# 13. Experimenteller Teil

Alle käuflichen Reagenzien wurden von den Firmen Acros, Aldrich und Merck bezogen und wenn nicht anders angegeben ohne weitere Reinigung eingesetzt. Die verwendeten Lösungsmittel wurden nach den üblichen Methoden gereinigt und getrocknet. Für Arbeiten unter Schutzgasatmosphäre wurde Stickstoff 4.0 bzw. 5.0 der Firmen Linde und Messer Griesheim verwendet, und die Lösungen und Suspensionen durch mehrmaliges Durchlaufen eines Evakuieren-Belüften-Zyklus entgast.

**Analytik**

*NMR-Spektroskopie*

Die NMR-Spektren wurden an WH 270 MHz oder AC 500 MHz-Geräten der Firma Bruker aufgenommen, wobei als interner Standard das Signal des Lösungsmittels selbst diente. Alle Messungen wurden bei RT durchgeführt, die chemischen Verschiebungen sind in ppm angegeben. Die Kopplungskonstanten *J* sind in Herz angegeben. Die deuterierten Lösungsmittel wurden von den Firmen Merck bzw. Deutero GmbH bezogen.

*Massenspektrometrie*

Die Aufnahmen von Massenspektren erfolgte mit Varian MAT 771 bzw. MAT 112 S.

*Elementaranalyse*

Zur Elementaranalyse diente ein EA 240 der Firma Perkin-Elmer.

*Schmelzpunkte*

Die Schmelzpunkte sind unkorrigiert und wurden an einem Büchi 510 gemessen.

*UV/Vis-Spektroskopie*

Die UV/Vis-Spektren wurden an einem Perkin-Elmer 16 UV, die Fluoreszenzspektren an einem Perkin-Elmer LS50-B FL

*Dünnschichtchromatographie*

Die Dünnschichtchromatographie wurde auf DC-Fertigplatten der Firma Merck durchgeführt (Art. 5554, Kieselgelbeschichtung Si 60 mit Fluoreszenzindikator $F_{254}$). Zur Detektion diente UV-Licht mit Wellenlängen von $\lambda = 254$ nm bzw. $\lambda = 366$ nm.

*Säulenchromatographie*

Zur Säulenchromatographie wurde Kieselgel der Firma Merck verwendet (Kieselgel 60, 230-400 mesh ASTM, Korngröße 40-60 pm).

*Analytische Gel-Permeations-Chromatographie*

Die GPC wurde mit einem Waters Assoc. 150-c Alc/GPC Chromatograph durchgeführt. Es wurde der Säulensatz Waters Styragel HR Columns mit THF als mobiler Phase verwendet. Die Detektion erfolgte mit einem Waters 484 UV/Vis-Detektor gegen Polystyrol als Eichstandard.

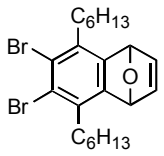
*Präparative Gel-Permeations-Chromatographie*

Die Trennung erfolgte auf eine Anlage der Firma Waters mit UV-Detektion und THF als Laufmittel. Als Trennsäulen dienten Waters Styragel HR Columns.

*Röntgenstrukturanalyse*

Die Einkristall-Röntgenstrukturanalysen wurden mit einem BRUKER-AXS SMART 1000 CCD mit MoK\α-Strahlung durchgeführt.

**6,7-Dibromo-1,4-epoxy-5,8-dihexylnaphthalene[35] (36)**

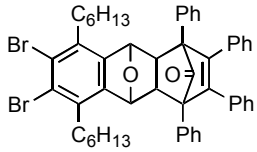



A solution of 1,2,4,5-tetrabromo-3,6-dihexylbenzene (42,24 g, 75 mmol) and furan (50 ml) in dry toluene (150 ml) was prepared under nitrogen. The solution was cooled to -20 °C and 42 ml of a PhLi solution (1.8 M in cyclohexane/ether) were added within 30 min. The solution was stirred for 4 h while it was allowed to warm to room temperature. The reaction was quenched by adding 20 ml water. After two times washing with water, and phase separation the solvent was evaporated *in vacuo*. The raw product was purified by column chromatography on silica gel using hexane/ethyl acetate as eluens to give 28 g of a colorless solid (mp 68-70° C; $R_F$ 0.33) in 79 % yield.

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.89 (t, *J* 6.7 Hz, 6H, $CH_3$), 1.32 (m, 12H, γ-ε-$CH_2$), 1.51 (m, 4H, β-$CH_2$), 2.79 (m, 4H, α-$CH_2$), 5.74 (s, 2H, H-1,4), 7.00 (s, 2H, H-2,3)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.05 ($CH_3$), 22.56, 29.24, 29.76, 31.75, 34.74 (alkyl-$CH_2$), 81.74 (C-1,4), 124.46, 134.84, 142.64 (arom-C), 147.54 (C-2,3)

**2,3-Dibromo-5,10-epoxy-1,4-dihexyl-6,7,8,9-tetraphenyl-6,9-carbonyloanthracene[35] (33)**

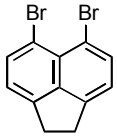



A solution of **36** (22.2 g, 47 mmol) and tetracyclone (18 g, 46.8 mmol) in ethanol (200 ml) was refluxed for 16 h. After cooling to room temperature the mixture was filtered with suction and the precipitate was washed two times with 50 ml ethanol. Drying *in vacuo* gave 38.7 g of a pale pink solid in 96.5 % which was suitable for further work.

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.92 (t, *J* 7.0 Hz, 6H, $CH_3$), 1.39 (m, 8H, $CH_2$), 1.55 (m, 6H, β-γ-$CH_2$), 1.77 (m, 2H, β-$CH_2$), 2.97 (m, 4H, α-$CH_2$), 3.10 (s, 2H, H-5a,9a), 5.82 (s, 2H, H-5,10), 6.85 (m, 4H, phenyl-H), 6.96 (m, 6H, phenyl-H), 7.33 (m, 10-H, phenyl-H)

**$^{13}$C-**NMR (68 MHz, $CDCl_3$): δ 14.05, 22.66, 29.73, 31.49, 35.73, 46.79, 64.14, 80.86, 126.56, 126.78, 127.53, 128.27, 129.28, 129.81, 134.02, 134.92, 135.35, 138.53, 145.13, 196.23

**5,6-Dibromoacenapnthene[42] (39)**



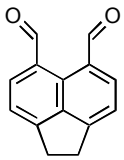

This was prepared by the method of Kasai[42] with modifications.

A suspension of NBS (1 kg, 5.62 mol) in DMF (2 l) was added in portions to an ice cooled suspension of acenaphthene (400 g, 2.59 mol) in DMF (500 ml) over a period of 5 h. Attention was paid that the mixture didn't warm up over 15 °C. The mixture was stirred for another 12 h while allowed to warm to room temperature. The precipitate was filtered with suction washed three times with 500 ml of ethanol and purified by stirring over night in 3 l of refluxing ethanol. After cooling to room temperature, filtration, washing with ethanol, and drying *in vacuo* 206 g (25 %) of a beige crystalline solid were isolated (mp. 169-172 °C) which was suitable for further work. Recrystallization of a sample in chloroform raised the melting point to 173-175 °C (lit. 174-176 °C).

**$^{1}$H-NMR** (270 MHz, $CDCl_3$): δ 3.28 (s, 4H, H-1,2), 7.06 (d, 2H, *J* 7.49 Hz, H-3,8), 7.76 (d, 2H, *J* 7.49 Hz, H-4,7)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 29.99 (C-1,2), 114.31, 120.87, 131.80, 135.77, 141.75, 147 (arom.-C)

**5,6-Diformylacenaphthene (40)**




A solution of **39** ( 5 g, 16 mmol) in dry ether (150 ml) was prepared under nitrogen atmosphere and cooled to –55 °C. To this solution 10 ml BuLi (1.6 M solution in hexane) were added at once. The reaction mixture was stirred for 5 h while it was allowed to warm to room temperature. Dry DMF (5ml) was added at once and the mixture stirred for additional 45 min. Finally the reaction was quenched by adding a saturated $NaHCO_3$ solution. Dilution with $CH_2Cl_2$, washing with water, phase separation and evaporation of the solvent of the organic layer yielded the crude product. This was purified by column chromatography on silica gel using $CH_2Cl_2$ as eluens to give 2.25 g (67 %) of a pale brown solid (mp 173-175 °C decomp).

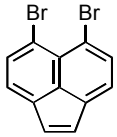
**$^{1}$H-NMR** (270 MHz, $CDCl_3$): δ 3.42 (s, 4H, H-1,2), 7.44 (d, 2H, $^{3}J$ 7.3 Hz, H-3,8 or H-4,7), 8.05 (d, 2H, $^{3}J$ 7.3 Hz, H-3,8 or H-4,7), 10.25 (s, 2H, CHO)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 30.62 (C-1,2), 120.44, 125.27, 130.34, 136.86, 140.11, 154.28 (arom-C), 191.24 (CHO)

**EIMS** (80 eV, 130 °C): m/z (rel intensity) 210 (65) [$M^+$], 181 (75) [$M^+$-CHO], 153 (100) [$M^+$-2CHO+H]

**Analytical** calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.74; H, 5.02

**5,6-Dibromoacenaphtylene[43] (41)**




**41** was prepared according to literature starting from 5,6-Dibromacenaphthene (2 g, 6.4 mmol) to give 853 mg of a yellow solid in 43 % (mp 129-131; °C Lit. 132-133 °C) ($R_F$(hexane ethyl acetate 10:1) = 0.35).

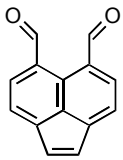
**$^{1}$H-NMR** (270 MHz, $CDCl_3$): δ 6.90 (s, 2H, H-1,2), 7.37 (d, 2H, $^{3}J$ 7.1 Hz, H-3,8 or H-4,7), 7.84 (d, 2H, $^{3}J$ 7.1 Hz, H-3,8 or H-4,7)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 121.00, 125.11, 12.67, 129.11, 131.05, 135.42, 140.29

**EIMS** (80 eV, 120 °C): m/z (rel intensity) 308 (49) [$M^+$], 229 (10) [$M^+$-Br]

**Analytical** calcd for $C_{14}H_{10}O_2$: C, 46.50; H, 1.95. Found: C, 45.89; H, 1.90

**5,6-Diformylacenaphthylene (42)**




The procedure was similar to **40** starting from **41** (0.4 g, 1.3 mmol) to give 51 mg (18 %) of an orange solid ($R_F(CH_2Cl_2)$ = 0.41).

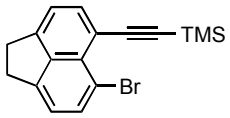
**$^{1}$H-NMR** (270 MHz, $CDCl_3$): δ 7.06 (s, 2H, H-1,2), 7.68 (d, 2H, $^{3}J$ 7.1 Hz, H-3,8 or H-4,7), 8.02 (d, 2H, $^{3}J$ 7.1 Hz, H-3,8 or H-4,7), 10.28 (s, 2H, CHO)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 121.89, 124.09, 129.68, 132.53, 134.46, 136.07, 144.90 (arom-C), 191.81 (CHO)

**EIMS** (80 eV, 120 °C): m/z (rel intensity) 208 (100) [$M^+$], 179 (65) [$M^+$-CHO], 152 (80) [$M^+$-2CHO]

**Analytical** calcd for $C_{14}H_{10}O_2$: C, 80.76; H, 3.87. Found: C, 79.80; H, 3.79

**5-Bromo-6(trimethylsilyethynyl)acenaphthene (43)**




A solution of **39** (3.9 g, 12.5 mmol) and trimethysilyl acetylene (4 ml) in 200 ml triethylamine was prepared under nitrogen. To the refluxing solution $(PPh_3)_2PdCl_2$ (10 mg) and Cu(I)I (10 mg) were added. After 20 h the mixture was allowed to cool to room temperature. The solvent was evaporated *in vacuo* and the residue was taken up with ether (200 ml) and washed with water. The separated organic layer was purified by column chromatography on silica gel using hexane as eluens to yield 1.68 g (41 %) of a colorless solid ($R_F$ = 0.1).

