of diethyl ether was added, and the organic layer was washed with 5 ml of 5% Na_2CO_3 solution, 5 ml of water and 10 ml of a satd. sodium chloride solution. Drying with $MgSO_4$, evaporation of the solvent and column chromatography of the residue yielded the methano-bridged helicenes.

Method B: A solution of 0.31 mmol of the alcohol and 0.49 mmol of triethylamine in 5 ml of dichloromethane was kept at 0 °C, then 1 ml of a 0.43 M solution of methanesulfonyl chloride in dichloromethane was added dropwise with stirring within 5 min. The reaction mixture was stirred for 3 h at room temperature and the reaction quenched by the addition of 10 ml of water and 15 ml of dichloromethane. The organic layer was washed with three portions (3 ml each) of 2 N hydrochloric acid, 3 ml of water, three portions (5 ml each) of 5% NaOH, and 5 ml of a satd. sodium chloride solution and dried with $MgSO_4$. After evaporation of the solvent the methano-bridged helicene was isolated by chromatography.

10,11-Methanodibenzo[c,g]phenanthrene (**2-H**): According to the above procedure (method B), 95 mg (0.31 mmol) of **1-H** was converted to 81 mg (90%) of **2-H** (after chromatography, R_f = 0.32, hexane/dichloromethane, 4:1), m.p. 158 °C (hexane/dichloromethane, 5:2). – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2960, 1440, 1260, 1080, 1020, 840, 780, 760, 720, 680. – ^1H NMR (400 MHz, $CDCl_3$): δ = 4.40 (br. s, 2H, Ar_2CH_2), ABC system [δ_A = 7.65, δ_B = 7.68, δ_C = 7.81, $^3J_{BC}$ = 6.6, $^3J_{AB}$ = 7.2, $^4J_{AC}$ = 2.4 Hz, 6H, 7(8,9,12,13,14)-H], AB system [δ_A = 7.13, δ_B = 7.87, $^3J_{AB}$ = 9.0 Hz, 4H, 1(2,5,6)-H], 8.13 [s, 2H, 3(4)-H]; coalescence temperature 294 K. – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 44.89 (–, Ar_2CH_2), 125.33 (+), 126.04 (+), 126.96 (+), 127.51 (+), 128.09 (+), 130.5 (Φ), 131.0 (Φ), 132.6 (Φ), 133.3 (Φ), 138.6 (Φ). – MS (70 eV): *m/z* (%) = 290 (100) [M^+], 289 (64) [$M^+ - H$], 144 (31) [$M^{++} - 2H$].

$C_{23}H_{14}$ Calcd. 290.1096 Found 290.1120 (MS)

12-Methyl-10,11-methanodibenzo[c,g]phenanthrene (**2-Me**): Reaction of 175 mg (0.54 mmol) of **1-Me** according to method A above gave, after filtration through silica gel (R_f = 0.94, hexane/dichloromethane, 4:1), 150 mg (91%) of **2-Me**, pale yellow needles, m.p. 122–123 °C (hexane/dichloromethane, 20:1). – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 1435, 1315, 1160, 840, 825, 790, 770, 760, 750, 715. – ^1H NMR (400 MHz, $C_6D_5NO_2$, 20 °C): δ = 2.78 (s, 3H, Ar-CH_3), 3.60 (d, ^2J = 12.7 Hz, Ar_2C-H^{endo}), 4.37 (d, ^2J = 12.7 Hz, Ar_2C-H^{exo}), 7.54–8.17 (m, 11H, aromatic H); coalescence temperature 350 K. – ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 131.3–138.4 (11 C, Φ, C-Ar), 124.2–129.8 (11 C, +, C-Ar), 38.4 (–, Ar-CH_2-Ar), 20.3 (+, Ar-CH_3). – MS (70 eV): *m/z* (%) = 304 (100) [M^+].

$C_{24}H_{16}$ (304.4) Calcd. C 94.70 H 5.30
Found C 94.85 H 5.29

12,15-Dimethyl-10,11-methanodibenzo[c,g]phenanthrene (**16a-Me**): According to the above procedure (method A) 25 mg (0.074 mmol) of **15a-Me** was converted to 21 mg (89%) of **16a-Me** (*endo:exo* = 5:1), m.p. 154–155 °C (hexane). – IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1}, 2940, 2900, 1438, 1353, 1292, 1163, 1010, 830, 775, 750, 715, 675. – *exo*-**16**: ^1H NMR (270 MHz, $CDCl_3$): δ = 1.06 (d, ^3J = 7.6 Hz, 3H, Ar_2CH-CH_3), 2.89 (s, 3H, Ar-CH_3), 5.08 (q, ^3J = 7.6 Hz, 1H, Ar_2CH-CH_3), 7.56–8.17 (m, 11H, aromatic H). – *endo*-**16**: ^1H NMR (270 MHz, $CDCl_3$): δ = 1.87 (d, ^3J = 7.6 Hz, 3H, Ar_2CH-CH_3), 2.91 (s, 3H, Ar-CH_3), 4.49 (q, ^3J = 7.6 Hz, 1H, Ar_2CH-CH_3), 7.42–8.19 (m, 11H, aromatic H). – MS (70 eV): *m/z* (%) = 318 (62) [M^+], 303 (100) [$M^+ - CH_3$].

