Synthesis and Spectroscopic Properties of a Hexapyrenylbenzene Derivative

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Supporting Information

General: Reagents and solvents were purchased from Acros, Aldrich, and Fluka and were used as received. 4,5,9,10-tetrahydropyrene was synthesized according to a literature procedure¹. Dioxane and THF were distilled from Na/benzophenone. Benzene was distilled from CaH₂. All reactions except the first were carried out under a dry N₂ atmosphere. ¹H and ¹³C NMR spectra were measured on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. Coupling constants (J) are given in Hz. Resonance multiplicities are described as s (singlet), d (doublet), t (triplet), or m (multiplet). MALDI mass spectra were obtained on a Bruker Daltonics Autoflex II instrument using DCTB as the matrix.

2,7-Dibromo-4,5,9,10-tetrahydropyrene.

To a stirred solution of 4,5,9,10-tetrahydropyrene (4.00 g, 19.4 mmol) in 130 ml acetic acid a solution of sodium hydroxide (1.71 g, 42.7 mmol) and bromine (6.82 g, 2.19 ml, 42.7 mmol) in 130 ml water was added dropwise over a period of 30 min at ambient temperature. The reaction mixture was stirred overnight and the precipitate was removed by filtration, washed with water and dried in vacuo. The white solid was recrystallized from benzene to give 2,7-dibromo-4,5,9,10-tetrahydropyrene (3.96 g, 10.8 mmol, 56 %). Mp: 218-219 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.82 (s, 8H), 7.20 (s, 4H). CA: [17533-36-7].

2-Bromo-4,5,9,10-tetrahydro-7-pyrenecarboxylic acid octylester (3).

To a solution of 2,7-dibromo-4,5,9,10-tetrahydropyrene (1.08 g, 2.97 mmol) in 100 ml tetrahydrofuran, *n*-butyllithium solution in hexane (1.6 M, 1.85 ml, 2.97 mmol) was added dropwise during 5 min at -90 °C and stirred for 25 min. Then octylchloroformate (1.71 g, 1.74 ml, 8.90 mmol) was added in one portion and stirring was continued for further 15 min. The reaction mixture was poured on crushed ice and some drops conc. hydrochloric acid and was extracted three times with dichloromethane. The organic phase was dried with MgSO₄ and evaporated. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate 98:2 as eluent to yield **3** as a white solid (0.95 g, 2.15 mmol, 73 %). Mp: 103 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.89 (t, 3H), 1.2-1.5 (10H), 1.78 (m, 2H), 2.89 (m, 8H), 4.32 (t, 3H), 7.25 (s, 2H), 7.75 (s, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 14.2 (CH₃), 22.8 (CH₂), 26.2 (CH₂), 28.08 (CH₂), 28.10 (CH₂), 28.9 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 32.0 (CH₂), 65.3 (CH₂), 121.9 (q), 127.4 (CH), 129.0 (q), 129.2 (q + CH), 134.3 (q), 135.2 (q), 138.3 (q), 166.9 (C(O)=O). MS (EI): m/z (%), 440.2 (100)

2-Bromo-7-pyrenecarboxylic acid octylester (4).

A solution of **3** (760 mg, 1.72 mmol) and DDQ (821 mg, 3.62 mmol) in dry benzene was refluxed for 24 - 48 h under nitrogen atmosphere (reaction status controlled by TLC). After removal of the solvent the residue was treated with cold ethanol to give a white solid which was filtered off (470 mg, 1.08 mmol, 62 %). Mp: 131-132 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (t, 3H), 1.2-1.5 (10H), 1.90 (m, 2H), 4.49 (t, 2H), 8.02 (AA', 2H), 8.16 (BB', 2H), 8.32 (s, 2H), 8.85 (s, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 14.3 (CH₃), 22.8 (CH₂), 26.3 (CH₃), 29.0 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 32.0 (CH₂), 65.8 (CH₂), 121.4 (q), 123.1 (q), 126.6 (CH), 126.7 (q), 127.2 (CH), 127.7 (CH), 128.2 (q), 129.2 (CH), 130.8 (q), 133.4 (q), 167.2 (C(O)=O). MS (EI): m/z (%), 436.3 (100). HRMS (EI): calcd. m/z = 436.10388, found m/z = 436.10333.

7-(Trimethylsilylethynyl)-2-pyrenecarboxylic acid octylester (5).

Compound **4** (300 mg, 0.69 mmol) was dissolved in 7 ml dioxane (slightly heating required) under nitrogen atmosphere. To this solution copper(I)iodide (3.20 mg, 17.1 μmol), bis(benzonitrile)palladium(II)chloride (7.90 mg, 20.6 μmol), tri-*tert*-

butylphosphine solution in hexane (0.33 M, 0.21 ml, 68.8 μ mol) , trimethylsilylacetylene (84.2 mg, 121 μ l, 0.86 mmol) and diisopropylamine (86.7 mg, 121 μ l, 0.86 mmol) were added. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue extracted with dichloromethane and water. After drying the organic phase with MgSO₄ the dichloromethane was evaporated and the residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate 95:5 as eluent to yield **5** (220 mg, 0.48 mmol, 70 %) which still contains minor impurities. Mp: 120-122 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.34 (s, 9H), 0.90 (t, 3H), 1.2-1.5 (10H), 1.90 (m, 2H), 4.48 (t, 2H), 8.04 (AA', 2H), 8.14 (BB', 2H), 8.30 (s, 2H), 8.83 (s, 2H). MS (EI): m/z (%), 454.2 (100), 439.2 (15). HRMS (EI): calcd. m/z = 454.23287, found m/z = 454.23232

7-Ethynyl-2-pyrenecarboxylic acid octylester (**6**).

