

Supplementary Information

Conformational Polymorphism of 1,8-Dipyridylnaphthalene and Encapsulation of Chains of Fused Cyclic Water Pentamers in a Hydrophobic Crystal Environment

Xuefeng Mei and Christian Wolf*

Department of Chemistry, Georgetown University, Washington, DC 20057, USA

cw27@georgetown.edu

CCDC 268403 (**1**-(H₂O)₃), 268402 (form II) and 268401 (form I) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htm or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

All chemicals were of reagent grade and were purchased from Aldrich. All reactions were carried out under nitrogen atmosphere under anhydrous conditions. Flash chromatography was carried out on SiO₂ (Merck Kieselgel 60, particle size 0.032-0.063 mm). GC-MS was performed using a Fison Instruments MD800 capillary GC-Mass spectrometer. NMR spectra were obtained at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR) on a Varian FT-NMR spectrometer using CDCl₃ as the solvent. Chemical shifts are reported in ppm relative to TMS.

Preparation of 1,8-Dipyridylnaphthalene **1**

A solution of 1,8-diiodonaphthalene (0.6 g, 1.58 mmol), 4-trimethylstannylpyridine (1.0 g, 4.14 mmol), and tetrakis(triphenylphosphane)palladium(0) (100 mg, 5.5 mol%) in 3 mL anhydrous DMF was refluxed for 5 h. The reaction mixture was allowed to cool to room temperature, poured into 10% NH₄OH, and extracted with CH₂Cl₂. The combined organic layers were washed

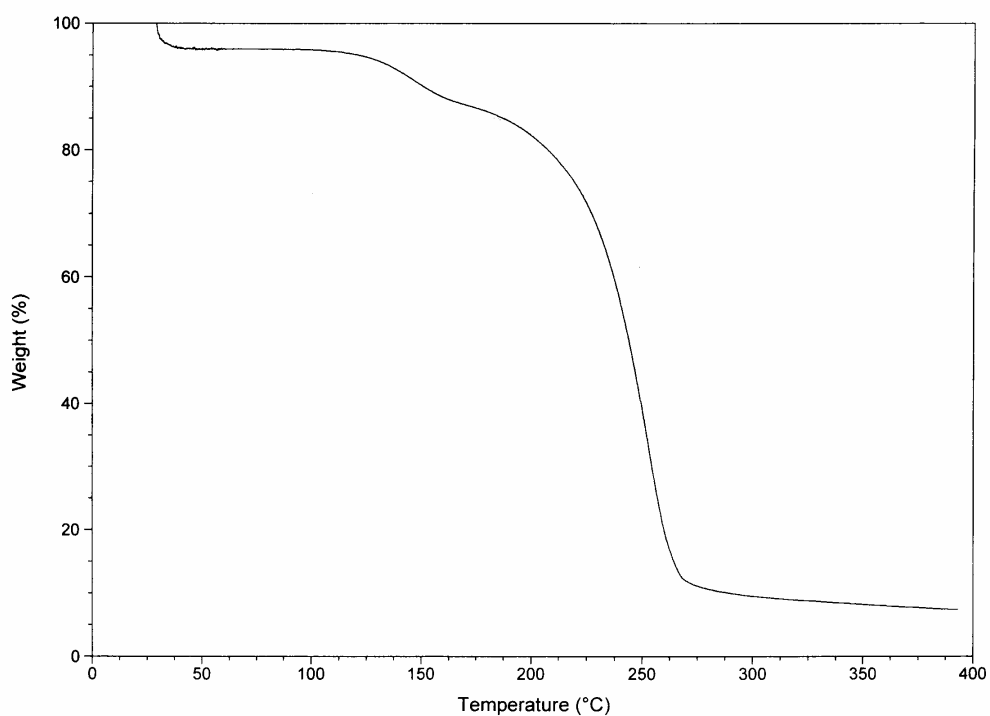
with water, dried over MgSO_4 , and the filtrate was concentrated under reduced pressure. Recrystallization from EtOAc afforded **1** (300 mg, 1.06 mmol, 67%) as light yellow crystals (mp 279-280 °C). ^1H NMR: δ 6.93 (dd, $J = 1.7$ Hz, $J = 4.4$ Hz, 4H), 7.43 (dd, $J = 1.1$ Hz, $J = 7.2$ Hz, 2H), 7.62 (dd, $J = 1.1$ Hz, $J = 8.2$ Hz, 2H), 8.04 (dd, $J = 7.2$ Hz, $J = 8.2$ Hz, 2H), 8.23 (dd, $J = 1.7$ Hz, $J = 4.4$ Hz, 4H). ^{13}C NMR: δ 14.4, 125.5, 128.0, 129.7, 131.1, 135.2, 137.0, 148.8, 150.3. EI-MS (70 eV): m/z (%) = 282 (100) [M^+], 254 (25) [$\text{M}^+ - \text{CH}_2\text{N}$], 226 (19) [$\text{M}^+ - 2 \text{CH}_2\text{N}$], 202 (26) [$\text{M}^+ - \text{H}$, -Py], 127 (25) [$\text{M}^+ - \text{H}$, -2Py]. Anal. Calc. for $\text{C}_{20}\text{H}_{14}\text{N}_2$: C, 85.00; H, 5.00; N, 9.92. Found: C, 84.66; H, 5.08; N, 9.91.

Preparation of 4-Trimethylstannylpyridine.

Commercially available 4-bromopyridine hydrochloride (3.1 g, 15.4 mmol) was partitioned between 2N NaOH and CH_2Cl_2 . The organic layers were dried over anhydrous MgSO_4 and CH_2Cl_2 was removed under reduced pressure. A yellow oil of 4-bromopyridine (2.4 g, 15.2 mmol, 99 %) was obtained and used without further purification. The crude material was dissolved in 20 mL anhydrous Et_2O and cooled to -78°C . *n*-Butyllithium in hexanes (10.4 mL, 1.6M) was added and the reaction mixture was stirred for one hour. A solution of trimethylstannyl chloride (3.8 g, 19 mmol) in 10 mL anhydrous Et_2O was added dropwise. The mixture was allowed to stir at room temperature for 5 hours. Following the work-up procedure described above gave a brown residue. Purification by flash chromatography (EtOAc/hexanes/ Et_3N 250:250:1) afforded 4-trimethylstannylpyridine (2.41g, 10.0 mmol, 66%) as a light orange oil. ^1H NMR: δ 0.33 (s, 9H), 7.39 (dd, $J = 1.5$ Hz, $J = 4.2$ Hz, 2H), 8.51 (dd, $J = 1.5$ Hz, $J = 4.2$ Hz, 2H). ^{13}C NMR: δ -9.6, 131.0, 148.3, 152.8. EI-MS (70 eV): m/z (%) = 239

(29) [M⁺], 224 (100) [M⁺-Me], 209 (34) [M⁺-2Me], 194 (68) [M⁺-3Me], 161 (18) [Me₃Sn], 131
(50) [MeSn], 116 (30) [Sn], 78 (17) [C₅H₄N].

TGA of 1-(H₂O)₃



Thermogravimetric analysis was performed under nitrogen with a heating rate of 5°C/min using a TA Instruments TGA 2050 Analyzer