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High Temperature Synthesis to Bowl-Shaped Subunits of Fullerenes - IV.[1] From 4-[9*H*-Fluorenylidene-(9)]-4*H*-cyclopenta[def]phenanthrene to Fluoreno[1,9,8-abcd]corannulene and Difluoreno[1,9,8,7-cdefg;2′,1′,9′,8′-klmno]anthracene[2]

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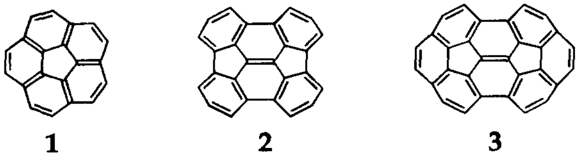
Abstract: Fluoreno[1,9,8-abcd]corannulene (**4**) and difluoreno[1,9,8,7-cdefg;2′,1′,9′,8′-klmno]-anthracene (**8**) have been synthesized by multistage thermal and catalytic dehydrocyclization reactions starting from 4-[9*H*-fluorenylidene-(9)]-4*H*-cyclopenta[def]phenanthrene and benzo[p]naphtho-[1,8,7-ghi]chrysene, respectively.

Bowl-shaped polycyclic aromatic hydrocarbons (PAH), representing curved subunits of buckminsterfullerenes, have recently attracted attention in organic chemistry. Interesting features, as for example the bowl-to-bowl inversion of derivatives of corannulene (**1**) and sandwich structures of polyanions of **1**, have been investigated.[3,4] High temperature syntheses are almost always necessary to overcome the inherent strain energy of the carbon frameworks of the target compounds.[3,5-7] The potential of pyrolytic methods in the generation of PAH with highly curved surfaces was demonstrated by the syntheses of **1**,[5] diindeno[1,2,3,4-defg;1′,2′,3′,4′-mnop]chrysene (**2**)[6] and diacenaphtho[3,2,1,8-cdefg;3′,2′,1′,8′-lmnop]chrysene (**3**)[8] (Scheme 1).

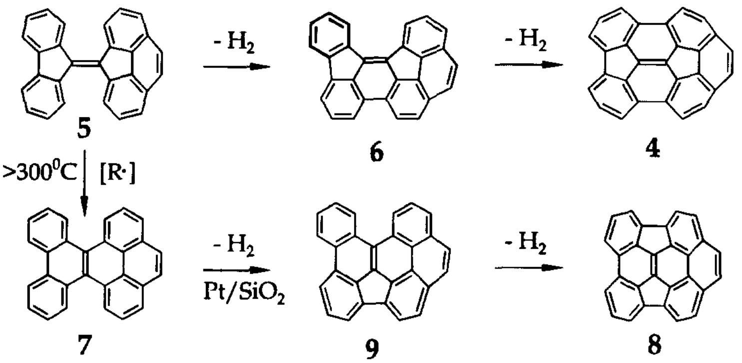
Scheme 1



In the course of our investigations on methylene bridged PAH as parent compounds for the generation of aromatics with highly curved structures, we synthesized fluoreno[1,9,8-abcd]corannulene (**4**) starting from 4-[9*H*-fluorenylidene-(9)]-4*H*-cyclopenta[def]phenanthrene (**5**) by double thermal dehydrocyclization

(Scheme 2). As well as **2** and **3** the PAH **4** belongs to that group of aromatic hydrocarbons which have a pyracyclene core surrounded by four to six pericondensed benzene rings.

Scheme 2



At a temperature of 780 °C, the Flow Pyrolysis (FP, 101 kPa) of **5** in nitrogen as carrier gas yields diindeno[4,3,2,1-cdef;1′,2′,3′-hi]chrysene (**6**) and benzo[p]naphtho[1,8,7-ghi]chrysene (**7**). The formation of **6** is thought to occur via an electrocyclic ring closure followed by hydrogen loss, and that of **7** via a homoallyl-cyclopropyl-carbinyl rearrangement.[9,10]

The isomerization of **5** to **7** is obviously initiated by hydrogen atoms as well as by other small radicals. Compared to the thermal conversion in nitrogen the ratio (r) of the selectivities (S) of the products **6** and **7** [r = S(**7**)/S(**6**)] can be increased by the factor of 3.2 in H_2 as carrier gas, and decreased by the factor of 3.4 using N_2 with addition of 3 vol. % of toluene. The reaction of highly reactive chain carrier radicals with toluene results in conjugatively stabilized and relatively bulky benzyl radicals, which are sterically hindered in the addition to the central double bond of **5** and the initiation of the homoallyl-cyclopropyl-carbinyl rearrangement is suppressed. [6]