A solution of **5** (211 mg, 0.46 mmol) in 5 ml tetrahydrofuran was treated with tetrabutylammonium fluoride solution (1M, 0.51 ml, 0.51 mmol) in tetrahydrofuran. After 2 h the solvent was removed in vacuo and the residue extracted with dichloromethane and water. The organic phase was dried with MgSO₄ and evaporated to dryness to yield 170 mg (0.45 mmol, 96 %). The crude product was used without further purification. Mp: 98°C. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (t, 3H), 1.2-1.5 (10H), 1.90 (m, 2H), 3.27 (s, 1H), 4.48 (t, 2H), 8.06 (AA', 2H), 8.16 (BB', 2H), 8.32 (s, 2H), 8.85 (s, 2H).

Ethynylene-di-2-(7-pyrenecarboxylic acid octylester) (7).

Compound **4** (72.0 mg, 16.5 μmol) was dissolved in 3 ml dioxane (slightly heating required) under nitrogen atmosphere. To the solution copper(I)iodide (3.15 mg, 16.5 μmol), bis(benzonitrile)palladium(II)chloride (3.35 mg, 8.27 μmol), tri-*tert*-butylphosphine solution in hexane (0.33M, 0.05 ml, 16.5 μmol), **6** (70.0 mg, 18.2 μmol) and diisopropylamine (20.1 mg, 27.8 μl , 0.86 mmol) were added. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue extracted with dichloromethane and water. After drying the organic phase with MgSO_4 the dichloromethane was removed and the residue was washed several times with cold dichloromethane to yield **7** (63.0 mg, 85.3 μmol , 52 %). Mp: 263-267 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 0.91 (t, 6H), 1.2-1.5 (20H), 1.91 (m, 4H), 4.49 (t, 4H), 8.12 (AA', 4H), 8.18 (BB', 4H), 8.46 (s, 4H), 8.48 (s, 4H). MS (EI): m/z (%), 738.3 (100), 626.2 (10). HRMS (EI): calcd. m/z = 738.37164, found = 738.37109

Hexa-7-(2-pyrenylcarboxylic acid, octyl ester)benzene (8).

A mixture of **7** (100 mg, 0.14 mmol) and 25 ml dioxane was heated to 60 °C under nitrogen. Then Co_2CO_8 (15.0 mg, 45.0 μmol) was added and the mixture was heated to reflux overnight. The solvent was removed in vacuo and the residue was purified by flash-chromatography on silica gel using petrol ether/dichloromethane 2:1 $\rightarrow$ 3:1 as eluent. The crude product was precipitated twice from dichloromethane and methanol to yield pure pale yellow **8** (25 mg, 35 μmol). Mp: 419 °C (decomp.). ^1H NMR (400 MHz, CDCl_3): 0.83 (t, 18H), 1.2-1.5 (60H), 1.73 (m, 12H), 4.30 (t, 12H), 7.55 (AA', 12H), 7.64 (BB', 12H), 8.08 (s, 12H), 8.43 (s, 12H). ^{13}C NMR (400 MHz CDCl_3): 14.2 (CH_3), 22.7 (CH_2), 26.1 (CH_2), 28.8 (CH_2), 29.27 (CH_2), 29.34 (CH_2), 31.9 (CH_2), 65.5 (CH_2), 122.2 (q), 125.4 (CH), 126.3 (q), 127.2 (q), 127.6 (2xCH), 128.3 (q), 130.5 (q), 130.6 (q), 139.1 (q), 141.9 (q), 167.2 ($\text{C}(\text{O})=\text{O}$). MS (MALDI), m/z (%) 2216.039 (100), calcd. 2216.11609 (100).

DFT calculations (B3LYP/6-31G*) of pyrene LUMO and HOMO

Pyrene LUMO

Pyrene HOMO

^{13}C NMR (CDCl_3) of **3**

^1H NMR (CDCl_3) of **3**

1) peak at 5.30 dichloromethane

^{13}C NMR (CDCl_3) of **4**

^1H NMR (CDCl_3) of **4**

^{13}C NMR (CDCl_3) of **8**

2) peak at 31.06 acetone CH₃

^1H NMR (CDCl_3) of **8**

3) peak at 5.30 dichloromethane

¹H NMR (CDCl₃) of **5**

¹H NMR (CDCl₃) of **6**

^1H NMR (CDCl_3) of **7**

(1) Conner, M. D.; Scott, D. A.; Collard, M. D.; Liotta, L. C.; Schiraldi, D. A. *J. Org. Chem.* **1999**, 64, 6888-6890.