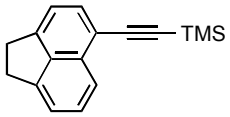
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.26 (s, 9H, $SiCH_3$), 3.30 (m, 4H, H-1,2), 7.07 (d, 1H, $^3J$ 7.4 Hz, arom-H), 7.17 (d, 1H, $^3J$ 7.3 Hz, arom-H), 7.67 (d, 1H, $^3J$ 7.4 Hz, arom-H), 7.74 (d, 1H, $^3J$ 7.3 Hz, arom-H)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ -0.38 ($SiCH_3$), 29.83 (C-1 or C-2), 30.56 (C-1 or C-2), 101.08 (acetylene-C), 115.67 (acetylene-C), 119.75, 120.79, 134.60, 137.73, 146.57, 148.09 (arom-C)

**EIMS** (80 eV, 80 °C): 328 (98) [$M^+$], 313 (56) [$M^+$-$CH_3$]

**Analytical** calcd for $C_{17}H_{17}BrSi$: C, 62.00; H, 5.20. Found: C, 61.72; H, 5.12

**6-(Trimethylsilyletynyl)acenaphthene (44)**




A solution of **43** (500 mg, 1.64 mmol) in dry diethyl ether (20 ml) was prepared under nitrogen atmosphere and cooled to 0 °C. BuLi (1.2 ml of a 1.6 M solution in hexane) was added at once. After 45 min the yellow solution was quenched with water. The organic layer was washed two times with water, the layers were separated, and the organic layer was brought to dryness *in vacuo*. Purification of the crude product by column chromatography using hexane as eluens gave 336 mg of a pale yellow oil in 90 % yield.

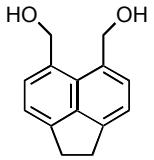
In a similar reaction **32** was obtained in 7 % yield by adding trethylamine and refluxing for 1 h prior to quenching with dilute hydrochloric acid.

**$^{1}$H-NMR** (270 MHz, $CDCl_3$): δ 0.39 (s, 9H, $SiCH_3$), 3.37 (s, 4H, H-1,2), 7.19 (d, 1H, $^{3}J$ 7.2 Hz, arom-H), 7.31 (d, 1H, $^{3}J$ 6.9 Hz, arom-H), 7.55 (dd, 1H, H-5), 7.69 (d, 1H, $^{3}J$ 7.2 Hz, arom-H), 7.93 (d, 1H, $^{3}J$ = 6.9 Hz)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 0.22 ($SiCH_3$), 30.35 (C-1 or C-2), 30.40 (C-1 or C-2), 80.49, 97.72, 103.26, 115.75, 118.75, 119.83, 119.92, 120.9, 121.08, 128.58, 131.90,132.51, 132.91, 138.77, 146.16, 147.43

**EIMS** (80 eV, 50 °C): 250 (95) [$M^+$], 235 (100) [$M^+$-$CH_3$]

**5,6-Bis(hydroxymethyl)acenaphthene (47)**




A suspension of **39** (40 g, 129 mmol) in dry diethyl ether was prepared under nitrogen and cooled to –30 °C. A 170 ml sample of 1.6 M BuLi (272 mmol) in hexane was added within 10 min. After further 30 min of stirring, 8 g paraformaldehyde (dried over $P_2O_5$) were added at once. The mixture was stirred for 3 h at –30 °C and for further 16 h while warming to room temperature. The reaction was quenched by adding 40 ml of 25 % hydrochloric acid. After 1 h of stirring the colorless precipitate was filtered with suction, suspended in 500 ml of diethyl ether filtered again and dried in vacuum at 50 °C. The dry material was powdered and suspended in 1% hydrochloric acid for 2 h, filtered, washed two times with 100 ml ethanol and dried again in vacuum at 50 °C yielding 20.51 g (74 %) of a colorless solid (mp 201-203°C) which was suitable for further work. Two times recrystallization of a sample from dioxane raised the melting point to 201-204 °C (lit[34c] 202-205 °C).

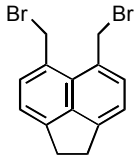
**$^{1}$H-NMR** (270 MHz, DMSO-$d_6$): δ 2.15 (s, 4H, H-1,2), 3.85 (d, 4H, $^{3}J$ 5.3 Hz, C$H_2$OH), 4.25 (t, 2H, $^{3}J$ 5.3 Hz, OH), 6.09 (d, 2H, $^{3}J$ 7.0 Hz, H-3,8 or H-4,7), 6.35 (d, 2H, $^{3}$J7.0 Hz, H-3,8 or H-4,7)

**$^{1}$H-NMR** (270 MHz, DMSO-$d_6$/ $D_2O$): 1.96 (s, 4H, H-1,2), 3.67 (s, 4H, C$H_2$OH), 5.95 (d, 2H, $^{3}J$ 7.0 Hz, H-3,8 or H-4,7), 6.34 (35 (d, 2H, $^{3}J$ 7.0 Hz, H-3,8 or H-4,7)

**$^{13}$C-NMR** (68 MHz, DMSO-$d_6$): δ 29.46 (C-1,2), 63.05 ($CH_2$OH), 118.96, 128.53, 129.70, 134.11, 140.24, 145.92 (arom.-C)

**EIMS**: (80eV, 100 °C), m/z (rel intensity): 214 (30)[$M^+$], 196 (100)[$M^+$-$H_20$], 167 (69) [$M^+$-$H_20$-HCO]

**Bis(bromomethyl)acenaphthene (48)**

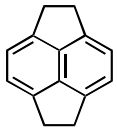



**46** was prepared from **45** (20 g, 93 mmol) according to literature in 83 % yield (26,24 g): mp 157-159 °C (decomp)(Lit[34c] 157-159 °C)

**$^1$H-NMR** (270 MHz $CDCl_3$): δ 3.33 (s, 4H, H-1,2 ), 5.28 (s, 4H, C*H*$_2$Br), 7.26 (d, 2H, $^3J$ 7.23 Hz, H-3,8), 7.55 (d, 2H, $^3J$ 7.23 Hz, H-4,7)

**$^{13}$C-NMR** ($CDCl_3$, 68 MHz): δ 30.16 (C-1,2), 36.81 ($CH_2Br$), 119.96, 127.75, 129.44, 134.02, 140.92, 149.34 (C-arom.)

**Pyracene (49)**



This was prepared by the method of Trost with modifications.

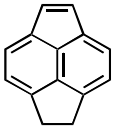
A solution of **46** (28 g, 82 mmol) in of dry diethyl ether (120 ml) was prepared under nitrogen atmosphere. To the ice cooled mixture a sample of PhLi (50 ml, 90 mml, 1.8 M solution in cyclohexane/ether) was added over a period of 10 min. After 4 h stirring the mixture was quenched with 10 ml water. The organic solvent was evaporated, the residue dissolved in 1 l of $CH_2Cl_2$, and the organic layer was washed with water. Drying and evaporation of the solvent yielded crude pyracene which was further purified by digeration in warm diethylether. After cooling to room temperature the precipitate was filtered and dried in vacuum. This procedure was repeated one time to yield 13.7 g (93 %) of a colorless solid (mp 205-209 °C) which was suitable for further work. Sublimation of a sample raised the melting point to 212-216 °C (lit.[2] 214-217 °C)

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 3.42 (s, 8H, H-1,2,5,6), 7.19 (s, 4H, H-2,3,7,8)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 31.60 (C-1,2,5,6), 120.33, 138.35, 140.81 (arom-C)

**EIMS**:(80eV, 100 °C) m/z (rel intensity) 180 (100)[$M^+$]

**1,2-Dihydropyracylene (32)**

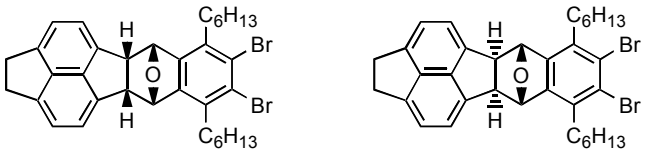


Under nitrogen atmosphere, a solution of **47** (13.7 g, 76 mmol) and TMEDA (30 ml) in dry cyclohexane (250 ml) was prepared. To this solution BuLi (110 ml of a 1.6 M solution in hexane) was added within 10 min at room temperature. The color changed quickly over dark red to dark green. After 1 h heating to reflux temperature, the mixture was allowed to cool for 15 min. Under nitrogen atmosphere the solution was added dropwise to an ice cooled suspension of Cu(II)$(acac)_2$ (50 g, 190 mmol) in dry cyclohexane (150 ml) within a period of 15 min.. The mixture was stirred for another 30 min and than purred on a short column ($Al_2O_3$, basic, activity grade V, height of column 5 cm) and washed with hexane until the filtrate became colorless. The solvent was evaporated in vacuum and the yellow brown crude product was purified by column chromatography (silica gel, hexane / ehtyl acetate 10:1)($R_F$ 0.57) to yield 10.01 g (74 %) of a yellow crystalline solid (mp 154-156 °C) (lit[34c] 156-157 °C)

**$^1$H-NMR**(270 MHz, $CDCl_3$): δ 3.50 (s, 4H, H-1,2), 7.16 (s, 2H, H-5,6), 7.41 (d, 2H, *J* 6.9 Hz, H-3,8), 7.77 (d, 2H, *J* 6.9 Hz, H-4,7)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 32.37 (C-1,2), 120.46 (C-3,8), 126.01 (C-3,4,7,8), 127.93 (C-8c), 128.22 (C-5,6), 134.90 (C-8b), 135.22 (C-4a,6a), 146.60 (C-2a,8a)

**1,2,4b,5,10,10a-Hexahydro-7,8-dibrom-5,10-epoxy-6,9-dihexyl-benzo[k]cyclopenta[c,d]fluoranthen (51)**




A solution of **32** (3.56 g, 19.8 mmol) and (16.9 g, 19.8 mmol) **33** in toluene (300 ml) was prepared under nitrogen atmosphere and refluxed for 24 h. After cooling to room temperature the solvent was evaporated *in vacuo*. To remove 82 % of the side product tetraphenylbenzene the residue was suspended in 50 ml of a 2:1 mixture of hexane/toluene and stirred for 30 min. The suspension was filtered with suction and the residue washed two times with 25 ml of a 2:1 mixture of hexane/toluene. The combined organic layers were brought to dryness *in vacuo*. Purification and separation of the isomeres was done by column chromatography (silica gel, hexane/toluene 2:1 as eluens) to give 2.12 g of **51-*exo***

(mp 126-127 °C, $R_F$ 0.20) and 8.61 g of **51-*endo*** (mp 92-94 °C, $R_F$ 0.14) in a combined yield of 97 %.

**51-*exo***

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.96 (t, 6H, *J* 7.1 Hz, $CH_3$), 1.3-1.6 (m, 12H, alkyl-$CH_2$), 1.73 (m, 4H, β-$CH_2$), 2.95 (m, 4H, α-$CH_2$), 3.43 (s, 4H, H-1,2), 3.92 (s, 2H, H-4b,10a), 5.41 (s, 2H, H-5,10), 7.28 (d, 2H, *J* 6.9 Hz, H-3,12), 7.37 (d, 2H, *J* 6.9 Hz, H-4,11)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.12, 22.61, 29.46, 31.56, 31.69, 35.09 (alkyl-C and C-1,2), 55.14 (C-4b,10a), 83.44 (C-5,10), 120.67, 126.16, 134.34, 138.13, 140.41, 142.49, 144.56 (arom-C)

**EIMS** (80 eV, 240 °C): m/z (rel intensity) 622 (5.6) $[M]^+$, 440 (100) $[M^+-C_{14}H_{10}]$, 365 (62.4) $[M^+-C_{14}H_{10}-Br]$ 178 (69.4) $[C_{14}H_{10}^+]$

**Analalytical** calcd for $C_{34}H_{38}Br_2O$: C, 65.60; H, 6.15. Found: C, 65.89; H 6.29

**51-*endo***

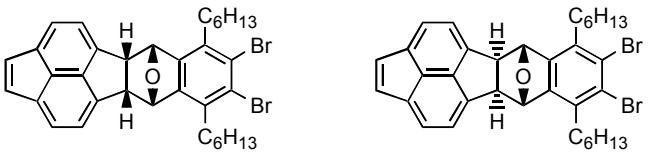
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.91 (t, 6H, *J* 6.6 Hz, *$CH_3$*), 1.2-1.6 (m, 16H, alkyl-*$CH_2$*), 2.48 (t, 4H, *$^3J$* 7.7 Hz α-*$CH_2$*), 3.27 (m, AA´BB´, 4H, H-1,2), 4.65 (m, 2H, *J* 3.4 Hz, H-4b,10a), 5.73 (m, 2H, *J* 3.4 Hz, H-5,10), 7.00 (d, 2H, *J* 6.9 Hz, H-3,12); 7.14 (d, 2H, *J* 6.9 Hz, H-4,11)

**$^{13}$C-NMR (125 MHz, $CDCl_3$)**: δ 14.13, 22.63, 28.81, 29.53, 31.38, 31.62, 35.22 (alkyl-C and C-1,2), 54.11 (C-4b,10a), 80.85 (C-5,10), 119.80, 120.76, 125.27, 134.41, 135.71, 138.09, 139.51, 14.72, 142.51 (arom-C)

**EIMS** (80 eV, 210 °C) m/z (rel intensity) 622 (6.8) $[M]^+$, 444 (100) $[M^+-C_{14}H_{10}]$, 365 (52) $[M^+-C_{14}H_{10}-Br]$ 178 (51) $[C_{14}H_{10}^+]$

**Analytical** calcd for $C_{34}H_{38}Br_2O$: C, 65.60; H, 6.15; Found: C, 65.56; H, 6.13

**4b,5,10,10a-Tetrahydro-7,8-dibrom-5,10-epoxy-6,9-dihexyl-benzo[k]cyclopenta[cd]fluoranthene (52)**




**52-*endo***

To a refluxing solution of **51-*endo*** (8.6 g, 13.8 mmol) in toluene (150 ml) DDQ (3.2 g, 14 mmol) was added under nitrogen atmosphere. After 90 min at reflux the solution was allowed to cool for 15 min and concentrated to a volume of 80 ml *in vacuo*. The product

was isolated from this solution by column chromatography (silica gel, toluene) as 7.3 g of a yellow solid ($R_F$ 0.54) in 85 % yield.