The evaporation of **5** is accompanied by the formation of coke-like products in the evaporation zone. Other side reactions are indicated by the formation of traces of dibenzo[g,p]chrysene, benzo[e]indeno[1,2,3-hi]acephenanthrylene and tetrabenzo[de,hi,mn,qr]naphthacene. These PAH are products of the thermal conversions of 9,9′-bi-9*H*-fluorenylidene [6] and 4,4′-bi-4*H*-cyclopenta[def]phenanthrenylidene [1] which are not inherent in the starting material (**5**) but they possibly can be formed in part by decomposition of the polymerizate of **5** on heating.

At 980 °C (FP) in nitrogen as carrier gas, **6** yields traces (0.6 %) of the bowl-shaped **4** by further thermal dehydrocyclization. The strain energy of the target compound **4** and the geometry of the starting PAH **6** can account for the low yield. A thermal electrocyclic ring closure in **6** (followed by hydrogen elimination) is inhibited because all three participating double bonds in **6** are incorporated in aromatic systems and the carbon atoms forming the new CC-bond exhibit an unfavourably large distance. The strained carbon framework in **4** causes a relatively high difference in the heats of formation for **4** and **6** ($\Delta[\Delta_F H(\mathbf{4}) - \Delta_F H(\mathbf{6})] = 58.3$ kcal/mol, see Table 1), which necessitates the high reaction temperature for its synthesis.

Due to the facts, that thermal rearrangements of PAH have been observed at temperatures of about 1000 °C, [6,11] and that the structural isomer of **4**, the difluoreno[1,9,8,7-cdefg;2′,1′,9′,8′-klmno]anthracene (**8**), might give similiar analytical data, we synthesized **8** by a twofold dehydrocyclization starting from **7** (see Scheme 2). The first step was performed on a 0.7 wt. % Pt/SiO_2 catalyst at temperatures of 750 °C resulting in indeno[1,2,3,4-defg]naphtho[1,8,7-pqr]chrysene (**9**, yield 25 %). With regard to the formation of five-membered carbon rings in PAH, catalytic dehydrocyclization presents great advantages in comparison to thermal, noncatalytic reactions, because only less, or no target products, could be observed under FP or Flash Vacuum Pyrolysis (FVP) conditions. [1,6,12,13]

The second cyclization step from **9** to **8** was performed at 980 °C in N_2 (FP) and results in a very low yield of only 0.2 %, for which the explanation already given for the formation of **4** is also applicable ($\Delta[\Delta_F H(\mathbf{8}) - \Delta_F H(\mathbf{9})] = 57.5$ kcal/mol, see Table 1). The activation energy of the thermal ring closure should be very high, because the reaction is assumed to occur initially by a C-H bond breaking in the fjord region of **9**, followed by cycloaddition of the resulting aryl radical as has been suggested by Plater. [13] Additionally, the compounds **2**, **3** and **4** decompose at temperatures above 300-330 °C without melting, [6,7] and the PAH **8** decomposes immediately after melting, which indicates not only the relatively low thermal stabilities of these highly curved PAH (compared to the majority of the normal planar PAH), but it also lets understand the basically low yields of the syntheses of this type of aromatics at very high temperatures as an intrinsic phenomenon.

Despite the low contents of **4** and **8** in the corresponding pyrolysates, their separation is possible with acceptable efforts by column chromatography because of their significantly shorter retention volumes in comparison with those of planar PAH of similiar size. This seems to be a common feature of bowl-shaped PAH which is valid for **1**, **2**, **4** and **8** at least, and it agrees with a similiar behavior observed in RP-HPLC.[14]

The structural assignment of the PAH, synthesized in this work, is given by the data from UV/VIS, ^{1}H NMR, IR (in part) and mass spectra (see experimental part). On comparing the electron absorption spectra of the PAH **6** and **9** with those ones previously synthesized, [1,6] bathochrome shifts for the β- and p-bands can be noted in passing from benzo[g]indeno[1,2,3,4-mnop]chrysene (**10**) to indeno[1,2,3,4-defg]naphtho-[1,8,7-pqr]chrysene (**9**) and finally to dibenzo[mn,qr]fluoreno[2,1,9,8,7-defghi]naphthacene (**11**), due to the linear benzanellation to the central naphthalene unit (see Figure 1). A similiar anellation effect was given for the PAH dibenzo[g,p]chrysene, benzo[p]naphtho[1,8,7-ghi]chrysene (7) and tetrabenzo[de,hi,mn,qr]naphthacene by Clar et al. [15] and is in accordance with our own data. [1,6]

