Hassan, Mohammad R.

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Department of Chemistry and Biochemistry

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Short Note

1,5-(4,4'-Dipyridyl)naphthalene

Mohammad R. Hassan and René T. Boeré *

Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive W., Lethbridge, AB T1K 3M4, Canada; E-Mail: mrh1@ualberta.ca

* Author to whom correspondence should be addressed; E-Mail: boere@uleth.ca; Tel.: +1-403-329-2045; Fax: +1-403-329-2057.

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**Abstract:** The title compound has been prepared from 1,5-dibromonaphthalene (obtained from 1,5-diaminonaphthalene) using Suzuki-Miyaura cross-coupling to 4-pyridylboronic acid. The crystal and molecular structure was determined by single-crystal X-ray diffraction.

**Keywords:** synthesis; structure; supramolecular chemistry

Introduction

There is currently strong interest in using (4,4'-dipyridyl)naphthalenes for diverse applications in supramolecular chemistry, including the synthesis of flexible pillared metal organic frameworks (MOFs) [1–4], hydrogen-bonded templates for supramolecular structures prepared by mechanochemistry used for solid-state photodimerization reactions [5–9] and the stabilization of porphyrinic catenanes [10,11]. To date, only four isomers of the parent (4,4'-dipyridyl)naphthalenes (Scheme 1, molecular formula C_{22}H_{16}N_{2}) have been reported in the literature: 1,4-, 1 [1], 1,8-, 2 [5–9] 2,7-, 3 [10,11] and 2,6-, 4 [2–4]. Herein we report the preparation, characterization and structure determination by single-crystal X-ray diffraction of the new 1,5-isomer, 5.

Results and Discussion

The synthesis (Scheme 2) started from commercially available 1,5-diaminonaphthalene, 6, to afford 1,5-dibromonaphthalene, 7, in 14% yield [12]. Suzuki-Miyaura cross-coupling was employed using conditions previously reported for coupling of 4-pyridylboronic acid with aryl bromides [13,14]. The
same catalyst, [Pd(PPh₃)₄], was used (10 mol % catalyst loading) but K₂CO₃ was used in place of K₃PO₄ because the former was on hand and is also often employed for such reactions. We employed 1,4-dioxane as solvent and refluxed the mixture for 3 days under an inert gas, which afforded 5 as colorless crystals (CHCl₃/CH₃OH), in 44% yield. A fitting mass spectrum as well as ¹H and ¹³C NMR spectroscopic data, which could be fully assigned, were obtained (see Experimental Section and Supplementary Information).

Scheme 1. Known isomers (1–4) of (4,4'-dipyridyl)naphthalenes.

Scheme 2. Synthetic route to 1,5-(4,4'-dipyridyl)naphthalene, 5.

Figure 1. Displacement ellipsoids plot (40% probability) of the structure of 5 as found in the crystal; the crystallographic centre of symmetry is indicated as a red dot. Selected bond lengths [Å] and bond angles [°]: N11–C12 1.340(2); N11–C16 1.3365(19); C1–C2 1.372(2); C1–C8A' 1.4298(19); C1–C14 1.4952(17); C2–C3 1.4104(18); C3–C8' 1.3670(19); C12–N11–C16 116.06(11); C2–C1–C8A' 119.84(11); C2–C1–C14 118.74(12); C8A'–C1–C14 121.41(11); C1–C2–C3 121.13(12).
The molecular structure of 5 as found in the crystal lattice is depicted in Figure 1. The molecule crystallizes at a crystallographic centre of symmetry (as indicated) so that the asymmetric unit consists of half a molecule. The pyridyl rings are twisted because of the steric hindrance between the pyridyl and naphthyl hydrogen atoms, resulting in a dihedral angle between the 4-pyridyl and naphthalene ring least-squares planes of 59.10(6)°. Bond distance and angle data for 5 are not remarkable and are very close to those found in three independent crystallographic structure determinations of 2 [6]. The inter-planar dihedral angles in 5 are also quite similar to those determined for 2 (range: 51.3–69.2°; mean of six = 63°). The shortest intermolecular contacts in the crystal structure of 5 are C12–C13' (3.468(2) Å) from offset π–π stacking and N11–H2 (2.54 Å). In contrast, all three structure determinations of 2 show C–H to π “T” interactions between the rings, in addition to the expected short contacts to nitrogen [6].