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.96 (t, 6H, *J* 6.5 Hz, $CH_3$), 1.2-1.6 (m, 16H, alkyl-$CH_2$), 2.54 (t, 4H, *J* 7.6 Hz, α-$CH_2$), 4.71 (m, 2H, *J* 3.7 Hz, H-4b,10a), 5,74 (m, 2H, *J* 3.7 Hz, H-5,10), 6.96 (s, 2H, H-1,2), 7.27 (d, 2H, *J* 6.9 Hz, H-4,11), 7.51 (d, 2H, *J* 6.9 Hz, H-3,12)

**$^{13}$C-NMR (68 MHz, $CDCl_3$)**: δ 14.10, 22.63, 28.85, 29.53, 31.64, 35.30 (alkyl-C), 54.96 (C-4b,10a), 80.32 (C-5,10), 120.83, 125.27, 125.68, 127.16, 129.00, 134.45, 136.55, 136.67, 141.23, 141.45 (arom.-C and C-1,2)

**EIMS** (80 eV, 130 °C): m/z (rel intensity) 620 (5.6) [$M^+$], 444 (71.6) [$M^+$-$C_{14}H_8$], 365 (100) [$M^+$-$C_{14}H_8$-Br ]

**Analytical** calcd for $C_{34}H_{36}Br_2O$: C, 65.82; H, 5.85. Found: C, 65.94; H 5.62.

**52-exo** was prepared from **51-*exo*** (2.12 g, 3.4 mmol) by a similar procedure as described above to give 1.52 g of a yellow solid in 72 % yield ($R_F$ 0.72, mp 152-154 °C)

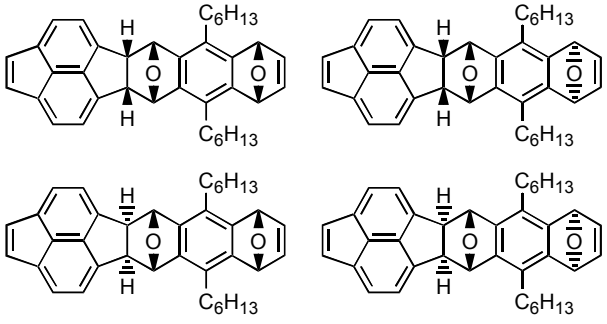
**1H-NMR** (270 MHz, $CDCl_3$): δ 0.97 (t, 6H, *J* 6.9 Hz, $CH_3$), 1.38 (m, 12H, alkyl-$CH_2$), 1.62 (m, 4H, β-$CH_2$), 2.95 (m, 4H, α-$CH_2$), 3.97 (s, 2H, H-4b,10a), 5.43 (s, 2H, H-5,10), 7.14 (s, 2H, H-1,2), 7.52 (d, 2H, *J* 6.86 Hz, H-3,12), 7.79 (d, 2H, *J* 6.86 Hz, H-4,11)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.13, 22.61, 29.47, 29.49, 31.57, 35.13 (alkyl-C), 55.92 (C-4b,10a), 82.53 (C-5,10), 120.73, 126.15, 126.35, 126.95, 129.16, 134.48, 136.64, 137.10, 143.72, 144.12 (arom.-C)

**EIMS** (80 eV, 230 °C): m/z (rel intensity) 620 (1.9) [$M^+$], 444 (38.2) [$M^+$-$C_{14}H_8$], 365 (33) [$M^+$-$C_{14}H_8$-Br ], 176 (100) [$C_{14}H_8^+$]

**Analytical** calcd for $C_{34}H_{36}Br_2O$ : C, 65.82; H, 5.85. Found: C, 65.66; H, 5.80

**4b,5,7,10,12,12a-Hexahydro-5,12,7,10-diepoxy-6,11-dihexyl-cyclopenta[cd]naphtho-[2,3-k]fluoranthen (53)**



**53-*endo-syn*** and **53-*endo-anti***

A solution of **52-*endo*** (5.44 g, 8.8 mmol) in dry toluene (350 ml) and dry furan (30 ml) was prepared under nitrogen. This solution was cooled to –30 °C and 6 ml of a 1.6 M solution of BuLi were added drop wise within 1 h. The solution was stirred for additional 2 h at –30 °C. The reaction was quenched by adding 5 ml water. After warming to room temperature the volume of the mixture was reduced to 30 ml in vacuum. This solution was chromatographed on silica gel using toluene as eluens to give the mixture of isomeres as yellow oil ($R_F$ = 0.28). This oil revealed a syn/anti ratio of 1:1.5 by $^1$H-NMR spectroscopy. The isomeres were separated by column chromatography (silica gel, hexane/methylenechlorid 2:1) to yield 930 mg of **53-*endo-anti*** ($R_F$ 0.23) as yellow oil and 1.53 g **53-*endo-syn*** ($R_F$ 0.17) as yellow solid (mp 91-93 °C) in a total yield of 53 %.

**53-*endo-syn***

**$^1$H-NMR** (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, *J* 6.9 Hz, $CH_3$), 1.35 (m, 16H, alkyl-$CH_2$), 2.00 (m, 2H, α-$CH_2$), 2.33 (m, 2H, α-$CH_2$), 4.63 (m, 2H, *J* 4.2 Hz, H-4b,12a), 5.28 (s, 2H, H-7,10), 5.68 (m, 2H, *J* 4.6 Hz, H-5,12), 6.08 (s, 2H, H-8,9), 6.89 (s, 2H, H-1,2), 7.18 (d, 2H, *J* 6.9 Hz, H-4,13), 7.39 (d, 2H, *J* 6.9 Hz, H-3,14)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.08, 22.56, 29.34, 30.72, 30.83, 31.68 (alkyl-C), 55.01 (C-4b,12a), 80.02 (C-5,12 or C-7,10), 80.71 (C-7,10 or C-5,12), 120.23, 124.42, 125.88, 128.44, 135.89, 136.01, 138.27, 141.29, 142.59, 146.55

**EIMS** (80 eV, 190 °C): m/z (rel intensity) 528 (1.84) [$M^+$], 352 (100) [$M^+$-$C_{14}H_8$], 176 (14.81) [$C_{14}H_8^+$]

**HRMS** calcd for $C_{38}H_{40}O_2$: 528.302831; Found: 528.30395

**53-*endo-syn***

**1H-NMR** (500 MHz, CDCl3): δ 0.90(t, 6H, *J* 6.8 Hz, $CH_3$), 1.28 (m, 14H, alkyl-$CH_2$, β-$CH_2$), 1.44 (m, 2H, β-$CH_2$), 2.26 (m, 2H, α-$CH_2$), 2.40 (m, 2H, α-$CH_2$), 4.67 (m, 2H, *J* 4.3 Hz, H-4b,12a), 5.33 (s, 2H, H-7,10), 5.68 (m, 2H, *J* 4.3 Hz, H-5,12), 6.79 (s, 2H, H-8,9), 6.92 (s, 2H, H-1,2), 7.25 (d, 2H, *J* 6.8 Hz, H-4,13), 7.48 (d, 2H, *J* 6.8 Hz, H-3,14)

**$^{13}$C-NMR** (125 MHz, CDCl3): δ 14.09, 22.56, 29.33, 30.27, 31.06, 31.69 (alkyl-C), 54.94 (C-4b,12a), 79.57 (C-5,12 or C-7,10), 80.49 (C-7,10 or C-5,12), 120.37, 125.04, 125.77, 127.05, 128.05, 136.39, 136.71, 138.74, 142.21, 143.02, 146.06

**EIMS** (80 eV, 215 °C): m/z (rel intensity) 528 (4.67) [$M^+$], 352 (100) [$M^+$-$C_{14}H_8$], 176 (14) [$C_{14}H_8^+$]

**HRMS** calcd for $C_{38}H_{40}O_2$: 528.302831; Found: 528.30420

**53-*exo-syn*** and **53-*exo-anti***

The procedure was similar to that for **53-*endo-syn*** and **53-*endo-anti*** starting from **52-*exo*** (1.73 g, 3.3 mmol). The isomeres were separated by column chromatography (silica gel, $CH_2Cl_2$) to obtain 424 mg of **53-*exo-syn*** ($R_F$ 0.15) and 457 mg of **53-*exo-anti*** ($R_F$ 0.27) in a total yield of 50 %.

**53-exo-anti**

**$^1$H-NMR** (500 MHz, $CDCl_3$): δ 0.95 (t, 6H, *J* 6.7 Hz, $CH_3$), 1.45 (m, 14H, $CH_2$, β-$CH_2$), 1.67 (m, 2H, β-$CH_2$), 2.71 (m, 2H, α-CH2), 2.81 (m, 2H, α-CH2), 3.95 (s, 2H, H-4b,12a), 5.38 (s, 2H, H-7,10), 5.83 (s, 2H, H-5,12), 7.03 (s, 2H, H-8,9), 7.13 (s, 2H, H-1,2), 7.51 (d, 2H, *J* 6.8 Hz, H-4,13), 7.78 (d, 2H, *J* 6.8 Hz, H-3,14)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.15, 22.60, 29.28, 30.24, 31.39, 31.71 (alkyl-C), 56.12 (C-4b,12a), 81.04 (C-5,12 or C-7,10), 81.87 (C-7,10 or C-5,12), 120.62, 126.08, 126.95, 129.04, 136.46, 137.21, 142.14, 142.92, 144.42, 147.15 (arom-C)

**EIMS** (80 eV, 220 °C): m/z (rel intensity) 528 (1.65) [$M^+$], 352 (100) [$M^+$-$C_{14}H_8$], 176 (9.52) [$C_{14}H_8^+$]

**HRMS** calcd for $C_{38}H_{40}O_2$: 528.302831; Found: 528.30475

**53-exo-syn**

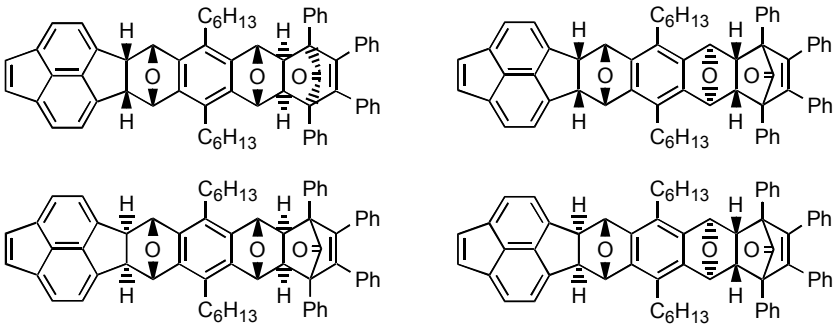
**$^1$H-NMR (500 MHz, $CDCl_3$)**: δ 0.96 (t, 6H, $^3J$ 6.7 Hz, $CH_3$), 1.42 (m, 12H, $CH_2$), 1.68 (m, 4H, β-$CH_2$), 2.79 (m, 2H, α-$CH_2$), 3.99 (s, 2H, H-4b,12a), 5.40 (s, 2H, H-7,10), 5.82 (s, 2H, H-5,12), 7.12 (s, 2H, H-8,9), 7.15 (s, 2H, H-1,2), 7.54 (d, 2H, *J* 6.8 Hz, H-4,13), 7.80 (d, 2H, *J* 6.8 Hz, H-3,14)