On the other hand the electron absorption bands of the PAH benzo[e]indeno[1,2,3-hi]acephenanthrylene (**12**), diindeno[4,3,2,1-cdef;1′,2′,3′-hi]chrysene (**6**) and diindeno[4,3,2,1-opqr;4′,3′,2′,1′-avut]picene (**13**) can not be compared in the same way (see Figure 2), because benzanellation to five-membered carbon rings does not result in comparable regular shifts. [16]

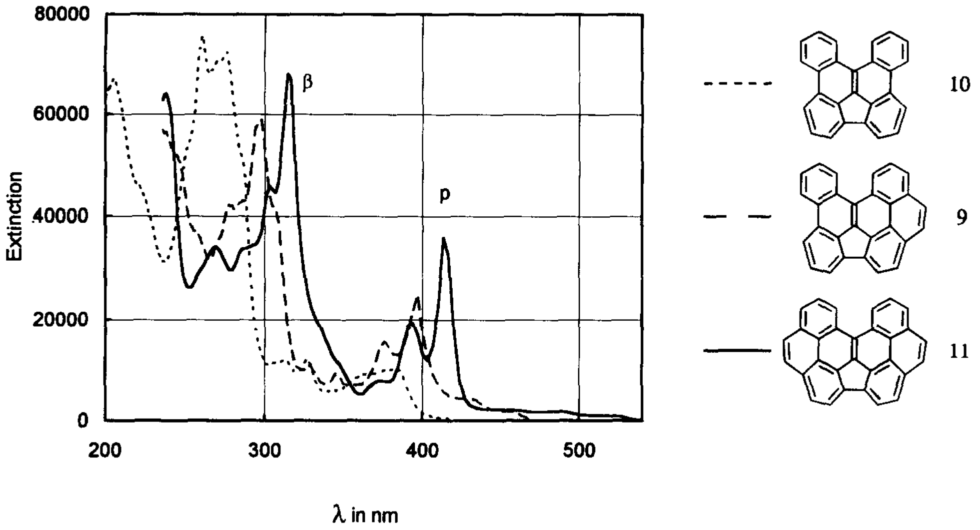


Figure 1. Electron absorption spectra of benzo[g]indeno[1,2,3,4-mnop]chrysene (**10**, in CH_3CN), indeno-[1,2,3,4-defg]naphtho[1,8,7-pqr]chrysene (**9**, in CH_2Cl_2) and dibenzo[mn,qr]fluoreno[2,1,9,8,7-defghi]-naphthacene (**11**, in CH_2Cl_2).

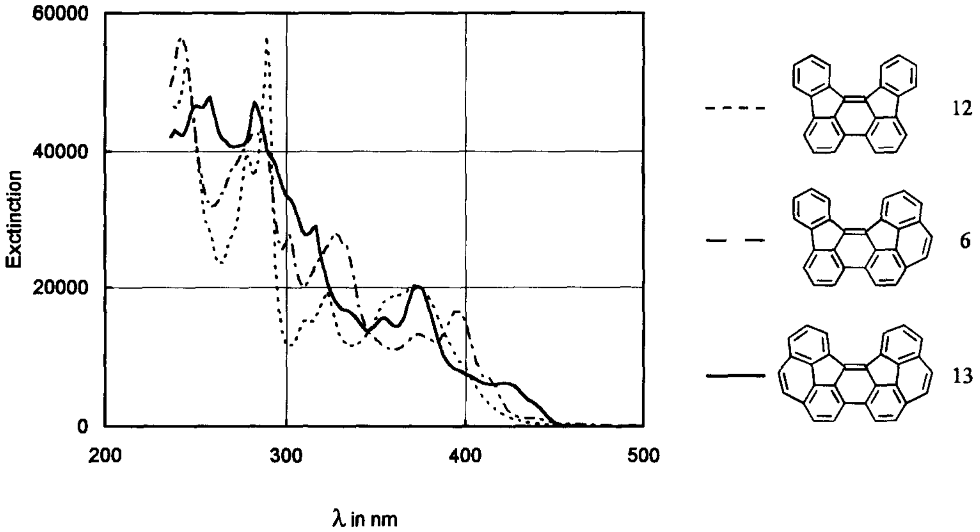


Figure 2. Electron absorption spectra of benzo[e]indeno[1,2,3-hi]acephenanthrylene (**12**, in CH_3CN), diindeno-[4,3,2,1-cdef;1′,2′,3′-hi]chrysene (**6**, in CH_2Cl_2) and diindeno[4,3,2,1-opqr;4′,3′,2′,1′-avut]picene (**13**, in CH_2Cl_2).

