Fourfold Fusion of Strained Benzodehydroannulenes to an Expanded Porphyrazine Core

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Synthesis and Characterization

General

Unless stated otherwise, all reagents were purchased from commercial suppliers and used without further purification. Known starting materials that were not commercially available were prepared according to literature procedures cited in the text. Anhydrous THF and 1,4-dioxane were freshly distilled from sodium benzenophene ketyl, whereas anhydrous diisopropylamine, triethylamine and piperidine were distilled from CaH₂. All reactions were carried out under an atmosphere of dry argon with oven-dried glassware and reactions yielding porphyrazines were conducted under exclusion of light. Flash chromatography was executed on Merck silica gel (230–400 mesh). Gel permeation chromatography was performed with a polystyrene resin cross-linked with divinylbenzene (Bio-beads® 1-SX, Bio-Rad, Munich), swollen in THF using THF as eluent. NMR spectra were recorded on Varian MR-400,Varian Unity INOVA 500 MHz or Varian 500 VNMRS instruments. ¹H-NMR spectra were referenced to the residual solvent peak at δ = 7.26 (CDCl₃); ¹³C-NMR spectra were referenced to the solvent peak at δ = 77.16 (CDCl₃). UV/Vis spectra were obtained on a Perkin-Elmer Lambda Lambda 40 instrument. All solvents used for optical measurements were purchased as analytically pure. Melting points were determined with a BÜCHI melting point M-565 hot stage and are uncorrected. Mass spectra were recorded with a Finnigan LCQ Deca (ESI and APCI ionisation). MALDI-TOF mass spectrometry was carried out on a Bruker Biflex IV MALDI-TOF mass spectrometer with a N₂-Laser (337 nm; 3 ns pulse length). High-resolution mass spectrometry was carried out on a Bruker micro-TOF equipped with an ApolloTM ion funnel.

Experimental Details

1-Bromo-3,4-dimethoxybenzene¹

\[
\text{MeO} \quad \text{MeO} \quad \text{Br}
\]

\(N\)-bromosuccinimide (53.4 g, 0.3 mol) was slowly added to a solution of 1,2-dimethoxybenzene in carbon tetrachloride (50 mL) and the resulting mixture was stirred for 7 h at 90 °C. After cooling to room temperature the precipitate was filtered and washed with a small amount of carbon tetrachloride. Excess solvents of the collected filtrate were removed under reduced pressure and the residue was further purified by distillation to yield a colorless liquid (51 g, 0.24 mol, 79%, Lit.¹: 90%). ¹H-NMR (400 MHz, CDCl₃): δₙ (ppm) = 7.05 – 7.00 (m, 1H, CH₃rom.), 6.97 (d, \(J_{H-H} = 2.3\) Hz, 1H, CH₃rom.), 6.73 (d, \(J_{H-H} = 8.1\) Hz, 1H, CH₃rom.), 3.86 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃); ¹³C-NMR (126 MHz, CDCl₃): δₙ (ppm) = 149.72, 148.31, 123.35, 114.77, 112.69, 112.47, 56.05, 56.01.
1-Bromo-2-iodo-4,5-dimethoxybenzene$^3$ (8)

A solution of iodine monochloride (76 mmol, 12.66 g, 4 mL) in glacial acetic acid (10 mL) was slowly added to a solution of 1-bromo-3,4-dimethoxybenzene (11 g, 51 mmol) in glacial acetic acid (120 mL). The resulting mixture was first stirred at room temperature for 15 min, then at 80 °C for 16 h. The mixture was cooled to room temperature, then slowly added to a 1M solution of Na$_2$S$_2$O$_3$ (150 mL). After decoloration the aqueous solution was extracted with diethyl ether (3 x 100 mL) and the organic layer was washed successively with water (2 x 100 mL), saturated aqueous NaHCO$_3$ (100 mL), saturated aqueous NaCl (100 mL), dried over Na$_2$SO$_4$ and filtered. Excess solvents were removed under reduced pressure, and the residue was crystallized from ethanol to furnish colorless needles (15.6 g, 45.4 mmol, 89%, Lit.$^2$: 91%). mp: 88-89 °C; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta_{H}$ (ppm) = 7.22 (s, 1H, CH$_{arom}$), 7.07 (s, 1H, CH$_{arom}$), 3.84 (s, 3H, OCH$_3$), 3.83 (s, 3H, OCH$_3$).