**$^{13}$C-NMR (125 MHz, $CDCl_3$)**: δ 14.11, 22.58, 29.27, 30.21, 31.15, 31.77 (alkyl-C), 56.34 (C-4b,12a), 81.12 (C-5,12 or C-7,10), 81.95 (C-7,10 or C-5,12), 120.41, 125.82, 126.07, 126.95, 129.02, 136.42, 137.39, 142.17, 144.42, 143.05, 147.63

**EIMS** (80 eV): m/z (rel intensity) 528 (2.92) [$M^+$], 352 (100) [$M^+$-$C_{14}H_8$], 176 (17.79) [$C_{14}H_8^+$]

**HRMS** calcd for $C_{38}H_{40}O_2$: 528.302831; Found: 528.30646

**4b,5,7,7a,8,11,11a,12,14,14a-Decahydro-8,11-carbonylo-5,14,7,12-diepoxy-6,13-dihexyl-8,9,10,11-tetraphenyl-acenaphtheno[1´,8´:2,3,4]cyclopenta[1,2-b]naphthacene (54)**



As a representative procedure for the synthesis of the four isomeres of **54** the one for **54-*endo-anti*** is given**.**

A suspension of **53-*endo-anti*** (830 mg, 1.57 mmol) and tetracyclone (604 mg, 1.57 mmol) in ethanol (100 ml) was refluxed for 2 h under nitrogen. The mixture was brought to dryness in vacuum and the residue was purified by column chromatography on silica gel using toulene as eluens. 960 mg of a pale yellow solid ($R_F$ 0.38) were obtained in 67 % yield.

**$^1$H-NMR** (500 MHz, $CDCl_3$): δ 0.97 (t, 6H, *J* 6.8 Hz, $CH_3$), 1.40 (m, 8H, alkyl-$CH_2$), 1.57 (m, 6H, β,γ-$CH_2$), 1.69 (m, 2H, β-$CH_2$), 2.48 (m, 2H, α-$CH_2$), 2.61 (m, 2H, α-$CH_2$), 2.82 (s, 2H, H-7a,11a), 4.75 (m, 2H, *J* 3.7 Hz, H-4b,14a), 5.45 (s, 2H, H-7,12), 5.80 (m, 2H, *J* 3.7 Hz, H-5,14), 6.73 (m, 4H, phenyl-H), 6.89 (m, 4H, phenyl-H), 6.93 (s, 2H, H-1,2), 6.96 (m, 2H, phenyl-H), 7,30 (m, 8H, phenyl-H), 7.35 (m, 4H, penyl-H and H-4,15), 7.51 (d, 2H, *J* 6.9 Hz, H-3-16)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.15, 22.76, 29.66, 30.25, 31.10, 31.46 (alkyl-C), 46.94 (C-7a,11a), 54.97 (C-4b,14a), 64.06 (C-8,11), 79.51 (C-5,14 or C-7,12), 79.59 (C-7,12 or C-5,14), 120.47, 124.54, 125.18, 126.55, 127.16, 127.25, 127.37, 128.10, 128.90, 129.31, 129.76, 134.97, 135.64, 136.53, 136.78, 138.27, 140.79, 142.99, 143.90 (arom-C and C-1,2), 196.52 (carbonyl-C)

**FABMS**: m/z (rel intensity) 913 (0.2) [$M^+$+H]

**Analytical** calcd for $C_{67}H_{60}O_3$: C, 88.12; H, 6.62. Found: C, 86.87; H, 6.67

**54-*endo-syn***

1.42 g of yellow crystals ($R_F$($CH_2Cl_2$) 0.43) in 54 % yield along with 664 mg (18 %) of the colorless bisadduct **55** were obtained. Single crystals of **54-*endo-syn*** for X-ray crystallographic analysis were obtained from recrystallization from ethanol.

**$^{1}$H-NMR** (500 MHz, $CDCl_3$): δ 0.88 (t, 6H, *J* 6.6 Hz, $CH_3$), 1.23 (s, 2H, H-7a,11a), 1.32 (m, 8H, alkyl-$CH_2$), 1.40 (m, 4H, γ-$CH_2$), 1.62 (m, 4H, β-$CH_2$), 2.17 (m, 2H, α-$CH_2$), 2.51 (m, 2H, α-$CH_2$), 4.73 (m, 2H, *J* 3.9 Hz, H-4b,14a), 5.28 (s, 2H, H-7,12), 5.80 (m, 2H, *J* 3.9 Hz, H-5,14), 6.19 (s, 2H, H-1,2), 6.77 (m, 4H, phenyl-H), 6.91 (m, 4H), 6.97 (m, 2H), 7.22 (m, 6H), 7.27 (m, 2H), 7.36 (m, 2H), 7.43 (m, 4H, phenyl-H and H-3,4,15,16)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.10, 22.48, 28.97, 30.89, 31.53, 31.76 (alkyl-C), 46.00 (C-7a,11a), 55.12 (C-4b,14a), 63.75 (C-8,11), 79.62 (C-5,14 or C-7,12), 80.17 (C-7,12 or C-5,14), 120.47, 124.15, 124.37, 125.92, 126.50, 127.04, 127.36, 127.95, 129.18, 129.34, 129.70, 135.00, 135.44, 135.52, 136.34, 138.26, 140.70, 142.66, 144.75 (arom-C and C-1,2), 195.31 (carbonyl-C)

**FABMS**: m/z (rel intensity) 913 (2) [$M^+$+H]

Analytical calcd for ($C_{67}H_{60}O_3$): C, 88.12; H,6.62. Found: C, 87.82; H, 6.68

**54-*exo-anti***

376 mg of a pale yellow solid in 67 % yield were obtained.

**1H-NMR** (500 MHz, $CDCl_3$): δ 0.93 (t, 6H, $^{3}J$ 7.1 Hz, CH3), 1.44 (m, 8H, CH2), 1.63 (m, 4H, γ-$CH_2$), 1.83 (m, 4H, β-$CH_2$), 2.91 (m, 2H, α-$CH_2$), 2.96 (m, 2H, α-$CH_2$), 3.07 (s, 2H, H-7a,11a), 3.98 (s, 2H, H-4b,14a), 5.50 (s, 2H, H-7,12), 5.90 (s, 2H, H-5,14), 6.91 (m, 4H, phenyl-H), 6.98 (m, 6H, phenyl-H), 7.15 (s, 2H, H-1,2), 7.33 (m, 2H, phenyl-H), 7.40 (m, 4H, phenyl-H), 7.48 (m, 4H, phenyl-H), 7.56 (d, 2H, *J* 6.7 Hz, H-4,15), 7.80 (d, 2H, *J* 6.7 Hz, H-3,16)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.03, 22.58, 29.64, 30.83, 31.56, 31.61 (alkyl-C), 46.57 (C-7a,11a), 55.97 (C-4b,14a), 64.11 (C-8,11), 81.65 (C-5,14 or C-7,12), 82.58 (C-7,12 or C-5,14), 120.56, 124.57, 125.99, 126.59, 126.86, 127.29, 127.39, 128.17, 128.98, 129.27, 129.78, 135.01, 135.38, 136.43, 137.12, 138.43, 143.73, 144.06, 144.80 (arom-C and C-1,2), 196.39 (carbonyl-C)

**FABMS**: m/z (rel intensity) 913 (1) [$M^+$+H]

Analytical calcd for ($C_{67}H_{60}O_3$): C, 88.12; H,6.62. Found: C, 86,98; H, 6.69

**54-*exo-syn***

501 mg of a pale yellow solid in 75 % yield were obtained.

**$^{1}$H-NMR** (500 MHz, $CDCl_3$): δ 0.99 (t, 6H, *J* 7.2 Hz, CH3), 1.48 (m, 8H, $CH_2$), 1.66 (m, 4H, γ-$CH_2$), 1.83 (m, 4H, β-$CH_2$), 2.91 (m, 2H, α-$CH_2$), 3.01 (m, 2H, α-$CH_2$), 3.20 (s, 2H, H-7a,11a), 4.06 (s, 2H, H-4b,14a), 5.46 (s, 2H, H-7,12), 5.89 (s, 2H, H-5,14), 6.92 (m, 4H,

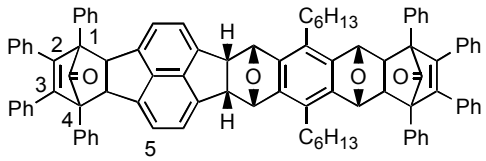
phenyl-H), 7.01 (m, 6H, phenyl-H), 7.14 (s, 2H, H-1,2), 7.33 (m, 2H, phenyl-H), 7.40 (m, 4H, phenyl-H), 7.51 (m, 4H, phenyl-H), 7.54 (d, 2H, *J* 6.8 Hz, H-4,15), 7.80 (d, 2H, *J* 6.8 Hz, H-3,16)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.14, 22.68, 28.88, 31.21, 31.70, 31.77 (alkyl-C), 47.05 (C-7a,11a), 56.35 (C-4b,14a), 64.30 (C-8,11), 80.21 (C-5,14 or C-7,12), 81.98 (C-7,12 or C-5,14), 120.59, 124.62, 126.14, 126.73, 127.05, 127.38, 127.53, 128.24, 129.11, 129.46, 129.91, 135.14, 135.72, 136.61, 137.26, 138.54, 144.01, 144.40, 144.99 (arom-C and C-1,2), 196.79 (carbonyl-C)

**FABMS:** m/z (rel intensity) 913 (3) [$M^+$+H]

**Analalytical** calcd for ($C_{67}H_{60}O_3$): C, 88.12; H,6.62. Found: C, 88.36; H, 6.23

**1,4,4a,6b,7,9,9a,10,13,13a,14,16,16a,18b-Tetradecahydro-1,4,10,13-dicarbonylo-7,16,9,14-diepoxy-8,15-dihexyl-1,2,3,4,10,11,12,13-octaphenyl-fluorantheno[3´,4´:2,3,4]cyclopenta[1,2-b]naphthacene (55)**



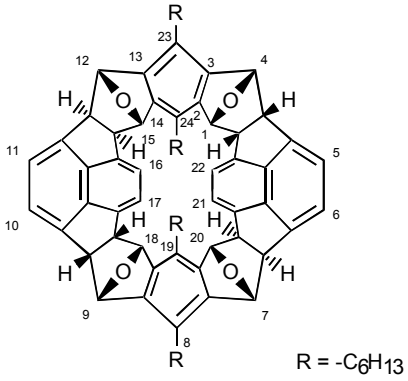

**$^{1}$H-NMR** (270 MHz, $CDCl_3$): δ 0.90 (t, 6H, *J* 6.4 Hz, CH3), 1.36 (m, 12H, $CH_2$), 1.57 (s, 2H, H-9a,13a), 1.64 (m, 4H, β-$CH_2$), 2.12 (m, 2H, α-$CH_2$), 2.48 (m, 2H, α-$CH_2$), 3.79 (m, 2H, H-6a,16a), 4.03 (s, 2H, H-4a,18b), 5.40 (s, 2H, H-9,14), 5.73 (m, 2H, H-7,16), 5,97 (d, 2H, *J* 7 Hz, H-5,18 or H-6,17), 6.61 (d, 2H, *J* 7 Hz, H-5,18 or H-6,17), 6.78 (m, 4H, phenyl-H), 7.10 (m, 26H, phenyl-H), 7.49 (m, 10H, phenyl-H)

**$^{13}$C-NMR** (67 MHz, $CDCl_3$): δ 14.04, 22.44, 28.95, 30.81, 31.50, 31.64 (alkyl-C), 46.27 (C-9a,13a), 53.81 (C-4a,18b or C-6b,16a), 55.78 (C-4a,18b or C-6b,16a), 63.48 (C-1,4 or C-10,13), 64.14 (C-1,4 or C-10,13), 79.91 (C-7,16 or C-9,14), 80.40 (C-7,16 or C-9,14), 120.43, 122.61, 124.16, 126.26, 126.33, 126.79, 126.98, 127.10, 127.56, 128.25, 129.58, 129.76, 129.93, 134.66, 134.74, 134.83, 135.37, 136.02, 138.20, 138.51, 138.93, 141.39, 144.23, 145.08, 197.06 (carbonyl-C), 201.94 (carbonyl-C)

**FABMS:** m/z (rel intensity) 1298 (1.5) [$M^+$+H]

**Analalytical** calcd for ($C_{96}H_{80}O_4$): C, 88.85; H,6.21. Found: C, 87.39; H, 6.28

**rel-(1*R*,4*S*,4a*S*,6b*S*,7*R*,9*S*,9a*S*,11b*S*,12*R*,15*S*,15a*R*,17b*R*,18*R*,20*S*,-20a*R*,22b*R*)-1,4:7,20:9,18:12,15-Tetraepoxy-8,19,23,24-tetrahexyl-1,4,4a,6b,7,9,9a,11b,12,15,15a,17b,18,20,20a,22b-hexadecahydro-2,14:3,13dimetheno-diindeno[1,2,3-c,d:1',2',3'-c',d']benzo[2,3-j:5,6-j']difluoranthene (57)**




Typical Procedure: A solution of **52-*exo-syn*** (230 mg, 0.25 mmol) in toluene (10 ml) was prepared under nitrogen and refluxed for 2 d. After cooling to room temperature and removal of solvent *in vacuo,* the residue was purified by column chromatography using $CH_2Cl_2$ as eluens affording a colorless solid (mp 286-287 °C, decomp.) in 43% yield ($R_F$ 0.25). Single crystals were grown by diffusion of ethanol to a chloroform solution.

