

## X-Ray characterization of 3-methyl-6,8-di(2-pyridyl)-[1,2,3]triazolo[5',1':6,1]pyrido[2,3-*d*]pyrimidine

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### Abstract

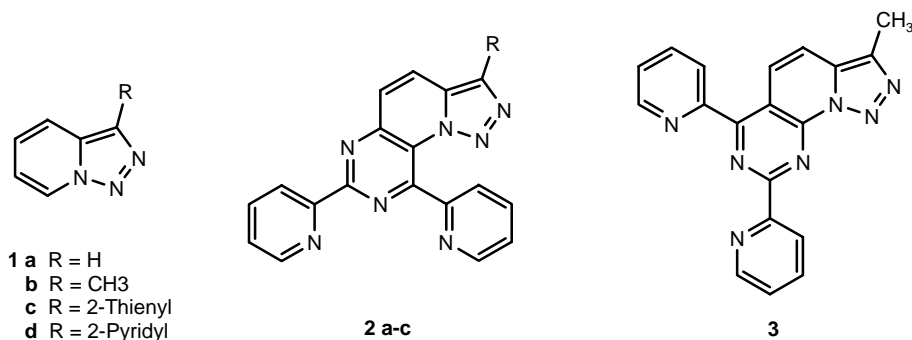
The structure of a new compound 3-methyl-6,8-di(2-pyridyl)[1,2,3]triazolo[5',1':6,1]pyrido[2,3-*d*]pyrimidine **3**, formed in the reaction of 3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine with 2-cyanopyridine, is determined by X-ray diffraction analysis.

**Keywords:** 3-Methyl-6,8-di(2-pyridyl)[1,2,3]triazolo[5',1':6,1]pyrido[2,3-*d*]pyrimidine, X-ray diffraction, structure

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### Introduction

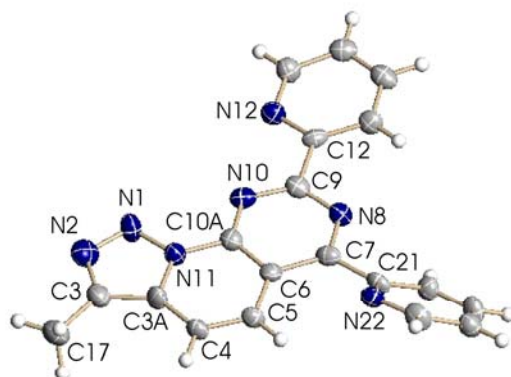
In the context of our work on new potential helicing ligands from [1,2,3]triazolo[1,5-*a*]pyridines **1**,<sup>1-3</sup> we discovered a novel heterocyclic system in the reaction of the corresponding 7-lithiotriazolopyridines with 2-cyanopyridine. On the basis of analytical and spectroscopic data the structure of this system was proposed to be 7,9-di(2-pyridyl)[1,2,3]triazolo[5',1':6,1]pyrido[3,2-*d*]pyrimidine **2**.<sup>2</sup> Following this research, we have now obtained suitable crystals for a X-ray diffraction analysis of the compound synthesized from **1b**. We wish to report here the result of this analysis that establishes its structure as 3-methyl-6,8-di(2-pyridyl)[1,2,3]triazolo[5',1':6,1]-pyrido[2,3-*d*]pyrimidine **3**.



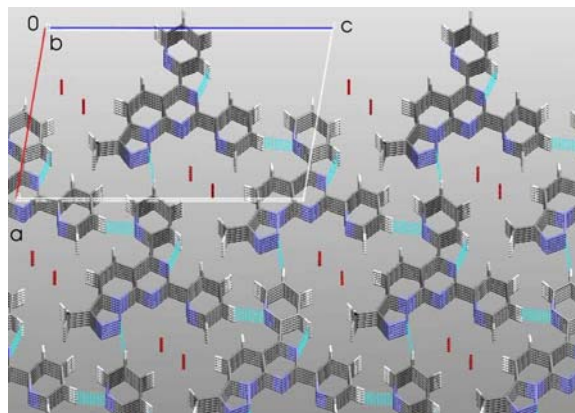
## Results and Discussion

Suitable crystals for X-ray analysis were obtained by recrystallisation from an ethyl acetate solution. The structure proved to be 3-methyl-6,8-di(2-pyridyl)[1,2,3]triazolo[5',1':6,1]pyrido[2,3-*d*]pyrimidine **3**, an isomer of the previously reported compound **2b**. The spectroscopic data are compiled in the experimental section.

Crystals of compound **3**·H<sub>2</sub>O suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate solution. Two half water molecules have been found in the asymmetric unit. The molecular structure shows a planar triazolopyridopyrimidine moiety (mean deviation 0.014 Å) and two pyridine rings, both rings being twisted in respect to that moiety (see figure 1). The pyridine ring corresponding to C(12) is slightly bent while the pyridine ring corresponding to C(21) is strongly twisted in respect to the triazolopyridopyrimidine plane (dihedral angles 6.1(3)° and 38.8(2)°, respectively). In the crystal, molecular layers through C-H···N weak hydrogen bonds are formed (see figure 2). The layers self-assemble along the *b* axis showing ring stacking with an interplanar distance of ca. 3.7 Å. The molecular assembly produces nanotubes along the *b* axis where the water molecules are included.