1-Bromo-2-trimethylsilyl ethyl-4,5-dimethoxybenzene$^3$ (9)

1-Bromo-2-iodo-4,5-dimethoxybenzene (2 g, 5.8 mmol), PdCl$_2$(PPh$_3$)$_2$ (126 mg, 3 mol%) and CuI (67 mg, 6 mol%) were dissolved in anhydrous THF (12 mL) and triethylamine (6 mL). Trimethylsilylacetylene (0.95 mL, 1.15 eq) was slowly added and the resulting mixture was stirred at room temperature for 16 h. 1N hydrochloric acid (50 mL) was added to the reaction mixture which was subsequently extracted with diethyl ether (2 x 50 mL). The organic layer was washed successively with saturated aqueous NH$_4$Cl (50 mL), water (2 x 50 mL), saturated aqueous NaCl (50 mL), dried over Na$_2$SO$_4$ and filtered. Excess solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to yield a pale yellow solid (1.4 g, 4.4 mmol, 76%, Lit.$^3$: 59%). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta_{H}$ (ppm) = 6.99 (s, 1H, CH$_{arom}$), 6.94 (s, 1H, CH$_{arom}$), 3.86 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$), 0.25 (s, 9H, CH$_3$); $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta_{C}$ (ppm) =150.00, 147.98, 117.21, 117.08, 115.41, 115.11, 103.36, 97.69, 56.23, 56.15, 18.89, 11.40, 0.00; ESI-MS: $m/z$ = 314.03 [M+H]$^+$.
4-Triisopropylsilylethyl-5-trimethylsilyl-1,2-dimethoxy-benzene (10)

![](image)

1-Bromo-2-trimethylsilyl-4,5-dimethoxybenzene (9) (2.2 g, 7 mmol), Pd(PPh₃)₄ (243 mg, 3 mol%) and Cul (80 mg, 6 mol%) were dissolved in anhydrous dioxane (30 mL) and anhydrous piperidine (10 mL). Triisopropylsilylethylene (0.95 mL, 1.15 eq) was slowly added and the resulting mixture was stirred for 16 h at 90 °C. The reaction mixture was diluted with diethyl ether (150 mL) and washed successively with 1N hydrochloric acid (100 mL), saturated aqueous NH₄Cl (100 mL), water (100 mL) and saturated aqueous NaCl (100 mL). The organic layer was separated, dried over Na₂SO₄, filtered and excess solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to obtain a yellow solid (2.4 g, 5.81 mmol, 83%). ¹H-NMR (400 MHz, CDCl₃): δₗ₁ (ppm) = 6.91 (s, 1H, CHₐrom.), 6.88 (s, 1H, CHₐrom.), 3.88 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 1.15 (s, 21H, CH₃isopropyl), 0.23 (s, 9H, CH₃).

1-Ethynyl-6-triisopropylsilylethyl-3,4-dimethoxy-benzene (3)

![Image]

A solution of 10 (2 g, 4.7 mmol) and potassium carbonate (1.2 g, 9.4 mmol) in a mixture of THF and methanol (2:1, 15 mL) was stirred for 3 h at 50 °C. Dichloromethane (75 mL) was added and the resulting mixture was washed successively with water (2 x 50 mL), saturated aqueous NaCl (50 mL), dried over Na₂SO₄ and filtered. Excess solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to yield a pale yellow oil (1.4 g, 4.2 mmol, 88%). ¹H-NMR (400 MHz, CDCl₃): δₗ₁ (ppm) = 6.91 (s, 1H, CHₐrom.), 6.89 (s, 1H, CHₐrom.), 3.87 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 3.17 (s, 1H, CHₐethyl), 1.12 (s, 21H, CH₃isopropyl); ¹³C-NMR (126 MHz, CDCl₃): δ₀ (ppm) = 149.11, 148.86, 119.78, 118.01, 114.49, 114.34, 104.85, 93.47, 82.40, 79.65, 55.98, 55.97, 26.88, 18.65, 11.77, 11.30; ESI-MS: m/z = 342.22 [M+H]⁺.