**1H-NMR** (270 MHz, $CDCl_3$): δ 0.88 (t, 12H, *J* 6.4 Hz, $CH_3$), 1.31 (m, 24H, alkyl-$CH_2$), 1.50 (s, 4H, H-6b,11b,15a,20a), 1.56 (m, 8H, β-$CH_2$), 2.00 (m, 4H, α-$CH_2$), 2.34 (m, 4H, α-$CH_2$), 4.71 (m, 4H, *J* 3.7 Hz, H-4a,9a,17b,22b), 5.13 (s, 4H, H-7,12,15,20), 5.73 (m, 4H, *J* 3.7 Hz, H-1,4,9,18), 7.03 (d, 4H *J* 6.9 Hz, H-5,10,17,21 or H-6,11,16,22), 7.19 (d, 4H, *J* 6.9 Hz, H-5,10,17,21 or H-6,11,16,22)

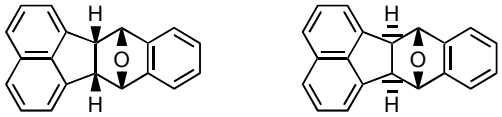
**1H-NMR** (270 MHz, benzene-$d_6$): δ 0.89 (t, 12H, *J* 6.6 Hz, $CH_3$), 1.22 (m, 16H, alkyl-$CH_2$), 1.35 (m, 8H, γ-$CH_2$), 1.50 (m, 8H, α-$CH_2$), 1.65 (s, 4H, H-6b,11b,15a,20a), 2.03 (m, 4H, α-$CH_2$), 2.28 (m, 4H, α-$CH_2$), 4.54 (m, 4H, *J* 3.7 Hz, H-4a,9a,17b,22b), 5.34 (s, 4H, H-7,12,15,20), 5.68 (m, 4H, *J* 3.7 Hz, H-1,4,9,18), 6.77 (d, 4H *J* 6.9 Hz, H-5,10,17,21 or H-6,11,16,22), 6.87 (d, 4H, *J* 6.9 Hz, H-5,10,17,21 or H-6,11,16,22)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.10, 22.54, 29.19, 31.15, 31.70, 31.75 (alkyl-*C*), 54.69 (C-4a,9a,17a,22b), 57.23 (C-6b,11b,15a,17a), 80.60 (C-1,4,9,18), 81.56 (C-7,12,15,20), 120.21, 121.16, 125.29, 138.62, 139.39, 139.60, 140.67, 141.80, 144.05 (arom.-C)

**EIMS** (80 eV, 140 °C): m/z (rel intensity): 1004 (1.8) [$M^+$], 828 (0.9) [$M^+$-$C_{14}H_8$], 502 (18) [$M^+$-$C_{36}H_{38}O_2$], 326 (100) [$M^+$-$C_{36}H_{38}O_2$-$C_{14}H_8$]

**Analytical**: calcd for $C_{72}H_{76}O_4$: C, 86.02; H 7.62. Found: C, 85.78; H, 7.58

**6a,7, 12,12a-Tetrahydro-7,12-epoxybenzo[k]fluoranthene (58)**



A solution of acenaphthylene (4.77 g, 31 mmol) and of the isobenzofurane precursor (16.39 g, 31 mmol) in toluene (250 ml) was refluxed for 16 h under nitrogen atmosphere. After cooling to room temperature the solvent was evaporated *in vacuo.* The residue was digerated in hot ethanol (250 ml) for 30 min and filtered hot, this was repeated one time. By this procedure 83 % of the side product tetraphenylbenzene were separated. The combined filtrates were brought to dryness *in vacuo*. Purification and separation of the isomeres was done by column chromatography on silica gel using hexane ethyl acetate (3:1) as eluens to give 5.87 g of **58-*endo*** (mp 190-191 °C, $R_F$ = 0.37 ) and 1.42 **58-*exo*** (mp 166-167 °C, $R_F$ = 0.43) in an overall yield of 87 % as colorless solids. Single crystals for X-ray crystallographic analysis were grown from ethanol solutions.

**58-*endo***

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 4.64 (m, 2H, *J* 4.0 Hz, H-6b,12a), 5.71 (m, 2H, *J* 4.0 Hz, H-7,12), 6.59 (AA'BB', 2H, H-8,11 or H-9,10), 6.68 (AA'BB', 2H, H-8,11 or H-9,10), 7.19 (d, 4H, *J* 6.6 Hz, H-1,6), 7.29 (dd, 2H, $^3J$ 6.6 Hz, $^3J$ 8.0 Hz, H-2,5), 7.37 (d, 2H, *J* 8.0 Hz, H-3,4)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 52.05 (C-6b,12a), 81.73 (C-7,12), 119.29, 120.35, 123.09, 125.52, 127.24, 131.21, 142.18, 142.27 (arom.-C)

**EIMS** (80 eV, 80 °C): m/z (rel intensity) 270 (76) [$M^+$], 252 (26) [$M^+$-$H_2O$], 152 (5) [$C_{12}H_8^+$], 118 (100) [$M^+$-$C_{12}H_8$]

**Analytical** calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.14; H, 5.18

**58-*exo***

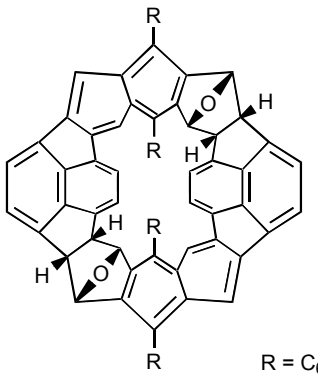
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 3.93 (s, 2H, H-6b,12a), 5.48 (s, 2H, H-7,12), 7.29 (AA'BB', 2H, H-8,11 or H-9,10), 7.46 (AA'BB', 2H, H-8,11 or H-9,10), 7.56 (m, 4H, H-1,6 and H-2,5), 7.74 (d, 2H, *J* 7.8 Hz, H-3,4)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 53.28 (C-6b,12a), 84.30 (C-7,12), 119.49, 119.53, 123.54, 126.94, 127.96, 131.37, 143.95, 145.87 (arom.-C)

**EIMS** (80 eV, 130 °C): m/z (rel intensity) 270 (18) [$M^+$], 252 (3) [$M^+$-$H_2O$], 152 (12) [$C_{12}H_8^+$], 118 (100) [$M^+$-$C_{12}H_8$]

**Analytical** calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.30; H, 5.17

**rel-(1*R*,4*S*,4a*S*,9*S*,9a*S*,17b*R*,18*R*,22b*R*)-1,4:9,18-Diepoxy-8,19,23,24-tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-2,14:3,13dimetheno-diindeno[1,2,3-c,d:1',2',3'-c',d']benzo[2,3-j:5,6-j']difluoranthene (59)**




A solution of **57** ( 60 mg, 0.06 mmol) in toluene (5 ml) was prepared under nitrogen atmosphere and heated to reflux temperature. *p*-TsOH monohydrate (45 mg) was added and the mixture was refluxed for 16 h. After cooling to room temperature the solution was washed three times with water and the organic layer was brought to dryness in *vacuo.* The residue was purified by column chromatography on silica gel using $CH_2Cl_2$ as eluens to give 27 mg of a pale yellow green solid (mp > 310 °C) in 47 % yield. Single crystals for X-ray crystallographic analysis were grown form diffusion of hexane to a chloroform solution.

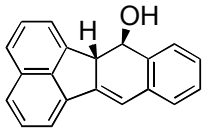
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.87 (t, 12H; $^3J$ = 6.3 Hz, $CH_3$), 1.1-1.5 (m, 24H, alkyl-$CH_2$), 1.58 (m, 8H, β-$CH_2$), 2.49 (m, 4H, α-$CH_2$), 2.74 (m, 4H, α-$CH_2$), 4.77 (m, 4H, *J* 3.9 Hz, H-4a,9a,17b,22b), 5.92 (m, 4H, *J* 3.9 Hz, H-1,4,9,18), 7.26 (d, 4H, *J* 7.0 Hz, H-5,10,17,21 or H-6,11,16,22), 7.47 (s, 4H, H-7,12,15,20), 7.49 (d, 4H, *J* 6.9 Hz, H-5,10,17,21 or H-6,11,16,22)

**$^{13}$C-NMR** (125 MHz, $CDCl_3$): δ 14.11, 22.61, 29.58, 30.93, 31.52, 31.76 (alkyl-C), 55.91 (C-4a,9a,17a,22b), 81.66 (C-1,4,9,18), 116.25, 119.39, 121.43, 128.87, 131.00, 133.49, 134.47, 136.28, 137.24, 137.44, 142.31 (arom.-C)

**EIMS** (80 eV, 260 °C): m/z (rel intensity): 968 (38) [$M^+$], 484 (100) [$M^+$-$C_{36}H_{36}O$ or $M^{2+}$], 413 (19) [$M^+$-$C_{36}H_{36}O$-$C_5H_{11}$]

**Analytical** calcd for $C_{72}H_{72}O_2$: C, 89.21; H, 7.49. Found: C, 88.50; H, 7.92

**6b,7-Dihydro-7-hydroxybezo[k]fluoranthene (62)**




A solution of a 1:1 mixture of **58-*endo*** and –***exo*** (400 mg, 1.48 mmol) in dry toluene (25 ml) was cooled to 0 °C. Water free *p*-TsOH (127 mg, 0.74 mmol) was added and the solution was stirred for 1 h. The reaction was stopped by adding $CH_2Cl_2$ (50 ml) followed by washing 5 times with ice cooled water until neutral reaction of the aqueous layer was reached. Phase separation and evaporation of the organic solvent yields the raw product which was purified by column chromatography (silica gel, hexane ethyl acetate 3:1) to yield **62** (37 mg, 9 %, $R_F$ 0.28) as pale yellow solid besides 43 mg (12 %) benzo[k]fluoranthene ($R_F$ = 0.51), 176 mg (44 %) **58-*exo***, 78 mg (20 %) **58-*endo***.

