Aryne-mediated syntheses of structurally related acene derivatives
Diego Rodríguez-Lojo, Diego Peña,* Dolores Pérez* and Enrique Guitián
Departamento de Química Orgánica, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain
diego.pena@usc.es; dolores.perez@usc.es

Organic & Biomolecular Chemistry

ELECTRONIC SUPPLEMENTARY INFORMATION

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1. Experimental details and spectroscopic data

1.1 General methods
All reactions were carried out under argon using oven-dried glassware. TLC was performed on Merck silica gel 60 F254; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh).

Aryne precursors 5 and 9, and phencyclone (8) were prepared following published procedures. Bu$_4$NF (TBAF) was used in solution in THF (1.0 M). Commercial reagents and anhydrous solvents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification.

![figure S1](image.png)

Figure S1

1.2 Synthesis of polyarenes 2-4

2,3,6,7-Tetrakis(hexyloxy)-10,11,12,13-tetraphenylbenzo[b]triphenylene (2)

Bu$_4$NF (153 µL, 1M, 0.153 mmol) was added dropwise to a solution of 5 (100 mg, 0.118 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (50 mg, 0.130 mmol) in THF (2.5 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. After this time, H$_2$O (2 mL) and Et$_2$O (2 mL) were added, the phases were separated and the aqueous layer was extracted with Et$_2$O. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane, then Et$_2$O/hexane 1:10 to 1:3), affording 2 (83 mg, 72%) as a brownish solid. M.p. 90-195 °C; $^1$H NMR (400 MHz, CDCl$_3$), δ: 8.66 (s, 2H), 7.74 (s, 2H), 7.65 (s, 2H), 7.44-7.28 (m, 10H), 7.00-6.87 (m, 10H), 4.20 (t, 4H), 3.99 (t, 4H), 2.00-1.83 (m, 8H), 1.66-1.30 (m, 24H), 1.05-0.85 (12 H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$), δ: 149.6 (2C), 149.1 (2C), 140.9 (2C), 140.1 (2C), 138.4 (2C), 138.3 (2C), 131.9 (4CH), 131.7 (4CH), 130.9 (2C), 127.8 (2C), 127.7 (4CH), 126.9 (4CH), 126.6 (2CH), 125.6 (2CH), 124.4 (2C), 124.0 (2C), 120.8 (2CH), 107.9 (2CH), 107.3 (2CH), 70.1 (2CH$_2$), 68.9 (2CH$_2$), 61.9 (2CH$_2$), 31.8 (2CH$_2$), 29.6 (2CH$_2$), 29.3 (2CH$_2$), 26.0 (2CH$_2$), 25.9 (2CH$_2$), 22.90 (2CH$_3$), 22.87 (2CH$_3$), 14.30 (2CH$_3$), 14.26 (2CH$_3$); MALDI-TOF MS, m/z (%): 982.61 (100); UV/Vis (CH$_2$Cl$_2$), $\lambda_{max}$ (ε): 329 (83900), 304 (84400), 278 (sh, 70400 mol$^{-1}$ dm$^3$ cm$^{-1}$) nm.

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4 A broad melting transition is probably due to liquid crystal behaviour.
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2,3,6,7-Tetrakis(hexyloxy)-10,19-diphenyltetrabenzo[a,c,j,l]tetracene (3)