Absorptions of the bowl-shaped PAH **4** and **8** as well as the spectra of **2** (see Figure 3 and 4) are dominated by strong peaks in the ultraviolet region and a couple of weaker bands and shoulders in the region above 300 nm. Similiar features are typical for the corresponding spectra of C_{60}- and C_{70}-fullerenes. [17] The absence of a vibrational fine structure can be explained by relatively flexible geometries in **2**, **4** and **8** in contrast to the electron absorption spectra of planar PAH. [16] Comparing the spectra of **2** and **8**, the bathochrome shift of 30 nm of the absorption bands at the highest wavelengths (340-390 nm) could be caused by the linear benzanellation to the central naphthalene unit from **2** to **8** (see Figure 3).

As can be predicted from the structures, the ^{1}H NMR spectra of **4** and **8** each exhibit one singlet (H-3, numeration see Figure 3 and 4), two doublets coupling with each other (H-1, H-2), and two doublets coupling with a double doublet (H-7, H-8, H-9). The pattern of coupling was assigned by coupling constants and by rooting of the doublets (**4**) as well as by a 2D-^{1}H-^{1}H COSY NMR spectra (**8**). The chemical shifts and the coupling constants are in the same region as the corresponding analytical data of the bowl-shaped PAH **2** and **3**. [6,7] The molecular ions of m/e = 348 and the absence of significant fragmentation patterns in the mass spectra are considered to be consistent with the structures of **4** and **8**.

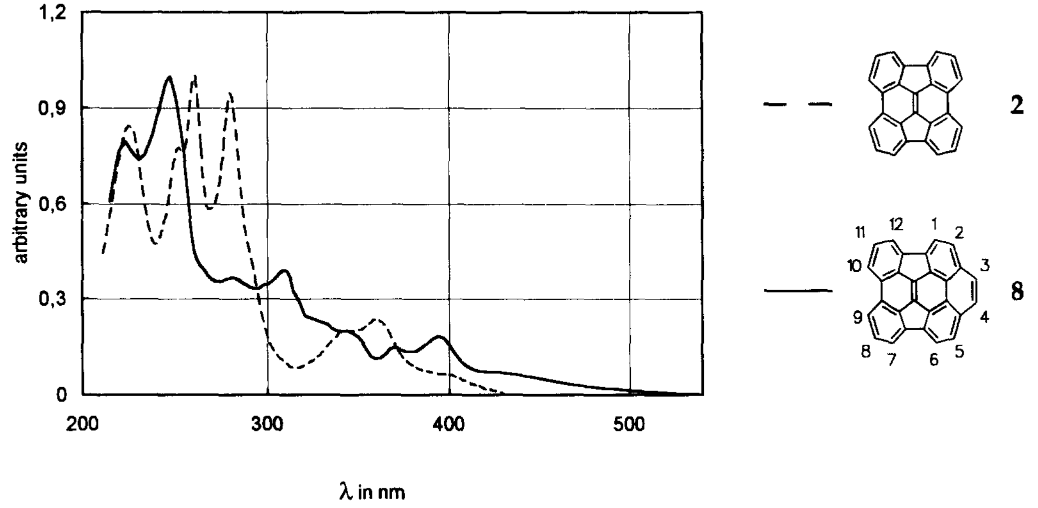


Figure 3. Electron absorption spectra of diindeno[1,2,3,4-defg;1′,2′,3′,4′-mnop]chrysene (**2**, in CH_2Cl_2) and difluoreno[1,9,8,7-cdefg;2′,1′,9′,8′-klmno]anthracene (**8**, in CH_2Cl_2).