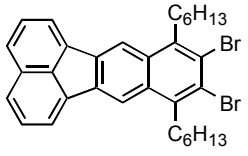
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 2.35 (d, 1H, $^3J$ 8.3 Hz, OH), 4.24 (d, 1H, $^3J$ 12.4 Hz, H-6b), 5.02 (dd, 1H, $^3J_{7,OH}$ 8.3, $^3J_{7,6b}$ 12.4 Hz, H-7), 7.05 (d, 1H, *J* 2.4 Hz, H-12), 7.33 (m, 3H, arom-H), 7.53 (m, 2H, arom-H) 7.67 (m, 5H, arom-H)

**$^1$H-NMR** (270 MHz, $CDCl_3/D_2O$): 4.24 (d, 1H, $^3J$ 14.3 Hz, H-6b), 5.02 (d, 1H, $^3J$ 14.3 Hz, H-7), 7.04 (d, 1H, *J* 2.2 Hz, H-12), 7.33 (m, 3H, arom-H), 7.53 (m, 2H, arom-H) 7.67 (m, 5H, arom-H)

**EIMS** (80 eV, 130 °C) m/z (rel intensity): 270 (100) [$M^+$], 252 (74) [$M^+$-$H_2O$], 239 (43) [$M^+$-$CH_2OH$], 118 (46) [$C_6H_5$-$CH_2OH^+$]

**Analytical** calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.52; H, 5.47

**9,10-Dibromo-8,11-dihexylbenzo[k]fluoranthene (66)**




A solution of acenaphthylene (761 mg, 5 mmol) and **33** (4.37 g, 5 mmol) in toluene (75 ml) was prepared under nitrogen atmosphere and refluxed for 1 d. To the refluxing solution *p*-TsOH monohydrate ( 1 g, 5.2 mmol) was added and heated for another 5 h. After cooling to room temperature the mixture was washed 3 times with water (50 ml). The layers were separated and the organic layer was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using hexane as eluens to give 1.88 g of a pale yellow solid in 65 % yield ($R_F$ 0.29)

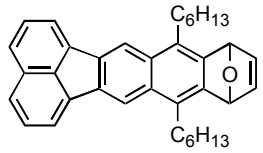
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.98 (t, 6H, *J* 6.6 Hz, $CH_3$), 1.45 (m, 8H, alkyl-$CH_2$), 1.62 (m, 4H, γ-$CH_2$), 1.73 (m, 4H, β-$CH_2$), 3.41 (m, 4H, α-$CH_2$), 7.68 (dd, 2H, *J* 8.2 Hz, *J* 6.9 Hz, H-2,5) 7.87 (d, 2H, *J* 8.2 Hz, H-1,6 or H-3,4), 8.02 (d, 2H, *J* 6.9 Hz, H-1,6 or H-3,4), 8.43 (s, 2H, H-7,12)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.12, 22.69, 29.42, 29.65, 31.58, 35.09 (alkyl-C), 117.10, 119.33, 125.61, 126.54, 128.13, 130.49, 131.48, 136.40, 138.04, 139.36 (arom-C)

**EIMS** (80 eV, 190 °C): m/z (rel intensity) = 576 (54) [$M^+$], 507 (27) [$M^+$-$C_5H_{11}$]

**Analytical** calcd for $C_{32}H_{34}Br_2$: C, 66.45; H, 5.92. Found: C, 66.57; H, 5.90

**9,12-Dihydro-9,12-epoxy-8,13-dihexylnaphtho[2,3:k]fluoranthene (67)**




A solution of **66** (1.7 g, 2.9 mmol) and dry furan (5ml) in touluene (100 ml) was prepared under nitrogen and cooled to –30 °C. Phenyllithium (1.7 ml of 1.8 M solution in cyclohexan/ether) was added dropwise within 30 min. The solution was stirred over night while it was allowed to warm to room temperature. The reaction was quenched by adding 10 ml of water. Washing the organic layer two times with water, followed by phase separation, and evaporation of the solvent *in vacuo* yielded the raw product. This was purified by column chromatography on silica gel using hexane ethyl acetate as eluens to give 960 mg of a yellow solid ($R_F$ 0.21) in 68 % yield.

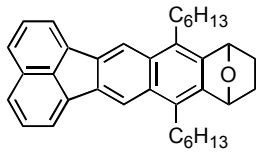
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.92 (t, 6H, *J* 6.5 Hz, $CH_3$), 1.38 (m, 12H, γ-ε-$CH_2$), 1.60 (m, 4H, β-$CH_2$), 3.10 (m, 4H, α-$CH_2$), 5.94 (s, 2H, H-9,12), 7.00 (s, 2H, H-10,11), 7.65 (dd, 2H, *J* 8.2 Hz, *J* 6.8 Hz, H-2,5), 7.82 (d, 2H, *J* 8.2 Hz, H-1,6 or H-3,4), 8.01 (d, 2H, *J* 6.8 Hz, H-3,4 or H-1,6), 8.39 (s, 2H, H-7,14)

**$^{13}$C-NMR (68 MHz, $CDCl_3$):** δ 14.06, 22.59, 29.52, 30.98, 31.66 (alkyl-C), 81.13 (C-9,12), 116.83, 118.94, 125.94, 127.89, 129.22, 130.97, 134.62, 137.05, 141.25, 141.70 (arom-C and C-10,11)

**EIMS** (80 eV, 210 °C): m/z (rel intensity) = 486 (100) [$M^+$], 458 (39) [$M^+$-CO], 387 (51) [$M^+$-CO-$C_5H_{11}$]

**Analytical** calcd for $C_{36}H_{38}O$: C, 88.84; H, 7.87. Found: C, 87.31; H, 8.10

**9,10,11,12-Tetrahydro-9,12-epoxy-8,13-dihexylnaphtho[2,3:k]fluoranthene (68)**




To a solution of **67** (900 mg, 1.9 mmol) in dioxane (50 ml) the catalyst Pd/C (10 %, 50 mg) was added and the mixture was heated to 50°C at a hydrogen pressure of 2 bar for 24 h. After cooling to room temperature the mixture was filtered with suction and concentrated *in vacuo* to a volume of 5 ml. This concentrate was taken up with $CH_2Cl_2$ and washed with water. The layers were separated and the organic one was brought to dryness *in vacuo*. Purification of the crude product by column chromatography using hexane ethyl acetate (6:1) yielded 826 mg (89 %) of a yellow solid ($R_F$ 0.31).

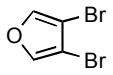
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 1.06 (t, 6H, *J* 6.9 Hz, $CH_3$), 1.53 (m, 8H, δ-ε-$CH_2$) 1.63 (m, 6H, γ-$CH_2$, and H-10,11 ), 1.85 (m, 4H, β-$CH_2$), 2.28 (m, 2H, H-10,11), 3.14 (m, 4H, α-$CH_2$), 5.76 (s, 2H, H-9,12 ), 7.67 (dd, 2H, *J* 8.2 Hz, *J* 6.9 Hz, H-2,5) , 7.83 (d, 2H, *J* 8.2 Hz, H-1,6 or H-3,4), 8.05 (d, 2H, *J* 6.9 Hz, H-1,6 or H-3,4), 8.50 (s, 2H, H-7,14)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.05, 22.57, 27.29 (alkyl-C), 29.68 (alkyl-C and C-10,11), 30.92, 31.60 (C-alkyl), 78.12 (C-9,12), 116.68, 118.71, 125.79, 127.50, 127.83, 130.29, 131.65, 134.91, 136.54, 137.08, 141.62 (arom-C)

**EIMS** ( 80 eV, 240 °C): m/z (rel intensity) 488 (80) [$M^+$], 460 (100) [$M^+$-$C_2H_4$]

**Analytical** calcd for $C_{36}H_{40}O$: C, 88.48; H, 8.25. Found: C, 88.22; H, 8.07

**3,4-Dibromofuran (76)**



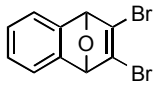

**76** was prepared according to literature[86] from *trans*-2,3-dibromo-2-buten-1,4-diol (100 g, 407 mmol) in 47 % yield to give 43.2 g of a colorless oil.

**$^1$H-NMR (270 MHz, $CDCl_3$):** 7.45 (s)

**$^{13}$C-NMR (68 MHz, $CDCl_3$):** 141.6, 103.9

**EIMS (80 eV, 40 °C):** m/z (rel intensity) 224 (50) [$M^+$], 197 (10) [$M^+$-HCO], 117 (41) [$M^+$-HCO-Br]

**1,4-Dihydro-2,3-dibromo-1,4-epoxynaphthaline (77)**




To a solution of **76** (34.3 g, 152 mmol) and isoamyl nitrite (46 ml) in a 1:1 mixture of $CH_2Cl_2$ and THF (300ml) a solution of anthranilic acid (23.3 g, 170 mmol) in THF (300 ml) was added dropwise within 1 h at room temperature. The mixture was refluxed for 1 h. After cooling to room temperature, the solvent was evaporated *in vacuo*. The residue was dissolved in $CH_2Cl_2$, washed with water, dried over $MgSO_4$, and dried again *in vacuo*. Purification of the crude product on silica gel (hexane / $CH_2Cl_2$ 6:1) gave 42.7 g of a pale beige solid in 93% yield: mp 116-118 °C; $R_F$ 0.46

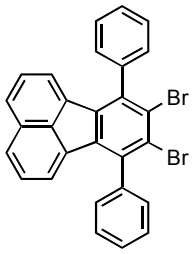
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 5.55 (s, 2H, H-1,4), 7.08 (AA'BB', 2H, H-5,8), 7.36 (AA'BB', 2H, H-6,7)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 88.10 (C-1,4), 120. 67 (arom-C), 126.15 (arom-C), 133.88 (arom-C), 145.74 (C-2,3)

**EIMS** (80 eV, 70 °C): *m/z* (rel. intensity) 300 (27) [$M^+$], 221 (83) [$M^+$-Br], 193 (100) [$M^+$-Br-CO]

**Analytical:** Calcd for $C_{10}H_6Br_2$: C, 39.78; H, 2.00. Found: C, 39.48; H, 1.95

**8,9-Dibromo-7,10-diphenylfluoranthene (79)**




A homogenized mixture of acecyclone (633 mg, 1.8 mmol) and **77** (2.7 g, 9 mmol) was heated to 130 °C for 24 h. After cooling to room temperature 572 mg of **79** were isolated by column chromatography using hexane / ethyl acetate 10:1 as eluens in 62 % yield as a yellow solid. mp > 250 °C; $R_F$ 0.59

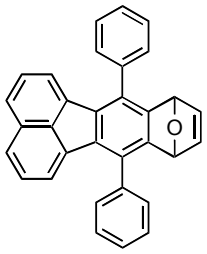
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 6.44 (d, 2H, *J* 7.1 Hz, H-1,6), 7.28 (dd, 2H, *J* 7.1 Hz, *J* 8.2 Hz, H-2,5), 7.42 (m, 4H, phenyl-H), 7.60 (m, 6H, phenyl-H), 7.74 (d, 2H, *J* 8.2 Hz, H-3,4)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 123.77, 126.08, 127.35, 127.8, 128.37, 128.98, 129.61, 135.17, 137.64, 139.53, 140.71

**EI-MS** (80 eV, 210 °C)**:** *m/z* (rel. intensity) 512 (100;$M^+$)

**Analytical:** Calcd for $C_{28}H_{16}Br_2$: C, 65.65; H 3.15. Found: C, 65.39; H, 3.24

**8,11-Dihydro-8,11-epoxy-7,12-diphenylbenzo[k]fluoranthene (80)**




A solution of **79** (556 mg, 1.1 mmol) and 3 ml furan in toluene (30 ml) was cooled to -35°C (± 5°C) and 0.68 ml of a 1.6 M solution of BuLi in hexane were added dropwise over a period of 15 min. The solution was stirred for 2 h. Afterwards 10 ml of water were added under vigorous stirring. The mixture was allowed to warm to room temperature, the layers were separated, the organic layer washed tree times with 25 ml of water, and dried in vacuum. Chromatographical work-up of the crude product using $CH_2Cl_2$ as eluens yielded 324 mg of a pale yellow solid in 71%. mp 215-217 °C; $R_F$ 0.46

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 5.59 (s, 2H, H-8,11), 7.01 (d, 2H, *J* 7.1 Hz, H-1,6 or H3,4), 7.09 (s, 2H, H-9,10), 7.29 (dd, 2H, *J* 7.1 Hz, *J* 6.6 Hz, H-2,5), 7.34 (d, 2H, *J* 6.6 Hz, H-3,4 or H-1,6), 7.55 (m, 6H, phenyl-H), 7.66 (m, 4H, phenyl-H)

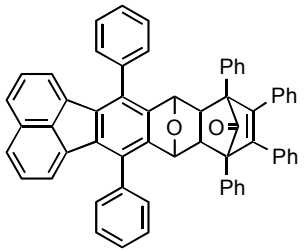
**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 81.90 (C-8,11), 123.08, 126.59, 127.48, 128.06, 128.90, 129.44, 138.01, 143.06, 147.84 (C-9,10)

**EI-MS** (80 eV, 170 °C): *m/z* (rel. intensity) 420 (64; $M^+$), 392 (100; $M^+$-CO)

**HRMS** calcd for $C_{32}H_{20}O$: 420.15142. Found: 420.15435

**8,8a,9,12,12a,13-Hexahydro-9,12-carbonylo-8,13-epoxy-7,9,10,11,1214-hexaphenylnaphtho[2,3-*k*]fluoranthene (81)**

A solution of **80** (298 mg, 0.71 mmol) and tetracyclone (260 mg, 0.68 mmol) in ethanol