$C_{25}H_{18}$ (318.4) Calcd. C 94.30 H 5.70
Found C 94.41 H 5.85

12-Methyl-15-phenyl-10,11-methanodibenzo[c,g]phenanthrene (**16b-Me**): According to the above procedure (method A) 40 mg (0.1 mmol) of **15b-Me** gave 34 mg (89%) of **16b-Me**, m.p. 220–221 °C (dichloromethane/hexane, 1:10), as colorless needles. – IR (KBr):

Table 1. Atomic coordinates [$\times 10^4$] and equivalent isotropic thermal parameters [$pm^2 \times 10^{-1}$] for non-hydrogen atoms of **2-Me** with e.s.d.'s of the least significant figure in parentheses; equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
C(1)	318(1)	-2727(2)	-9969(1)	47(1)
C(2)	820(2)	-3233(2)	-10658(1)	54(1)
C(3)	220(2)	-2979(2)	-11358(1)	56(1)
C(4)	-935(2)	-2375(2)	-11400(1)	50(1)
C(5)	-1500(2)	-1945(3)	-12128(1)	64(1)
C(6)	-2596(2)	-1291(3)	-12160(1)	66(1)
C(7)	-3286(2)	-1257(2)	-11491(1)	55(1)
C(8)	-4487(2)	-898(3)	-11611(1)	65(1)
C(9)	-5251(2)	-1284(3)	-11054(1)	64(1)
C(10)	-4837(2)	-2002(2)	-10344(1)	53(1)
C(11)	-5686(2)	-2743(3)	-9864(1)	63(1)
C(12)	-5371(2)	-3645(3)	-9220(1)	61(1)
C(13)	-4174(2)	-3676(2)	-8942(1)	50(1)
C(14)	-3868(2)	-4457(3)	-8230(1)	60(1)
C(15)	-2765(2)	-4270(3)	-7884(1)	60(1)
C(16)	-1955(2)	-3230(2)	-8241(1)	50(1)
C(17)	-2215(1)	-2495(2)	-8961(1)	41(1)
C(18)	-1356(1)	-1301(2)	-9302(1)	43(1)
C(19)	-833(1)	-2098(2)	-10002(1)	41(1)
C(20)	-1534(1)	-2089(2)	-10701(1)	42(1)
C(21)	-2796(1)	-1755(2)	-10746(1)	43(1)
C(22)	-3613(1)	-2121(2)	-10142(1)	43(1)
C(23)	-3309(1)	-2778(2)	-9363(1)	41(1)
C(24)	1052(2)	-2839(3)	-9225(1)	59(1)

$\tilde{\nu}$ = 3020 cm^{-1}, 2940, 1475, 1245, 1080, 1020, 850, 830, 795, 780, 740, 720, 710, 680. – ^1H NMR (400 MHz, $CDCl_3$): 1.54 (s, 1H, Ar_3CH), 2.98 (s, 3H, Ar-CH_3), AA'BB'C system [δ_A = 6.68, δ_B = 6.59, δ_C = 5.88, $^3J_{AB}$ = 7.2, $^3J_{BC}$ = 8.0 Hz, 5H, 4(3,5,2,6)-H], 7.64–7.98 (m, 11H, aromatic H). – MS (70 eV): *m/z* (%) = 380 (100) [M^+].

$C_{30}H_{20}$ (380.5) Calcd. C 94.70 H 5.30 Found C 94.23 H 5.42
C 94.35 H 5.36

X-Ray Structure Analysis of **2-Me**[13]: $C_{24}H_{16}$ (304.4); monoclinic crystals, space group $P2_1/n$, a = 1142.1(2), b = 775.2(2), c = 1723.9(3) pm, β = 93.06(3)°, Z = 4, V = 1.5241(5) nm^3, ϱ = 1.362 g cm^{-3}. Diffractometer: Syntex $P2_1$, total number of reflections 3068, Mo-K_α, $2\Theta < 50°$. Direct methods using SHELX-76, and SHELXL-92 for refinement on R^2 to $R1$ = 5.9%. For atomic coordinates and U(eq)values, see Table 1.

☆ Dedicated to Professor *Henry Shine* on the occasion of his 70th birthday.

[1] For a review see: W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130.
[2] R. H. Martin, M. J. Marchant, *Tetrahedron* **1974**, *30*, 347–349.
[3] H. J. Lindner, *Tetrahedron* **1975**, *31*, 281–284.
[4] C. Puls, Dissertation, Universität Hamburg, **1989**.
[5] R. H. Martin, *Angew. Chem.* **1974**, *86*, 727–738; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660.
[6] The skeletons of all compounds called helicenes in the text are numbered according to the original suggestion by M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770. The dibenzo[*c*,*g*]phenanthrene nomenclature refers to the IUPAC rules.
[7] H. Numan, H. Wynberg, *Tetrahedron Lett.* **1975**, 1097–1100.
[8] [8a] R. H. Martin, J. Jespers, N. Defay, *Tetrahedron Lett.* **1975**, *13*, 1093–1096. – [8b] J. H. Borkent, P. H. F. M. Rouwette, W. H. Laarhoven, *Tetrahedron* **1978**, *34*, 2569–2571.
[9] P. Hugelshofer, J. Kalvoda, K. Schaffner, *Helv. Chim. Acta* **1960**, *43*, 1322–1332.
[10] [10a] For recent examples see: L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769–3775. – [10b] K. Deshayes, R. D. Broene, I. Chao, C. B. Knobler, F. Diederich, *J. Org. Chem.* **1991**, *56*, 6787–6795.
[11] Photocyclization was carried out in a falling-film-reactor purchased from NORMAG, Otto Fritz GmbH, D-6238 Hofheim/Taunus, Germany.
[12] M. Gorsane, R. H. Martin, *Bull. Soc. Chem. Belg.* **1985**, *94*, 205–214.
[13] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-57306, the names of the authors, and the journal citation.
[14] Cf. H. Günther, *NMR-Spektroskopie*, 3. ed., Thieme, Stuttgart, **1992**, p. 310f.

[467/92]