Bu$_4$NF (153 µL, 1M, 0.153 mmol) was added dropwise to a solution of 5 (100 mg, 0.118 mmol) and phenycyclone (8, Figure S1, 64 mg, 0.165 mmol) in THF (2.5 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. After this time, H$_2$O (2 mL) and Et$_2$O (2 mL) were added, the phases were separated and the aqueous layer was extracted with Et$_2$O. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane, then CH$_2$Cl$_2$/hexane 1:8 to 1:3), affording 3 (63 mg, 55%) as a yellow solid. M.p. 138 ºC; $^1$H RMN (400 MHz, CDCl$_3$), δ: 8.94 (s, 2H), 8.26 (d, 2H), 7.77-7.63 (m, 12H), 7.60 (s, 2H), 7.57 (s, 2H), 7.00 (dd, 2H), 4.21 (t, 4H), 4.05 (t, 4H), 2.00-1.85 (m, 8H), 1.63-1.47 (m, 8H), 1.46-1.29 (m, 16H), 1.03-0.81 (12 H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$), δ: 149.8 (2C), 149.2 (2C), 142.4 (2C), 135.3 (2C), 133.1 (4CH), 132.3 (2C), 131.8 (2C), 131.0 (2CH), 130.7 (2C), 129.1 (4CH), 128.7 (2C), 127.9 (2C), 127.8 (2CH), 127.1 (2CH), 126.1 (2CH), 124.5 (2C), 124.1 (2C), 123.6 (2CH), 120.5 (2CH), 107.9 (2CH), 107.5 (2CH), 70.1 (2CH$_2$), 69.1 (2CH$_2$), 31.9 (2CH$_2$), 31.8 (2CH$_2$), 29.9 (2CH$_2$), 29.6 (2CH$_2$), 26.02 (2CH$_2$), 14.3 (4CH$_3$) ppm; MS (FAB$^+$), m/z (%): 981 (100), HRMS (FAB$^+$), m/z: calcd for C$_{70}$H$_{77}$O$_4$ [M + H$^+$]: 981.5744, found: 981.5822. UV/Vis (CH$_2$Cl$_2$), λ$_{max}$ (ε): 354 (103900), 261 (sh, 43100 mol$^{-1}$ dm$^3$ cm$^{-1}$) nm.

15,16,19,20-Tetrakis(hexyloxy) dibenzo[f,j]triphenylene[2,3-s]picene (4)

Finely powdered anhydrous CsF (103 mg, 0.676 mmol) was added to a solution of 5 (41 mg, 0.048 mmol), 9 (48 mg, 0.121 mmol), 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, 20 mg, 0.085 mmol) and Pd$_2$(dba)$_3$ (5.0 mg, 0.005 mmol) in CH$_3$CN/CH$_2$Cl$_2$ 5:1 (3.6 mL), and the mixture was stirred at room temperature for 15 h. After this time, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography (silica gel; hexane, then Et$_2$O/hexane 1:10 to 1:3), affording 4 (13 mg, 30 %) as a yellow solid. M. p. 121 ºC; $^1$H RMN (500 MHz, CDCl$_3$), δ: 9.99 (s, 2H), 9.19 (d, 2H), 8.85 (d, 2H), 8.66 (d, 2 H), 8.15 (s, 2 H), 8.01 (d, 2H), 7.87 (s, 2 H), 7.81 (m, 4 H), 7.58 (m, 4H), 4.35-4.28 (m, 8H), 2.05-1.94 (m, 8H), 1.68-1.58 (m, 8H), 1.50-1.36 (m, 16H), 1.03-0.94 (12 H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$), δ: 150.0 (2C), 149.5 (2C), 132.1 (2C), 130.9 (2C), 130.7 (2CH), 129.9 (2C), 129.6 (2C), 129.4 (2C), 129.1 (2CH), 128.9 (2C), 127.8 (2C), 127.1 (2CH), 126.8 (2CH), 126.4 (2CH), 125.6 (2CH), 124.9 (2C), 124.1 (2C), 123.8 (2CH), 123.4 (2CH), 122.9 (2CH), 107.7 (2CH), 107.5 (2CH), 70.0 (2CH$_2$), 69.5 (2CH$_2$), 31.9 (4CH$_2$), 29.5 (4CH$_2$), 26.1 (4CH$_2$), 22.9 (4CH$_2$), 14.3 (4CH$_3$) ppm; MS (FAB$^+$), m/z (%): 979 (100), HRMS (FAB$^+$), m/z: calcd for C$_{70}$H$_{75}$O$_4$ [M + H$^+$]: 979.5744, found: 979.5822. UV/Vis (CH$_2$Cl$_2$), λ$_{max}$ (ε): 354 (103900), 261 (sh, 43100 mol$^{-1}$ dm$^3$ cm$^{-1}$) nm.
2. $^1$H and $^{13}$C NMR spectra
Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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