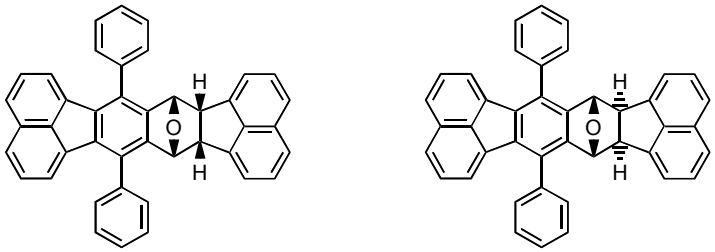
(30 ml) was refluxed over night. After cooling to room temperature the solvent was evaporated *in vacuo*. The residue was purified by column chromatography using $CH_2Cl_2$ as eluens to give 502 mg of a pale yellow solid in 88% yield. mp 223-225 °C decomp; $R_F$ 0.73

**$^1$H-NMR (270 MHz, $CDCl_3$)**: δ 3.09 (s, 2H, H-8a,12a), 5.73 (s, 2H, H-8,13), 6.76 (2d, 4H, Ar-H), 6.98 (m, 12H, Ar-H), 7.15 (m, 6H, arom-H), 7.34 (dd, 2H, H-2,5), 7.62 (m, 2H, arom-H), 7.70 (m, 10H, arom-H)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 47.05 (C-8a,12a), 64.30 (C-9,12), 81.03 (C-9,12), 123.19, 126.58, 126.86, 127.07, 127.42, 127.68, 128.12, 128.42, 128.96, 129.38, 129.55, 129.71, 129.84, 135.10, 135.27, 135.76, 136.98, 138.12, 138.58,145.30, 196.38 (carbonyl-C)

**FABMS** (MNBA/$CH_2Cl_2$): *m/z* (rel. intensity) 805 (0.8) [$M^+$+H], 787 (1.8) [$M^+$+H-$H_2O$], 394 (100) [$M^+$-CO-$C_{30}H_{22}$]

**6b,7,16,16a-Tetrahydro-7,16-epoxy-8,15-diphenylfluorantheno[8,9-*k*]fluoranthene (82)**




A solution of **81** (464 mg, 0.58 mmol) and acenaphthylene (96 mg, 0.63 mmol) in toluene (20 ml) was refluxed for 2 d. After cooling to room temperature the solvent was evaporated *in vacuo* and the residue purified by column chromatography using $CH_2Cl_2$ as eluens to give 67 mg **82-*endo*** and 190 mg **82-*exo*** as pale yellow solids in 82% over all yield.

**82-*endo***: mp 254-257 °C decomp**;** $R_F$ 0.31

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 4.47 (m, 2H, H-6b,16a ), 5.85 (m, 2H, H-7,16), 6.69 (2d, 4H), 6.83 (m, 2H, H-1,6 ), 7.14 (2d, 2H), 7.23 (2d, 2H), 7.37 (d, 2H, *J* 8.2), 7.55 (m, 8H, phenyl-H)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 52.20 (C-6b,16a), 80.99 (C-7,16), 120.87, 122.43, 123.63, 126.24, 126.97, 127.34, 127.86, 128.65, 129.05, 129.28, 130.92, 131.08, 131.75, 135.96, 137.70, 140.62, 141.00, 141.50

**EIMS** (80 eV, 170 °C): *m/z* (rel. intensity) 546 (0.2) [$M^+$], 528 (1.5) [$M^+$-$H_2O$], 394 (100) [$M^+$-$C_{12}H_8$]

**HRMS** calcd for $C_{42}H_{26}O$–$H_2O$ 528.1878. Found 528.1864

**82-*exo*:** mp 258-260 decomp; $R_F$ 0.54

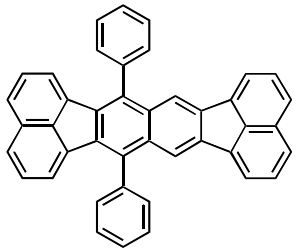
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 4.05 (s, 2H, H-6b,16a ), 5.32 (s, 2H, H-7,16 ), 7.13 (d, 2H. *J* 7.0, H-1,6 ), 7.31 (d, 2H, *J* 6.8), 7.37 (d, 2H, *J* 7.7), 7.49 (dd, 2H), 7.67 (m, 14H)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 53.50 (C-6b,16a), 83.88 (C-7,16), 119.39, 123.05, 123.51, 126.68, 127.54, 127.83, 128.18, 128.66, 128.98, 129.03, 129.41, 129.53, 130.30, 131.30, 132.71, 135.91, 136.64, 138.06, 141.39, 143.76, 144.63

**EI-MS (80 eV, 170 °C):** *m/z* (rel. intensity) 546 (0.1) [$M^+$], 528 (0.9) [$M^+$-$H_2O$], 394 (100) [$M^+$-$C_{12}H_8$]

**HRMS** calcd for $C_{42}H_{26}O$–$H_2O$ 528.18780. Found 528.18452

**7,16-Diphenylfluorantheneo[8,9-k]fluoranthene**



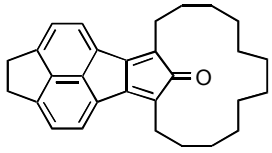
To a refluxing solution of **82-*endo*** (59 mg, 0.11 mmol) in toluene (20 ml) *p*-TsOH monohydrate (21 mg, 0.11 mmol) were added. After 1h the solution was allowed to cool to room temperature, washed three times with water, and the organic layer was dried *in vacuo*. The crude product was purified by chromatography using hexane ethyl acetate (10:1) as eluens to give 43 mg of a yellow green solid in 76% yield. Crystals were grown from slow evaporation of a dilute hexane solution. mp > 300 °C; $R_F$ 0.28

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 6.60 (d, 2H, *J* 7.1, H-1,6 ), 7.31 (dd, 2H, H-2,5 ), 7.65 (m, 16H), 7.84 (d, 2H, *J* 6.9 ), 8.09 (s, 2H, H-8,15 )

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 119.17, 119.56, 122.26, 125.95, 126.18, 127.83, 128.04, 129.34, 130.18, 130.34, 132.77, 135.08, 135.48, 135.73, 136.63, 136.79, 137.47, 139.07

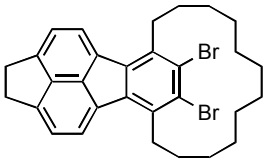
**EIMS** (80 eV, 260 °C): *m/z* (rel. intensity) 528 (100) [$M^+$], 450 (10) [$M^+$-$C_6H_5$-H]

**5,6-(3´,4´-Cyclopentadienondiyl-2´,5´-α,ω-dodecadiyl)acenaphthene (87)**




**87** was taken form the workgroups stock as a mixture with the dimer.

**1,2-Dihydro-6,7-dibromo-5,8-´-α,ω-dodecadiyl-cyclopenta[c,d]fluoranthene (88)**



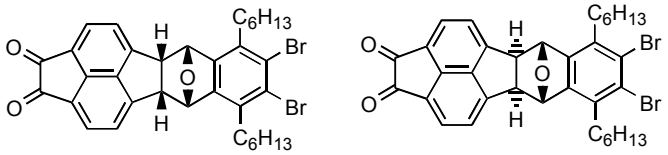

A homogenized mixture of **87** (523 mg, 1.3 mmol) and **77** (2.7 g, 9 mmol) was heated to 130 °C for 16 h. After cooling to room temperature 408 mg of **88** were isolated by column chromatography on silica gel using hexane/$CH_2Cl_2$ 2:1 as mobile phase in 56 % yield as a yellow solid. $R_F$ 0.53

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.60 (m, 4H, $CH_2$), 0.87 (m, 8H, $CH_2$), 1.17 (m, 4H, γ-$CH_2$), 1.83 (m, 4H, β-$CH_2$), 3.46 (m, 2H, α-$CH_2$), 3.49 (s, 4H, H-1,2), 3.60 (m, 2H, α-$CH_2$), 7.41 (d, 2H, *J* 7.1, H-3,10), 7.96 (d, 2H, *J* 7.1, H-4,9)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 25.07, 26.40, 26.98, 27.52, 27.67, 32.17, 34.08 (alkyl-C and C-1,2), 120.89, 125.67, 127.54, 130.20, 131.90, 136.50, 138.41, 138.58, 146.31 (arom-C)

**EIMS** (80 eV, 160 °C): *m/z* (rel. intensity) 550 (48) [$M^+$], 472 (9) [$M^+$-Br+H], 392 (100) [$M^+$-2Br]

**1,2,4b,5,10,10a-Hexahydro-7,8-dibrom-5,10-epoxy-6,9-dihexyl-benzo[k]cyclopenta[c,d]fluoranthen-1,2-dion (95)**




A solution of diketopyracene **94** (750 mg, 3.6 mmol) and **33** (3.08 g, 3.6 mmol) in toluene (150 ml) was prepared under nitrogen atmosphere and refluxed for 24 h. After cooling to room temperature the solvent was evaporated *in vacuo*. To remove parts of the side product tetraphenylbenzene the residue was suspended in 50 ml of a 2:1 mixture of

hexane/toluene and stirred for 30 min. The suspension was filtered with suction and the residue washed two times with 25 ml of a 2:1 mixture of hexane/toluene. The combined organic layers were brought to dryness *in vacuo*. Purification and separation of the isomeres was done by column chromatography on silica gel using $CH_2Cl_2$ to give 1.4 g **95-*endo*** (mp 215-217 °C, $R_F$ 0.35) and 0.41 g **95-*exo*** (mp 216-219 °C, $R_F$ 0.26) as yellow solids in a combined yield of 82 %.

**95-*endo***

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, *J* 6.5, $CH_3$), 1.34 (m, 16H, β-ε-$CH_2$), 2.43 (m, 4H, α-$CH_2$), 4.84 (m, 2H, *J* 3.7, H-4b,10a ), 5.83 (m, 2H, *J* 3.7, H-5,10), 7.53 (d, 2H, *J* 7.1, H-3,12 or H-4,11), 7.80 (d, 2H, *J* 7.1, H-4,11 or H-3,12)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.04, 22.57, 28.89, 29.42, 31.57, 35.38 (alkyl-C), 55.18 (C-4b,10a ), 80.46 (C-5,10), 121.90, 123.46, 125.32, 126.22, 134.39, 138.77, 140.71, 144.31, 147.54 (arom-C), 186.61 (carbonyl-C)

**EIMS** (80 eV, 250 °C): m/z (%) = 648 (0.3)[$M^+$], 442 (52) [$M^+$-$C_{14}H_6O_2$], 363 (68) [$M^+$-$C_{14}H_6O_2$-Br], 206 (25) [$M^+$-$C_{20}H_{28}Br_2O$]

**Analytical** calcd for $C_{34}H_{34}Br_2O_3$: C, 62.78; H, 5.27. Found: C, 62.65; H, 5.21

**95-*exo***

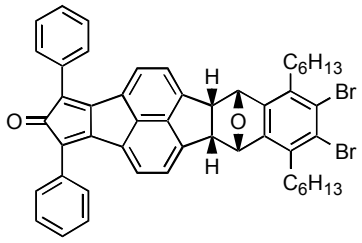
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.92 (t, 6H, *J* 7.0, $CH_3$), 1.42 (m, 12H, γ-ε-$CH_2$), 1.67 (m, 4H, β-$CH_2$), 2.94 (m, 4H, α-$CH_2$), 4.12 (s, 2H, H-4b,10a ), 5.50 (s, 2H, H-5,10), 7.76 (d, 2H, *J* 7.1, H-3,12 oder H-4,11 ), 8.09 (d, 2H, *J* 7.1, H-4,11 oder H-3,12)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.07, 22.61, 29.49, 29.60, 31.61, 35.25 (alkyl-C), 56.33 (C-4b,10a), 83.06 (C-5,10), 121.66, 122.03, 124.39, 125.52, 127.02, 134.76, 135. 01, 140.08, 143.74, 144.87, 149.63 (arom-C), 186.89 (carbonyl-C)

**MS (FAB(+), Xe, $CH_2Cl_2$/m-$NO_2$-Benzyl-OH):** m/z (%) = 649 (0.3)[$M^+$+H], 442 (10) [$M^+$-$C_{14}H_6O_2$], 363 (18) [$M^+$-$C_{14}H_6O_2$-Br], 207 (100) [$M^+$+H-$C_{20}H_{28}Br_2O$]

**Analytical** calcd for $C_{34}H_{34}Br_2O_3$: C, 62.78; H, 5.27. Found: C, 61.75; H, 5.07

**2,5b,6,11,11a-Pentahydro-8,9-dibrom-6,11-epoxy-7,10-dihexyl- pentaleno[1,2,3:c,d] benzo[k]fluoranthen-2-on (96)**



To a suspension of **95-*endo*** (1.2 g, 1.8 mmol) and 1,3-diphenylacetone (380 mg, 1.8 mmol) in ethanol (50 ml), 5 ml of a solution of KOH in methanol (10 %) was added. The mixture was stirred for 2 h. 5 ml of hydrochloric acid (25 %) were added an the solution stirred for another 15 min. The precipitate was filtered with suction, washed several times with ethanol an dried *in vacuo* to give 995 mg (67 %) of dark blue solid.