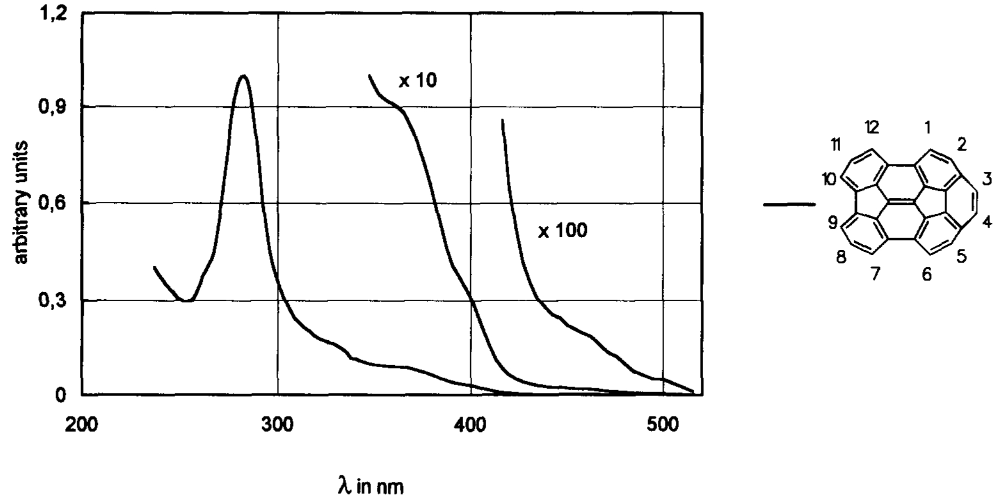


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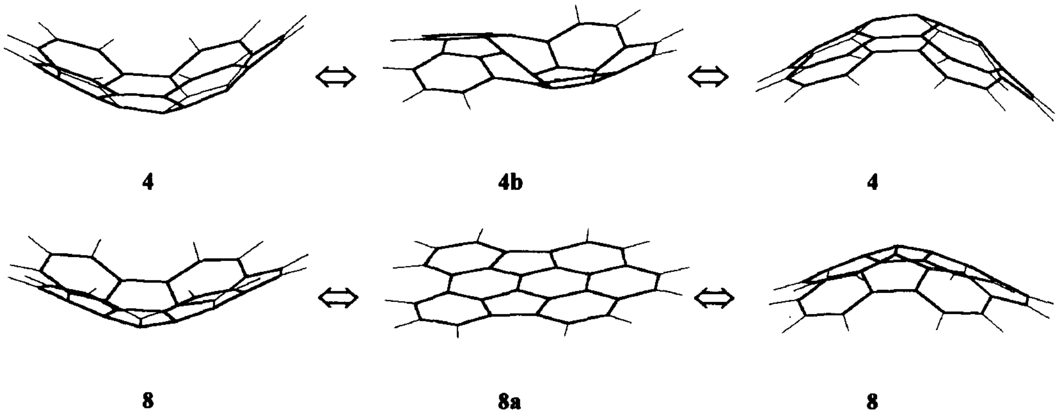
Figure 4. Electron absorption spectra of fluoreno[1,9,8-abcd]corannulene (4, in CH_2Cl_2, including a 10-fold and a 100-fold magnificaton of the corresponding parts).

Semi-empirical geometry optimization using the PM3 parameter set predicts the bowl-shaped C_s topology of the PAH **4** and **8**, which exhibits no imaginary vibrational frequency (see Table 1). [18] In contrast to **3**, which has an additional local minimum at the potential energy surface with a folded chair topology (**3a**, C_{2h}) [7], no analogous conformation was found for **4** and **8**. Frequency analyses of the structures listed in Table 1 indicate a transition state with a folded chair geometry for **4** (**4b**, C_s, see Scheme 3), and a planar transition state for **8** (**8a**, C_{2v}). An equivalent planar transition state (**2a**) has been previously calculated for **2**. [6] All transition conformations (**2a**, **4b** and **8a**) show only one imaginary vibrational frequency.



Scheme 3. Prediction of the bowl-to-bowl inversion of the PAH **4** and **8** according to the optimized structures and frequency analyses given in Table 1.