3,6-dibromo-2,7-bis(tri-p-tolylpropynyl)phenanthrene-9,10-di(ethyleneglycol)ketal (2)

![Image]

3,6-dibromo-2,7-diiodo-9,10-di(ethylene-glycol)ketal¹ (2.82 g, 4 mmol), tri-p-tolylpropyne⁵ (2.1 g, 8.1 mmol), Pd(PPh₃)₄ (277 mg, 6 mol%) and Cul (91 mg, 12 mol%) were stirred at 85 °C in anhydrous dioxane (40 mL) and anhydrous diisopropylamine (20 mL) for 6 h. The reaction mixture was slowly
added to an aqueous solution of EDTA/NH₄Cl (200 mL). The resulting precipitate was collected by filtration and successively washed with water (2 x 50 mL), methanol (2 x 50 mL) and diethyl ether (2 x 15 mL). The residue was further purified by column chromatography on silica gel (petroleum ether/methylene chloride 3:1 → 1:1) to yield a colorless solid (3.21 g, 3 mmol, 75%). mp: 337 °C; ¹H-NMR (400 MHz, CDCl₃): δ_H (ppm) = 8.02 (s, 2H, CHphenan.), 7.82 (s, 2H, CHphenan.), 7.24 (d, 3J_H-H = 8.0 Hz, 12H, CHarom.), 7.11 (d, 3J_H-H = 8.0 Hz, 12H, CHarom.), 4.19 (bs, 4H, OCH₂), 3.64 (bs, 4H, OCH₂), 2.35 (s, 18H, CH₃); ¹³C-NMR (126 MHz, CDCl₃): δ_C (ppm) = 142.34, 136.57, 132.45, 132.36, 131.36, 129.26, 128.84, 128.06, 127.89, 126.90, 102.52, 92.07, 83.39, 61.57, 55.70, 21.17; MALDI-TOF MS (DCTB, positive ion mode): m/z = 1070.43 [M]+, calculated for [C₆₆H₅₆O₄Br₂]^+ = 1070.96.

3,6-Di(1-ethyl-6-triisopropylethyl-3,4-dimethoxy-benzene)-2,7-bis(3,3,3-tri-p-tolylprop-1-ynyl)phenanthrene-9,10-di(ethylene glycol)ketal (4)

1-Ethyl-6-triisopropylsilylethyl-3,4-dimethoxy-benzene (3, 880 mg, 2.57 mmol), 2 (1.3 g, 1.21 mmol), Pd(PPh₃)₄ (84 mg, 6 mol%) and CuI (28 mg, 12 mol%) were stirred at 90 °C in anhydrous dioxane (15 mL) and anhydrous diisopropylamine (7.5 mL) for 5 h. After cooling to room temperature, the reaction mixture was diluted with methylene chloride (100 mL) and washed successively with 1N hydrochloric acid (50 mL), saturated aqueous NH₄Cl (50 mL), water (50 mL) and saturated aqueous NaCl (50 mL). The organic layer was separated, dried over Na₂SO₄, filtered, and excess solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to yield a colorless solid (1.35 g, 0.85 mmol, 70%). mp: 196-198 °C; ¹H-NMR (400 MHz, CDCl₃): δ_H (ppm) = 7.93 (s, 2H, CHphenan.), 7.75 (s, 2H, CHphenan.), 7.17 (d, 3J_H-H = 8.2 Hz, 12H, CHarom.), 6.90 (s, 2H, CHarom.), 6.89 (d, 3J_H-H = 8.2 Hz, 12H, CHarom.), 6.58 (s, 2H, CHarom.), 4.14 (bs, 4H, OCH₂), 3.85 (s, 6H, OCH₃), 3.61 (bs, 4H, OCH₂), 3.33 (s, 6H, OCH₃), 2.19 (s, 18H, CH₃), 0.93 (s, 42H, CHisopropyl); ¹³C-NMR (126 MHz, CDCl₃): δ_C (ppm) = 148.80, 148.59, 142.42, 136.07, 132.49, 131.31, 129.71, 128.97, 128.57, 127.70, 127.64, 126.72, 119.07, 118.84, 114.61, 114.34, 105.17, 101.08, 93.58, 92.92, 92.09, 90.18, 83.74, 56.00, 55.52, 55.43, 20.89, 18.65, 11.27; HR/ESI-MS: m/z = 1699.693 [M+Ag]^+, calculated for [C₁₅₈H₁₁₂O₈Si₂Ag]^+ = 1699.694.
3,6-di(1-ethinyl-6-ethinyl-3,4-dimethoxy-benzene)-2,7-bis(3,3,3-tri-p-tolylprop-1-ynyl)phenanthrene-9,10-di(ethyleneglycol)-ketal (5)