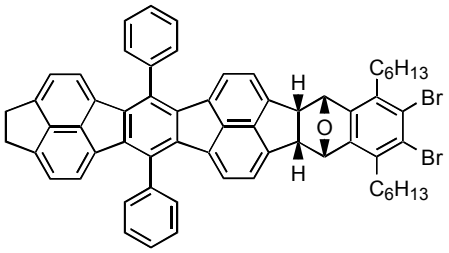
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.90 (t, 6H, *J* 6.6), 1.41 (m, 16H, β-ε-$CH_2$), 2.46 (m, 4H, α-$CH_2$), 4.69 (m, 2H, H-5b,11a), 5.77 (m, 2H, H-6,11), 7.29 (d, 2H, *J* 7.2, H-4,13 or H-5,12), 7.38 (2d, 2H, *J* 7.2, H-4,13 or H-5,12), 7.49 (m, 4H, phenyl-H), 7.75 (m, 6H, phenyl-H)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.08, 22.60, 28.90, 29.50, 31.62, 35.33, 54.69 (C-5b,11a), 80.71 (C-6,11), 121.68, 121.82, 125.89, 128.11, 128.49, 128.86, 131.49, 134.44, 139.85, 141.23, 141.84, 143.16, 154.23 (C-1,3 and arom-C), 201.69 (carbonyl-C)

**EIMS** (80 eV, 260 °C): m/z (%) = 824 (1.8) [$M^+$], 444 (7) [$M^+$-$C_{29}H_{16}O$], 380 (100) [$M^+$-$C_{20}H_{28}Br_2O$]

**Analytical** calcd for $C_{49}H_{44}Br_2O$: C, 71.36; H, 5.38. Found: C, 71.44; H, 5.35

**1,2,7b,8,13,13a-Hexahydro-10,11-dibromo-8,13-epoxy-9,12-dihehyl-5,16-diphenyl-cyclopenta[f'g']acenaphteno[1',2'-5,6]indeno[1,2,3-cd]benzo[k]fluoranthene (97)**




A solution of **96** (850 mg, 1.0 mmol) and **32** (183 mg, 1.0 mmol) in 50 ml dry toluene was refluxed for 1 d. After cooling to room temperature the sovent was evaporated *in vacuo.* The residue was purified by column chromatography on silica gel using hexane/ethyl acetate as eluens to give 380 mg (38 %) of **97** as yellow solid, along with 462 mg (46 %) of **98** as pale yellow solid.

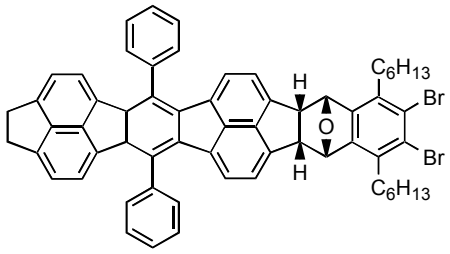
**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.91 (t, 6H, *J* 6.7, $CH_3$), 1.34 (m, 16H, β-ε-$CH_2$), 2.45 (m, 4H, α-$CH_2$), 3.41 (s, 4H, H-1,2 ), 4.67 (m, 2H, *J* 4.1, H-7b,13a), 5.69 (m, 2H, *J* 3.7, H-8,13), 6.43 (d, 2H, *J* 7.1, H-4,17 or H-6,15), 6.76 (d, 2H, *J* 7.0, H-4,17 or H-6,15), 7.07

(d, 2H, *J* 7.0, H-3,18 or H-7,14), 7.15 (d, 2H, *J* 7.1, H-3,18 or H-7,14), 7.65 (m, 10H, phenyl-H)

**$^{13}$C-NMR** (68 MHz, $CDCl_3$): δ 14.04, 22.62, 28.84, 29.59, 31.64, 32.17, 35.30 (C1,2 and alkyl-C), 54.71(C-7b,13a), 80.47 (C-8,13), 120.71, 121.17, 123.91, 124.81, 125.67, 127.94, 129.19, 129.39, 132.17, 133.92, 134.30, 134.54, 137.28, 137.94, 139.63, 140.22, 141.49, 145.72 (arom-C)

**EIMS** (80 eV, 310 °C): m/z (%) = 970 (0.6) [$M^+$]; 528 (100) [$M^+$- $C_{20}H_{28}Br_2O$]

**1,2,4b,7b,8,13,13a,16a-Octahydro-10,11-dibromo-8,13-epoxy-9,12-dihehyl-5,16-diphenyl-cyclopenta[f'g']acenaphteno[1',2'-5,6]indeno[1,2,3-cd]benzo[k]fluoranthene (98)**



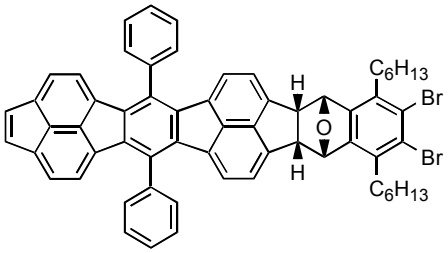

**$^1$H-NMR** ($CDCl_3$, 270 MHz): δ 0.90 (t, 6H, *J* 6.8, $CH_3$), 1.32 (m, 16H, β-ε-$CH_2$), 2.36 (m, 4H, α-$CH_2$), 3.30 (s, 4H, H-1,2), 4.59 (m, 2H, *J* 3.8, H-7b,13a ), 5.33 (s, 2H, H-4b,16a), 5.65 (m, 2H, *J* 3.8, H-8,13), 6.01 (d, 2H, *J* 7.0, H-6,15 ), 6.53 (d, 2H, *J* 7.2, H-4,17), 6.91 (2d, 4H, H-3,7,14,18), 7.56 (m, 10H, phenyl-H)

**$^{13}$C-NMR** ($CDCl_3$, 68 MHz): δ 14.04, 22.56, 28.80, 29.49, 31.47, 31.56, 35.20 (C1,2 and alkyl-C), 51.49 (C-4b,16a), 54. 43 (C-7b,13a), 80.67 (C-8,13), 119.34, 120.07, 120.71, 121.66, 125.41, 127.87, 128.88, 131.69, 133.18, 133.59, 134.43, 135.72, 137.40, 138.07, 139.20, 140.57, 140.63, 141.45, 14.68 (arom-C)

**EIMS** (80 eV, 300 °C): m/z (%) = 974 (0.3) [$M^+$], 530 (100) [$M^+$- $C_{20}H_{28}Br_2O$], 444 (10) [$M^+$-$C_{42}H_{28}$]

**Analytical** calcd for $C_{62}H_{54}Br_2O$: C, 76.38 ; H, 5.58. Found: C, 75.22; H, 5.32

**7b,8,13,13a-Tetrahydro-10,11-dibromo-8,13-epoxy-9,12-dihexhyl-5,16-diphenyl-cyclopenta[f'g']acenaphteno[1',2'-5,6]indeno[1,2,3-cd]benzo[k]fluoranthene (99)**



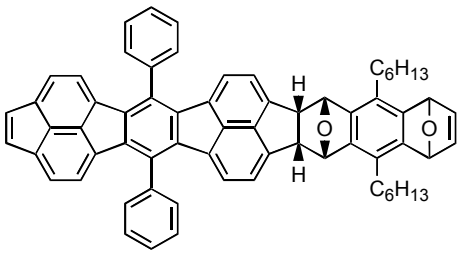

To a refluxing solution of **97** (350 mg, 0.36 mmol) in dry toluene (50 ml) DDQ (82 mg) was added under nitrogen atmosphere. After 16 h of heating, the reaction mixture was allowed to cool to room temperature and concentrated *in vacuo*. Chromatographical (silica gel; hexane/ ethyl acetate 6:1) workup yielded 146 mg (42 %) of an orange solid with ca. 5 % impurities.

**$^1$H-NMR** (270 MHz, $CDCl_3$): δ 0.90 (t, 6H, *J* 6.8, $CH_3$), 1.33 (m, 16H, β-ε-$CH_2$), 2.43 (m, 4H, α-$CH_2$), 4.65 (m, 2H, *J* 4.5 ), 5.66 (m, 2H, *J* 3.8), 5.97 (d, 2H, *J* 6.9, H-4,17 or H-6,15), 6.35 (s, 2H, H-1,2), 6.53 (d, 2H, *J* 7.1, H-4,17 or H-6,15), 6.76 (d, 2H, *J* 6.9, H-3,18 or H-7,14), 7.04 (d, 2H, *J* 7.1, H-3,18 or H-7,14), 7.60 (m, 19H, H-phenyl)

**$^{13}$C-NMR** ($CDCl_3$, 68 MHz): δ 14.08, 22.62, 28.85, 29.58, 31.64, 35.30 ( C-7b,13a), 54.75 ( C-8,13), 80.43, 121.16, 123.70, 124.39, 125.49, 125.72, 128.05, 128.83, 129.07, 129.34, 131.54, 133.42, 134.02, 134.54, 135.26, 138.46, 138.75, 140.33, 140.78, 141.44 (arom-C)

**MS (FAB(+), Xe, DMSO/m-$NO_2$-Benzyl-OH):** m/z (%) = 971 (5) [$M^+$+H]; 526 (100) [$M^+$-$C_{20}H_{28}Br_2O$]

**7b,8,10,13,15,15a-Hexahydro-11,12-dibromo-8,15,10,13-diepoxy-9,14-dihexhyl-5,18-diphenylcyclopenta[f'g']acenaphteno[1',2'-5,6]indeno[1,2,3-cd]naphto[2,3-k]fluoranthene (100)**




The procedure was similar to that of **52** and yielded the isomeres in two fractions (32 mg and 27 mg) with a purity of 85-90 % in a total yield of 31 % which were not suitable for further work.

**$^{1}$H-NMR** ($CDCl_3$, 270 MHz): δ 0.89 (t, 6H, *J* 6.7, $CH_3$), 1.26 (m, 16H, β-ε-$CH_2$), 1.95 (m, 2H, $CH_2$-α), 1.26 (m, 2H, $CH_2$-α), 4.56 (m, 2H, *J* 4.4, H-7b,15a), 5.28 (s, 2H, H-10,13), 5.63 (m, 2H, *J* 3.8, H-10,13), 5.97 (d, 2H, *J* 7.0, H-4,19 or H-6,17), 6.10 (s, 2H, H-10,13), 6.35 (s, 2H, H-1,2), 6.43 (d, 2H, *J* 7.1, H-4,19 or H-6,17), 6.76 (d, 2H, *J* 7.0 Hz, H-3,20 or H-7,16), 6.96 (d, 2H, *J* 7.1, H-3,20 or H-7,16 ); 7.60 (m, 10H, H-phenyl)

**$^{13}$C-NMR** ($CDCl_3$, 68 MHz): δ 14.09, 22.60, 29.42, 30.82, 30.91, 31.75 (alkyl-C), 54.88 (C-7b,15a), 80.22 (C-8,15), 80. 86 (C-10,13), 120.65, 123.68, 125.51, 125.99, 128.14, 128.51, 129.00, 129.32, 131.56, 132.68, 135.01, 138.41, 138.70, 138.85, 140.37, 141.61, 142.17, 146.60 (C-1,2 and arom-C)

**MS (FAB(+), Xe, $CH_2Cl_2$/m-$NO_2$-Benzyl-OH):** m/z (%) = 878 (4) [$M^+$]; 526 (60) [$M^+$-$C_{24}H_{32}O_2$]; 353 (13) [$M^+$+H-$C_{42}H_{22}$]; 307