The calculated activation energies for the bowl-to-bowl inversions increase from **2** (14.1 kcal/mol) to **4** (≈33.5 kcal/mol) and **8** (29.9 kcal/mol), respectively, due to the additional benzanellation in the peri-position. A further benzanellation from **4** to **3** results in an activation energy of more than 50 kcal/mol, as can be estimated from the energy difference between the bowl (**3**) and folded chair (**3b**) conformation. Ab initio calculation results in a value of about 57 kcal/mol.[7]

Table 1. Results of semiempirical geometry optimization, calculation of the heats of formation ($\Delta_F H$ in kcal/mol) and frequency analyses (imaginary vibrational frequencies) using the PM3 parameter set.[18]

compound	formula	symmetry	geometry (shape)	$\Delta_F H$ (kcal/mol)	imaginary frequencies
5	$C_{28}H_{16}$	C_1 (C_2)[a]	cross	158.2	-
7	$C_{28}H_{16}$	C_1 (C_2)[a]	cross	121.9	-
6	$C_{28}H_{14}$	C_1 (C_s)[a]	nearly planar	153.2	-
9	$C_{28}H_{14}$	C_1 (C_s)[a]	nearly planar	143.6	-
4	$C_{28}H_{12}$	C_s	bowl	211.5	-
4a	$C_{28}H_{12}$	C_{2v}	planar	264.9	159i, 102i
4b	$C_{28}H_{12}$	C_s	folded chair	≈ 245	≈ 25i
8	$C_{28}H_{12}$	C_s	bowl	201.1	-
8a	$C_{28}H_{12}$	C_{2v}	planar	231.0	123i
2	$C_{26}H_{12}$	C_{2v}	bowl	184.7	-
2a	$C_{26}H_{12}$	D_{2h}	planar	198.8	102i
3	$C_{30}H_{12}$	C_{2v}	bowl	237.2[b]	-
3a	$C_{30}H_{12}$	D_{2h}	planar	335.5[b]	192i, 151i
3b	$C_{30}H_{12}$	C_{2h}	folded chair	287.4[b]	-

[a] C_1 is the exact geometry with respect to a small curvature in parts of these molecules; otherwise C_2 or C_s geometry, respectively.

[b] Ab initio calculation at HF / 6-31G* // 3-21G level: $\Delta[\Delta_F H(\mathbf{3a}) - \Delta_F H(\mathbf{3})] = 76.1$ kcal/mol and $\Delta[\Delta_F H(\mathbf{3b}) - \Delta_F H(\mathbf{3})] = 51.0$ kcal/mol; no imaginary vibrational frequency for **3** and **3b**, two imaginary vibrational frequencies (150i and 126i) for **3a** at the HF / 3-21G level (Rabideau et al. [7])

ACKNOWLEDGEMENTS

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EXPERIMENTAL PART

Melting points were determined on a Boetius melting point apparatus and are uncorrected. - IR: Specord M80 (Carl-Zeiss-Jena). - UV/VIS: Specord M40 (Carl-Zeiss-Jena). - ^{1}H NMR: Bruker AM 250 (250 MHz), Varian Unity 400 (100.1 MHz), $\delta = 7.26$ for chloroform, 2.00 for [D$_6$]acetone as internal standard. - GC-MS: HP 5890 Series II (12 m glass capillary, Ultra 1, He, MSD HP 5971. - Column chromatography on aluminium oxide (Fluka 06300, neutral, 100-125 mesh) with cyclohexane/toluene; eluation by gradient method starting with cyclohexane (100%) up to cyclohexane (50%) / toluene (50%). - Thin layer chromatography (TLC) on aluminium oxide (Merck 5550, neutral) with cyclohexane/toluene. - Pyrolysis in a sectional, electrically heated quartz reactor with an evaporation zone (100 mm, 300 °C) and a reaction zone (l = 350 mm). The inner diameter (i.d.), the reaction temperature, and the respective carrier gas used are given below.

