

Short Note

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

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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

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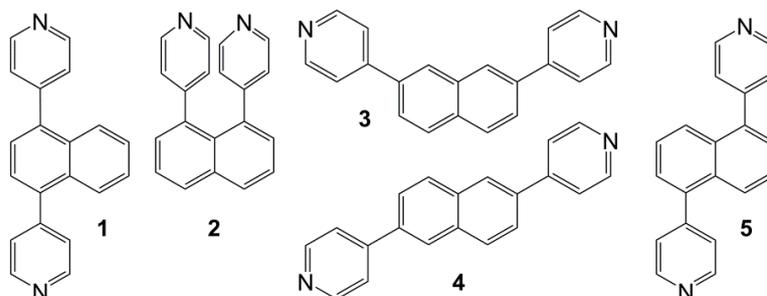
### Introduction

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<sub>22</sub>H<sub>16</sub>N<sub>2</sub>) 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**.

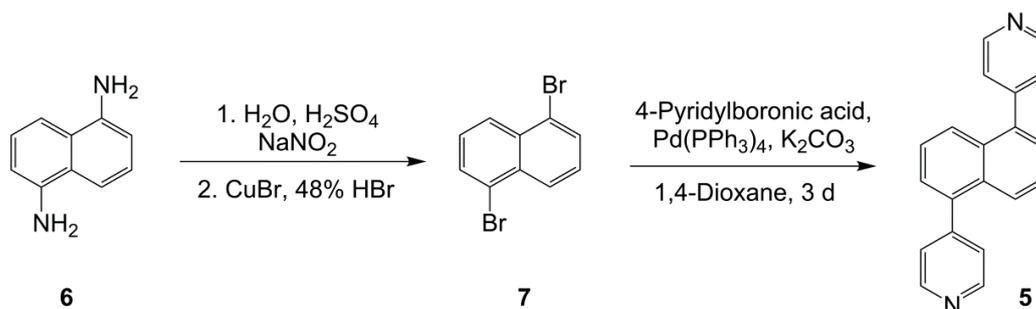
### Results and Discussion

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

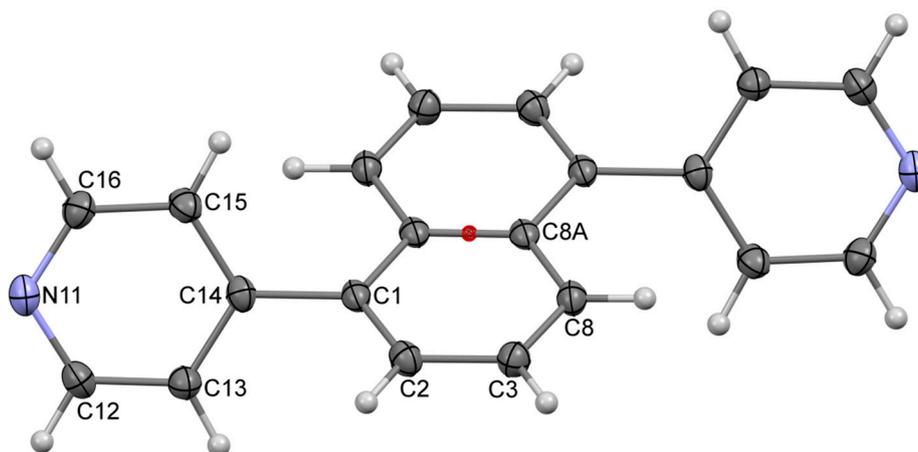
same catalyst,  $[\text{Pd}(\text{PPh}_3)_4]$ , was used (10 mol % catalyst loading) but  $\text{K}_2\text{CO}_3$  was used in place of  $\text{K}_3\text{PO}_4$  because the former was on hand and is also often employed for such reactions. We employed 1,4-dioxane as solvent and refluxed the mixture for 3 days under an inert gas, which afforded **5** as colorless crystals ( $\text{CHCl}_3/\text{CH}_3\text{OH}$ ), in 44% yield. A fitting mass spectrum as well as  $^1\text{H}$  and  $^{13}\text{C}$  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 [ $\text{\AA}$ ] and bond angles [ $^\circ$ ]: 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  $59.10(6)^\circ$ . 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:  $51.3\text{--}69.2^\circ$ ; mean of six =  $63^\circ$ ). The shortest intermolecular contacts in the crystal structure of **5** are C12–C13' ( $3.468(2)$  Å) from offset  $\pi$ – $\pi$  stacking and N11–H2 ( $2.54$  Å). In contrast, all three structure determinations of **2** show C–H to  $\pi$  “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).  $^1\text{H}$  (300.14 MHz) and  $^{13}\text{C}$  (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  $\text{H}_2\text{SO}_4/\text{NaNO}_2$  and slowly added to a solution of CuBr (5 g, 34.9 mmol) in 48% HBr (75 mL) and  $\text{H}_2\text{O}$  (75 mL). Extraction with  $\text{CHCl}_3$  followed by drying (anhyd.  $\text{MgSO}_4$ ) 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),  $\text{Pd}(\text{PPh}_3)_4$  (0.15 g, 0.13 mmol),  $\text{K}_2\text{CO}_3$  (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  $\text{N}_2$  for 3 days. After removal of 1,4-dioxane, the resulting mass was dissolved in 30 mL of  $\text{CHCl}_3$  giving a dark, slightly cloudy, liquid which was treated twice with 20 mL of brine. The  $\text{CHCl}_3$  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:  $110\text{--}112$  °C. Calcd for  $\text{C}_{20}\text{H}_{14}\text{N}_2$ : 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, 1312 m, 1261 s, 1183 vs, 1119 vs, 1070 vs, 992 s 799 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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  $[\text{M}]^+$ .

Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) diffraction data collected on a colourless prism ( $0.31 \times 0.18 \times 0.09$  mm<sup>3</sup>) 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  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$  for model refinement. Monoclinic,  $P2_1/n$ ,  $a = 9.096(6)$ ,  $b = 5.954(4)$ ,  $c =$

13.447(9) Å;  $\beta = 103.849(7)^\circ$ ;  $V = 707.0(8) \text{ \AA}^3$ .  $D_c = 1.326 \text{ Mg/m}^3$ ;  $\theta$ -range: 2.456 to  $28.616^\circ$ ,  $-12 \leq h \leq 11$ ,  $-8 \leq k \leq 7$ ,  $-17 \leq l \leq 17$ , 9908 reflections; 1740 indep. data ( $R_{\text{int}} = 0.030$ ); 99.9% complete; 100 parameters.  $R_1 = 0.0425$ ;  $wR_2 = 0.1075$ . Largest diff. peak and hole: 0.279 and  $-0.230 \text{ e/\AA}^3$ . 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](mailto: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

1. Culp, J.T.; Madden, C.; Kauffman, K.; Shi, F.; Matranga, C. Screening Hofmann compounds as CO<sub>2</sub> sorbents: Non-traditional synthetic route to over 40 different pore-functionalized and flexible pillared cyanonickelates. *Inorg. Chem.* **2013**, *52*, 4206–4216.
2. Lin, M.-J.; Jouaiti, A.; Kyritsakas, N.; Hosseini, M.W. Molecular tectonics: Control of interpenetration in cuboid 3-D coordination networks. *CrystEngComm* **2011**, *13*, 776–778.
3. Hauptvogel, I.M.; Bon, V.; Grüner, R.; Baburin, I.A.; Senkovska, I.; Mueller, U.; Kaskel, S. A family of 2D and 3D coordination polymers involving a trigonal tritopic linker. *Dalton Trans.* **2012**, *41*, 4172–4179.
4. Karagiari, O.; Bury, W.; Tylianakis, E.; Sarjeant, A.A.; Hupp, J.T.; Farha, O.K. Opening metal-organic frameworks vol. 2: Inserting longer pillars into pillared-paddlewheel structures through solvent-assisted linker exchange. *Chem. Mater.* **2013**, *25*, 3499–3503.
5. Wolf, C.; Ghebremariam, B.T. Synthesis of atropisomeric 1,8-bis(4',4'-dipyridyl)naphthalenes from 4-trimethylstannylpyridines. *Synthesis* **2002**, *2002*, 749–752.
6. Mei, X.; Wolf, C. Conformational polymorphism of 1,8-dipyridylnaphthalene and encapsulation of chains of fused cyclic water pentamers in a hydrophobic crystal environment. *CrystEngComm* **2006**, *8*, 377–380.
7. Mei, X.; Liu, S.; Wolf, C. Template-controlled face-to-face stacking of olefinic and aromatic carboxylic acids in the solid state. *Org. Lett.* **2007**, *9*, 2729–2732.

8. Atkinson, M.B.J.; Bučar, D.-K.; Sokolov, A.N.; Friščić, T.; Robinson, C.N.; Bilal, M.Y.; Sinada, N.G.; Chevannes, A.; MacGillivray, L.R. General application of mechanochemistry to templated solid-state reactivity: Rapid and solvent-free access to crystalline supermolecules. *Chem. Commun.* **2008**, 5713–5715.
9. Atkinson, M.B.J.; Sokolov, A.N.; Bučar, D.-K.; Mariappan, S.V.S.; Mwangi, M.T.; Tiedman, M.C.; MacGillivray, L.R. Applications of hydrogen-bond-acceptor templates to direct ‘in-phase’ reactivity of a diene diacid in the solid state. *Photochem. Photobiol. Sci.* **2011**, *10*, 1384–1386.
10. Beyler, M.; Heitz, V.; Sauvage, J.-P. The dual role of Cu(I) as a protective group and a template in the synthesis of a tetra-rhodium(III)porphyrin [2]catenane. *New J. Chem.* **2010**, *34*, 1825–1829.
11. Beyler, M.; Heitz, V.; Sauvage, J.-P. Coordination chemistry-assembled porphyrinic catenanes. *J. Am. Chem. Soc.* **2010**, *132*, 4409–4417.
12. Hodgson, H.H.; Whitehurst, J.S. 17. The tetrazotisation of 1:5- and 1:8-naphthylenediamines and the tetranitration of 1:5- and 1:8-di-*p*-toluenesulphonamidonaphthalenes. *J. Chem. Soc.* **1947**, 80–81.
13. Biradha, K.; Hongo, Y.; Fujita, M. Open square-grid coordination polymers of the dimensions  $20 \times 20 \text{ \AA}$ : Remarkably stable and crystalline solids even after guest removal. *Angew. Chem. Int. Ed.* **2000**, *39*, 3843–3845.
14. Marin, G.; Andruh, M.; Madalan, A.M.; Blake, A.J.; Wilson, C.; Champness, N.R.; Schröder, M. Structural diversity in metal-organic frameworks derived from binuclear alkoxo-bridged copper(II) nodes and pyridyl linkers. *Cryst. Growth Des.* **2008**, *8*, 964–975.

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