

# Hyperpolarized $^{129}\text{Xe}$ NMR spectroscopic investigation of potentially porous shape- persistent macrocyclic materials

*Kristopher J. Ooms, Katie Campbell, Rik R. Tykwinski and Roderick E. Wasylshen\**

## Supporting Information.

### General Experimental Details.

Column chromatography: Silica gel-60 (230–400 mesh) from *General Intermediates of Canada* or *Silicycle*. Thin Layer Chromatography (TLC): Plastic sheets coated with *silica gel G UV<sub>254</sub>* from *Macherey–Nagel*: visualization by UV light. Mp.: *Gallencamp* apparatus; uncorrected. IR spectra: *Nic–Plan IR Microscope* (cast from  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR: *Varian Gemini–300*, *–400*, or *–500* instruments at rt in  $\text{CD}_2\text{Cl}_2$ ; solvent peaks (5.32 ppm for  $^1\text{H}$  and 53.80 ppm for  $^{13}\text{C}$ ) as reference. EI MS (70 eV): *Kratos MS 50* instrument. ESI MS ( $m/z$ ): *Micromass Zabspec oaTOF* instrument; solvents as noted.

**Oligomer 6.** In dry glassware under  $\text{N}_2$ , 3,5–diethynylbenzene **4** (47 mg, 0.37 mmol) was dissolved in a mixture of dry, degassed THF (40 mL) and  $\text{Et}_2\text{NH}$  (3 mL). Vinyl triflate **5** (0.35 g, 0.75 mmol) was added to the solution, followed by  $\text{Pd}(\text{PPh}_3)_4$  (30 mg, 0.026 mmol) and  $\text{CuI}$  (10 mg, 0.053 mmol). The resulting mixture was stirred at 50

°C for 14 h. After cooling to room temperature, ether (25 mL) was added, and the resulting solution was washed with saturated NH<sub>4</sub>Cl (2 × 25 mL) and dried (MgSO<sub>4</sub>). Purification by column chromatography on silica (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 2:1) afforded oligomer **6** (0.28 g, 98%) as a golden oil. *R*<sub>f</sub> = 0.39 (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 2:1). IR (CH<sub>2</sub>Cl<sub>2</sub> cast) 3054, 2954, 2873, 2145, 1592, 1492 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.51 – 7.45 (m, 8H), 7.39 – 7.33 (m, 12H), 7.20 – 7.18 (m, 4H), 0.96 (t, *J* = 7.8 Hz, 18H), 0.60 (q, *J* = 8.0 Hz, 12H); <sup>13</sup>C {<sup>1</sup>H} NMR (125.3 MHz, APT, CD<sub>2</sub>Cl<sub>2</sub>) δ 157.6, 140.6, 140.4, 134.1, 131.6, 130.7, 130.6, 129.1, 129.0, 128.8, 128.1, 128.0, 123.7, 104.4, 102.1, 96.3, 90.9, 89.7, 7.6, 4.5; EI HRMS calcd. for C<sub>54</sub>H<sub>54</sub>Si<sub>2</sub> (M<sup>+</sup>) 758.3764, found 758.3789.

**Macrocycle 2.** Oligomer **6** (0.11 g, 0.14 mmol) was dissolved in wet THF (25 mL) and treated with TBAF (ca. 2.2 equiv.). The resulting solution was stirred, in the presence of air at room temperature, until TLC analysis indicated complete conversion to the desilylated intermediate. Ether (25 mL) was added, and the resulting solution was washed with saturated NH<sub>4</sub>Cl (2 × 25 mL) and dried. The solvent was reduced to ca. 1 mL and the deprotected polyynes were carried on, with no further purification. The deprotected polyynes were oxidatively coupled in the presence of CuI (0.40 g, 2.1 mmol), TMEDA (0.40 mL, 2.6 mmol) and air in dry CH<sub>2</sub>Cl<sub>2</sub> (350 mL) for 14 h at rt. Ether (300 mL) was added, and the resulting solution was washed with saturated NH<sub>4</sub>Cl (6 × 75 mL), saturated NaHCO<sub>3</sub> (2 × 75 mL), brine (2 × 75 mL), and dried. The solvent volume was reduced by approximately 80%, and acetone (3 mL) was added, resulting in the formation of a yellow precipitate. Isolation of the precipitate afforded **2** (29 mg, 39%) as an orange–yellow solid that was not sufficiently soluble for meaningful <sup>13</sup>C NMR analysis. Mp 184 °C (dec.). IR (CH<sub>2</sub>Cl<sub>2</sub> cast) 3053, (a *very* weak C≡C absorption is

observed at ca. 2150), 1595, 1486  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.60 (t,  $J = 1.5$  Hz, 2H), 7.49 – 7.31 (m, 40H), 7.18 (t,  $J = 7.6$  Hz, 2H), 7.01 (dd,  $J = 7.9, 1.6$  Hz, 4H); ESI MS ( $\text{NO}_2\text{Me}$ , AgOTf added,  $\text{C}_{84}\text{H}_{48}$ )  $m/z$  (rel. intensity): 1937 ( $[\text{M} + \text{Ag} + 3\text{AgOTf}]^+$ , 19), 1679 ( $[\text{M} + \text{Ag} + 2\text{AgOTf}]^+$ , 53), 1421 ( $[\text{M} + \text{Ag} + \text{AgOTf}]^+$ , 66), 1165 ( $[\text{M} + \text{Ag}]^+$ , 100).

### X-ray Crystallographic studies.

Unit cell parameters and intensity data were obtained at  $-80$  °C on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The structures were solved by direct methods using SHELXS-86<sup>18</sup> and refined by full-matrix least squares on  $F^2$  using SHELXL-93.<sup>19</sup> Data for **1** ( $\text{C}_{84}\text{H}_{50}\text{Cl}_4\text{N}_2$ ),  $F_w = 1229.06$ ; monoclinic crystal system; space group  $P2_1/n$  (an alternate setting of  $P2_1/c$  [No. 14]),  $a = 9.7664$  (9),  $b = 16.6488$  (15),  $c = 20.6911$  (18) Å;  $\beta = 101.1778$  (19)°;  $V = 3300.5$  (5) Å<sup>3</sup>;  $Z = 2$ ;  $\rho_{\text{calcd}} = 1.237$  g  $\text{cm}^{-3}$ ;  $2\theta_{\text{max}} = 52.84$ °;  $\mu = 0.227$   $\text{mm}^{-1}$ ; total data collected = 17480;  $R_1 = 0.0790$  (3035 observed reflections with  $F_o^2 \geq 2\sigma(F_o^2)$ );  $wR_2 = 0.1734$  for 379 variables and 6749 unique reflections with  $F_o^2 \geq -3\sigma(F_o^2)$ ; residual electron density = 0.178 and -0.150 e Å<sup>-3</sup>.

- (1) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
- (2) Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination, University of Göttingen, Göttingen (Germany), **1993**.