A solution of 4 (1 g, 0.63 mmol) and tetra-\textit{n}-butylammonium fluoride (800 mg, 4 eq) in a mixture of THF (5 mL) and methanol (2.5 mL) was stirred at 50 °C for 16 h. The reaction mixture was diluted with methylene chloride (50 mL) and washed successively with water (3 x 50 mL) and saturated aqueous NaCl (50 mL). The organic layer was separated, dried over Na$_2$SO$_4$, filtered, and excess solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) to yield a pale yellow solid (719 mg, 0.56 mmol, 89%). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta_{H}$ (ppm) = 8.08 (s, 2H, CH$_{phenan}$), 7.84 (s, 2H, CH$_{phenan}$), 7.29 (d, $^3$J$_{H-H}$ = 8.1 Hz, 12H, CH$_{arom}$), 7.00 (d, $^3$J$_{H-H}$ = 8.0 Hz, 12H, CH$_{arom}$), 6.99 (s, 2H, CH$_{arom}$), 6.65 (s, 2H, CH$_{arom}$), 4.20 (bs, 4H, OCH$_2$), 3.90 (s, 6H, OCH$_3$), 3.67 (bs, 4H, OCH$_2$), 3.44 (s, 6H, OCH$_3$), 3.14 (s, 2H, CH$_{ethinyl}$), 2.28 (s, 18H, CH$_3$); $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta_C$ (ppm) = 148.11, 148.04, 141.42, 135.18, 131.79, 130.40, 128.77, 128.02, 127.60, 126.82, 126.60, 125.54, 118.04, 116.65, 113.44, 113.36, 100.34, 91.41, 91.06, 89.78, 82.68, 81.23, 79.18, 54.98, 54.64, 54.49, 19.89; HR/ESI-MS: m/z = 1303.509 [M+Na]$^+$, calculated for [C$_{99}$H$_{72}$O$_6$+Na]$^+$ = 1303.512.

Dehydroannulenophenantherene-9,10-di(ethyleneglycol)-ketal (6)

A solution of 5 (500 mg, 0.39 mmol) and copper(II) acetate in pyridine (10 mL) was stirred for 2 h at 60 °C. After cooling to room temperature chloroform (50 mL) was added and the mixture was washed successively with 1N hydrochloric acid (50 mL), water (2 x 50 mL) and saturated aqueous NaCl (50 mL). The organic layer was separated, dried over Na$_2$SO$_4$, filtered, and excess solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with chloroform to yield a bright yellow solid (450 mg, 0.35 mmol, 90%). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta_{H}$ (ppm) =8.51 (s, 2H, CH$_{phenan}$), 7.74 (s, 2H, CH$_{phenan}$), 7.35 (d, $^3$J$_{HH}$ = 8.2 Hz, 12H, CH$_{arom}$), 7.10 (d, $^3$J$_{HH}$ = 8.2 Hz 12H, CH$_{arom}$), 7.08 (s, 2H, CH$_{arom}$), 6.42 (s, 2H, CH$_{arom}$), 4.19 (bs, 4H, OCH$_2$), 3.91 (s, 6H, OCH$_3$), 3.69 (bs, 4H, OCH$_2$), 3.39(s, 6H, OCH$_3$), 2.32 (s, 18H, CH$_3$); $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta_C$ (ppm) =149.69, 149.32, 142.56, 136.28, 132.79, 130.93, 130.24, 129.06, 128.99, 128.72,
128.24, 124.42, 118.43, 118.30, 116.33, 113.54, 101.14, 93.10, 92.46, 92.42, 83.76, 82.46, 56.03, 55.72, 55.46, 20.95; MALDI-MS (DCTB, positive ion mode): m/z = 1279.55 [M+H]⁺.

**Dehydroannuleno-2,3-dicyano-dibenzoquinoxaline (7)**

![Diagram of the molecule](image)