4-[9*H*-Fluorenylidene-(9)]-4*H*-cyclopenta[def]phenanthrene (5): 30 mmol butyllithium in 15 ml cyclohexane was added to a cooled solution (-30 °C) of 5.01 g (26.4 mmol) 4*H*-cyclopenta[def]phenanthrene [19] in 80 ml dry tetrahydrofuran (THF) and stirred for 45 min. 5.43g (30.2 mmol) Fluorenone in 20 ml THF was added dropwise to the orange slurry. The resulting dark red solution was stirred for 16 h, quenched with water, extracted with diethyl ether / THF (1:1), dried and evaporated to dryness. [20] The carbinol (F_p = 187 °C, ref. 188-189 °C [21]) and 0.1 g p-toluenesulfonic acid was dissolved in 200 ml toluene, refluxed for 2 h until no carbinol was detected by TLC. The reaction mixture was washed with water and dried. Recrystallization in ethanol/toluene results in 6.08 g (overall yield 68%) of **5** (red crystals). - mp 198-201.5 °C (ethanol/toluene, ref. 198 °C [21]). - IR (KBr): ν = 1496 cm^{-1}, 1448, 1416, 1356, 1320, 821 (s), 780, 762, 744, 720 (s), 644, 592. - UV (CH$_2$Cl$_2$): λ_{max} (lg ε) = 272 nm (4.566), 280 (4.504), 306 (4.048), 363 (4.073), 474 (4.253), 501 (4.221). - ^{1}H NMR (CS$_2$/[D$_6$]acetone = 3:1, 400 MHz): δ = 8.54 (d, J = 7.6 Hz, 2H), 8.40 (d, J = 7.6 Hz, 2H), 7.74 (s, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 7.2 Hz, 2H), 7.54 (dd, J = 7.6 Hz and J = 7.6 Hz, 2H), 7.32 (dd, J = 7.6 Hz and J = 7.6 Hz, 2H), 7.22 (dd, J = 7.6 Hz and J = 7.6 Hz, 2H). - GC-MS (70 eV), m/z (%): 353 (27) [M$^+$+1], 352 (100) [M$^+$], 351 (76) [M$^+$-1], 350 (56) [M$^+$-2], 175 (57) [M^{++}-2], 174 (44) [M^{++}-4].

Diindeno[4,3,2,1-cdef;1′,2′,3′-hi]chrysene (6) and **benzo[p]naphtho[1,8,7-ghi]chrysene (7)**: 3.08 g (8.75 mmol) of **5** was pyrolyzed in six equivalent portions at 780 °C (15 mm i.d., 30 l/h N$_2$). The purification of the accumulated pyrolyzate by column chromatography resulted in 680 mg (1.93 mmol, 22 %) of **7** (white crystals) and 390 mg (1.11 mmol, 13%) of **6** (canary-yellow needles). Traces (100 mg in sum) of dibenzo[g,p]chrysene, benz[e]indeno[1,2,3-hi]acephenanthrylene [6] and tetrabenzo[de,hi,mn,qr]naphthacene [1] were also separated.

(**6**): mp 295-296 °C (CHCl$_3$). - IR (KBr): ν = 1492 cm^{-1}, 1444, 824 (s), 784, 760, 750, 732 (s), 672, 636, 576. - UV (CH$_2$Cl$_2$): λ_{max} (lg ε) = 250 nm (4.851), 257 (4.889), 283 (4.877), 293 (sh, 4.804), 316 (4.668), 338 (sh, 4.450), 354 (4.400), 372 (4.494), 398 (4.148), 425 (sh, 3.999), 445 (3.760). - ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.58 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 7.2 Hz, 1H), 8.50 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H), 8.05 - 8.02 (m, 4H), 7.87 - 7.82 (m, 2H), 7.60 (dd, J = 7.6 Hz and J = 7.4 Hz, 1H), 7.55 (dd, J = 7.6 Hz and J = 7.2 Hz, 1H). - GC-MS (70 eV), m/z (%): 351 (30) [M^{+}+1], 350 (100) [M^{+}], 348 (23) [M^{+}-2], 175 (36) [M^{++}], 174 (38) [M^{++}-2].

(7): mp 267-268.5 °C (cyclohexane/toluene), ref. 259-261 °C[15]. - IR (KBr): ν = 1600 cm^{-1}, 1582, 1496, 1448, 1436, 1316, 1192, 1152, 1106, 1052, 832 (s), 796, 772, 764, 752, 732, 724 (s), 616, 592, 548, 512. - UV (CH_2Cl_2): λ_{max} (lg ε) = 241 nm (4.683), 249 (sh, 4.673), 272 (4.460), 278 (4.467), 291 (4.399), 303 (4.666), 317 (4.871), 366 (4.276), 378 (4.288), 401 (3.560). - ^{1}H NMR (CS_2/[D_6]acetone = 3:1, 400 MHz): δ = 8.92 (d, J = 8.0 Hz, 2H), 8.82 (d, J = 8.0 Hz, 2H), 8.68 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 7.6 Hz, 2H), 8.05 (s, 2H), 7.99 (dd, J = 7.6 Hz and J = 7.6 Hz, 2H), 7.66 (dd, J = 7.6 Hz and J = 7.6 Hz, 2H), 7.61 (dd, J = 7.6 Hz and J = 7.6 Hz, 2H). - GC-MS (70 eV), m/z (%): 353 (29) [M^{+}+1], 352 (100) [M^{+}], 351 (37) [M^{+}-1], 350 (35) [M^{+}-2], 175 (40) [M^{++}-2], 174 (45) [M^{++}-4].