Experimental Section

Reagents and solvents were commercial products and used as received (except 1,4-dioxane, distilled under nitrogen from Na). A Bruker Alpha FTIR with diamond ATR was used for IR data; an Elementar Americas Vario MicroCube instrument for EA (Mount Laurel, NJ, USA); EI-MS spectra measured on a Varian 4000 GC-MS (direct sample insertion) (Palo Alto, CA, USA). 1H (300.14 MHz) and 13C (62.9 MHz) NMR spectra were obtained on a Bruker Avance II instrument using the residual solvent signals for referencing (Bruker BioSpin GmbH, Rheinstetten, Germany).

1,5-diaminonaphthalene (6, 2 g, 12.6 mmol) was diazotized with H2SO4/NaNO2 and slowly added to a solution of CuBr (5 g, 34.9 mmol) in 48% HBr (75 mL) and H2O (75 mL). Extraction with CHCl3 followed by drying (anhyd. MgSO4) and evaporation afforded 1,5-dibromonaphthalene, 7, which was crystallized from chloroform (0.5 g, 14%). A mixture of 7 (0.37 g, 1.3 mmol), Pd(PPh3)4 (0.15 g, 0.13 mmol), K2CO3 (1.073 g, 7.8 mmol) and 4-pyridylboronic acid (0.48 g, 3.9 mmol) in 1,4-dioxane (40 mL) was refluxed under N2 for 3 days. After removal of 1,4-dioxane, the resulting mass was dissolved in 30 mL of CHCl3 giving a dark, slightly cloudy, liquid which was treated twice with 20 mL of brine. The CHCl3 layer was dried and evaporated; recrystallization from 1.0 mL chloroform layered with 1.0 mL methanol afforded 1,5-(4,4'-dipyridyl)naphthalene, 5.

Yield 0.160 g (44%), colourless crystals, Mp: 110–112 °C. Calcd for C20H14N2: C, 85.08; H, 4.99; N, 9.92. Found: C, 84.71; H, 4.76; N, 9.90%. IR (diamond ATR): 1589 s, 1542 m, 1585 m, 1437 s, 1409 s, 1409 s, 1312 m, 1261 s, 1183 vs, 1119 vs, 1070 vs, 992 s 799 vs cm⁻¹. 1H NMR (CDCl3): δ 8.77 (d, J = 6.0 Hz, 4H, pyridyl H3,5), 7.91 (d, J = 8.7 Hz, 2H, naphthyl H4,8), 7.54 (t, J = 7.2 Hz, 2H, naphthyl H3,7), 7.46 (d, J = 6.3 Hz, 6H, naphthyl H2,6; pyridyl H2,6). 13C NMR (CDCl3): δ 149.9 (pyridyl C3,5), 148.6 (pyridyl C1), 138.0 (naphthyl C1,5), 131.1 (naphthyl C1',4'), 127.2 (naphthyl C4,8), 126.1 (naphthyl C3,7), 126.0 (naphthyl C2,6), 125.0 (pyridyl C2,6). Assignment of resonances determined from HSQC and HMBC 2D-NMR experiments. MS: m/z 282 [M]+.

Mo Kα radiation (λ = 0.71073 Å) diffraction data collected on a colourless prism (0.31 × 0.18 × 0.09 mm³) with a Bruker APPEX-II diffractometer at 173(2) K. After multi-scan absorption (max 0.798; min 0.767), the structure was solved by direct methods and refined using SHELXL-2013. H atoms were observed but were treated as riding on their attached aromatic carbon atoms with C–H = 0.95 Å and Uiso = 1.2Ueq(C) for model refinement. Monoclinic, P2₁/n, a = 9.096(6), b = 5.954(4), c =
13.447(9) Å; β = 103.849(7)°; V = 707.0(8) Å³. Dc = 1.326 Mg/m³; θ-range: 2.456 to 28.616°, −12 ≤ h ≤ 11, −8 ≤ k ≤ 7, −17 ≤ l ≤ 17, 9908 reflections; 1740 indep. data (Rint = 0.030); 99.9% complete; 100 parameters. R1 = 0.0425; wR2 = 0.1075. Largest diff. peak and hole: 0.279 and −0.230 e/Å³.

CCDC 1041753 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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Author Contributions

The synthesis, characterization and crystal structure data collection were undertaken by M.R.H. Crystal structure refinement and article writing was performed by R.T.B.

Conflicts of Interest

The authors declare no conflict of interest.

References


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