6 (300 mg, 0.23 mmol) and p-toluene sulphonic acid monohydrate (134 mg, 0.7 mmol) were heated in glacial acetic acid and o-dichlorobenzene at 140 °C for 2 h until the starting material was completely hydrolysed (TLC control). After cooling to 70 °C diaminomaleonitrile (40 mg, 0.35 mmol) was added and the solution was stirred for 3 h. The solution was cooled to room temperature and was slowly added to methanol (50 mL). The resulting brownish red precipitate was collected by filtration. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to yield a red solid (243 mg, 0.19 mmol, 82%).¹H-NMR (400 MHz, CDCl₃): δH (ppm) = 9.10 (s, 2H, CH₆phenan), 8.50 (s, 2H, CH₆phenan), 7.35 (d, JHH = 8.2 Hz, 12H, CH₆arom), 7.11 (d, JHH = 8.2 Hz, 12H, CH₆arom), 6.83 (s, 2H, CH₆arom), 6.21 (s, 2H, CH₆arom), 3.69 (s, 6H, OCH₃), 3.36 (s, 6H, OCH₃), 2.36 (s, 18H, CH₃); ¹³C-NMR (126 MHz, CDCl₃): δC (ppm) = 149.69, 149.32, 142.56, 136.28, 132.79, 130.93, 130.24, 129.06, 128.99, 128.72, 128.24, 124.42, 118.43, 118.30, 116.33, 113.54, 101.14, 93.10, 92.46, 92.42, 83.76, 82.46, 56.03, 55.72, 55.46, 20.95; HR/ESI-MS: m/z = 1369.3836 [M+Ag]⁺, calculated for [C₉₀H₉₂N₆O₄+Ag]⁺ = 1369.3817; UV/VIS (CHCl₃): λmax/nm (ε₁₀⁵ M⁻¹ cm⁻¹ = 312 (1.06), 351 (0.66), 374 (0.48), 409 (0.53).
Tetra(benzodehydroannuleno)dibenzoquinoxalinoporphyrazine (1)

Magnesium turnings (8 mg, 0.33 mmol) and a small crystal of iodine were stirred in n-butanol (3 mL) under an argon atmosphere for 3 h at 160 °C. The dicyanodibenzoquinoxaline 7 (70 mg, 55 μmol) was dissolved in the minimal amount of o-dichlorobenzene (ca. 0.5 mL), and the resulting solution was added to the refluxing solution of magnesium butanolate. The reaction mixture was stirred for another 3 h at 160 °C and, after cooling to room temperature, the brown-green solution was poured into methanol saturated with NH₄Cl (10 mL). The precipitate was filtered, washed sequentially with water (3 x 10 mL), methanol (3 x 10 mL) and hexane (2 x 10 mL). The crude product was filtered through a pad of silica (THF) and purified by gel permeation chromatography using THF as solvent. The olive-green band was collected to furnish, after removal of excess solvents under reduced pressure, 1 as an olive-brown solid (10 mg, 0.002 mmol, 15%). MALDI-TOF MS (dithranol, positive ion mode): m/z =5078 [M]+, calculated for [C₃₆₀H₂₄₈N₁₆O₁₆Mg]+ = 5078.22; UV/VIS (CHCl₃) : λmax/nm (ε / 10⁶ M⁻¹ cm⁻¹) = 317 (2.30), 382 (1.19), 417 (1.23), 721 (1.18).
NMR Spectra

$^1$H-NMR-Spectrum of 4 in CDCl$_3$:

$^{13}$C-NMR-Spectrum of 4 in CDCl$_3$:
$^1$H-NMR-Spectrum of 5 in CDCl₃:

$^{13}$C-NMR-Spectrum of 5 in CDCl₃:
$^1$H-NMR-Spectrum of 6 in CDCl$_3$:

$^{13}$C-NMR-Spectrum of 6 in CDCl$_3$: 
$^1$H-NMR-Spectrum of $\mathbf{7}$ in CDCl$_3$:

$^{13}$C-NMR-Spectrum of $\mathbf{7}$ in CDCl$_3$:
MALDI-TOF mass spectrum

Maldi-TOF mass spectrum of 1 (dithranol, positive ion mode)

\[ 5078.708 \text{ g/mol} \]

\(^1\text{O}_2\)-emission of 1

Compound 1 was irradiated between 680 – 800 nm with a 100W QTH (quartz tungsten halogen) light source (Oriel Q-series). The excitation light was directed via fibre optics through a temperature-controlled cuvette from Ocean Optics (CUV QPOD). For detection of the \(^1\text{O}_2\)-phosphorescence at 1270 nm a Cornerstone\textsuperscript{TM} 260i 1/4m monochromator from Newport Physics with a blazed grating (600 lines/mm, 1250 nm), a cooled InGaAs semiconductor diode detector, a chopper system and an Oriel Merlin\textsuperscript{TM} digital lock-in radiometry system from Newport Physics was utilized. A filter (780 nm cut-on, range 800 – 2700 nm) was used to eliminate higher-order fluorescence in the range of 1270 nm.
References