Indeno[1,2,3,4-defg]naphtho[1,8,7-pqr]chrysene (9): 100 mg (0.284 mmol) of **7** was converted over a 0.7 wt.% Pt/SiO_2 catalyst at temperatures of 750 °C (catalysis zone 50 mm long, i.d. = 15 mm, 30 l/h N_2). The separation by column chromatography resulted in 7.5 mg (0.021 mmol, 7.5 %) of **7** and 24.8 mg (0.071 mmol, 25 %) of **9** (yellow needles). - mp 311.5-313.5 °C. - IR (KBr): ν = 1400 cm^{-1}, 836 (s), 808, 762 (s), 732 (s), 700, 660, 636, 580, 568, 536. - UV (CH_2Cl_2): λ_{max} (lg ε) = 280 nm (4.453), 287 (4.460), 297 (4.596), 328 (3.849), 346 (3.781), 376 (4.012), 396 (4.215), 430 (3.471), 453 (sh, 3.121). - ^{1}H NMR (CS_2/[D_6]acetone, 400 MHz): δ = 9.64 (d, J = 8.4 Hz, 1H), 9.51 (d, 8.4 Hz, 1H), 8.88 (d, J = 7.8 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.22-8.16 (m, 3H), 8.11 (s, 2H), 7.87 (dd, 1H), 7.800 - 7.780 (m, 2H). - GC-MS (70 eV), m/z (%): 351 (31) [M^{+}+1], 350 (100) [M^{+}], 348 (24) [M^{+}-2], 175 (17) [M^{++}], 174 (24) [M^{++}-2].

Fluoreno[1,9,8-abcd]corannulene (4): 200 mg (0.571 mmol) of **6** was pyrolyzed in four equivalent portions at 980 °C (6 mm i.d., 10 l/h N_2). The purification of the accumulated pyrolyzate by column chromatography resulted in 1.2 mg (3.45 µmol, 0.6%) of **4** (pale yellow crystals). - mp >300 °C (dark.). - UV (CH_2Cl_2): λ_{max} = 263 nm (sh), 282, 328 (sh), 365 (sh), 397 (sh), 453 (sh). - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.17 (d, J = 8.1 Hz, 2H, H-7/H-9), 8.16 (d, 8.9 Hz, 2H, H-1/H-2), 7.75 (d, J = 7.1 Hz, 2H, H-7/H-9), 7.72 (d, J = 8.9 Hz, 2H, H-1/H-2), 7.66 (s, 2H, H-3), 7.57 (dd, J = 8.1 Hz and J = 7.2 Hz, 2H, H-8). - GC-MS (70 eV), m/z (%): 349 (36) [M^{+}+1], 348 (100) [M^{+}], 346 (15) [M^{+}-2], 174 (23) [M^{++}], 173 (22) [M^{++}-2].

Difluoreno[1,9,8,7-cdefg;2′,1′,9′,8′-klmno]anthracene (8): 300 mg (0.857 mmol) of **9** was pyrolyzed in six equivalent portions at 980 °C (6 mm i.d., 10 l/h N_2). The purification of the accumulated pyrolyzate by column chromatography resulted in approximately 0.5 mg (1.4 µmol, 0.2 %) of **8** (red crystals). - mp = 337-340 °C (dark.). - UV (CH_2Cl_2): λ_{max} = 223 nm, 245, 280, 297, 307, 326 (sh), 343 (sh), 368, 390. - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, J = 8.0 Hz, 2H, H-7/H-9), 8.02 (d, 8.0 Hz, 2H, H-1/H-2), 7.90 (d, J = 8.0 Hz, 2H, H-1/H-2), 7.78 (s, 2H, H-3), 7.77 (d, J = 7.2 Hz, 2H, H-7/H-9), 7.54 (dd, J = 8.0 Hz and J = 7.2 Hz, 2H, H-8). - GC-MS (70 eV), m/z (%): 349 (28) [M^{+}+1], 348 (100) [M^{+}], 347 (10) [M^{+}-1], 346 (16) [M^{+}-2], 174 (23) [M^{++}], 173 (21) [M^{++}-2], 172 (12) [M^{++}-4].

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