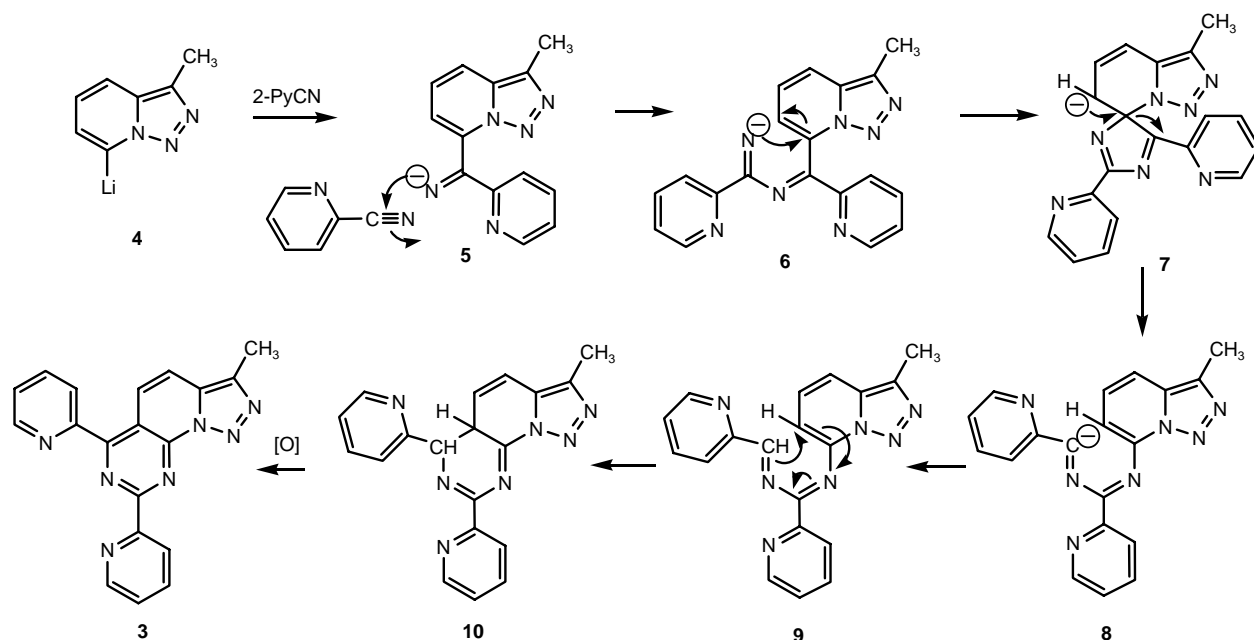
**Figure 1.** Ellipsoid plot of compound **3** (50% probability level).



**Figure 2.** Crystal view of compound **3**·H<sub>2</sub>O along the *b* axis, showing the molecular layers. Grey carbon, blue nitrogen and red oxygen atoms. Weak C-H...N hydrogen bonds [C14-H14...N22<sup>i</sup> (i:  $x+1/2, -y+2, z+1/2$ ): C14...N22<sup>i</sup> 3.334(10), H14...N22<sup>i</sup> 2.41 Å, C14-H14...N22<sup>i</sup> 164.6°; C24-H24...N1<sup>ii</sup> (ii:  $x-1, y-1, z$ ): C24...N1<sup>ii</sup> 3.745(11), H24...N1<sup>ii</sup> 2.85 Å, C24-H24...N1<sup>ii</sup> 156.5°] are shown in light blue colour.

To account for this structure we propose the mechanism shown in scheme 1. Reaction of the lithio derivative **4** with a mole of 2-cyanopyridine gives the intermediate **5**, which reacts with a second mole of reagent forming a new intermediate **6**, as we have proposed.<sup>2</sup> Attack to the activated 7-position towards nucleophilic substitution,<sup>4</sup> leads to the intermediate **7** that would in turn produce **8**. After protonation, a new intermediate **9** is formed, that undergoes an electrocyclic process ( $6\pi$ ) followed by oxidation to give **3**.

Compound **3** has potential fields of application based on its rich photophysical and photochemical properties,<sup>5</sup> or as luminescent molecular sensors.<sup>6</sup> At present, we are studying its ability as colourimetric and fluorescent cation and as anion chemosensor. The results of this study will be published elsewhere.



Scheme 1

## Experimental Section

**X-Ray data for compound 3·H<sub>2</sub>O.** Yellow spike, 0.34 x 0.24 x 0.12 mm size, monoclinic, Pn, a = 11.734(2), b = 3.7442(7), c = 19.385(4) Å, β = 99.57(3), V = 839.8(3) Å<sup>3</sup>, Z = 2, ρ<sub>calcd</sub> = 1.413 gcm<sup>-3</sup>, θ<sub>max</sub> = 26.37, Mo Kα, λ = 0.71073 Å, ω-scan, diffractometer Kappa CCD, T = 100(2) K, 5699 reflections collected of which 1718 were independent (R<sub>int</sub> = 0.114), direct primary solution and refinement on F<sup>2</sup> (SHELXS-97 and SHELXL-97, G.M. Sheldrick, University of Göttingen, 1997), 251 refined parameters, two disordered half water molecules, isotropic water molecules oxygen atoms, water molecules hydrogen atoms were not found, rigid methyl and other hydrogen atoms riding, the largest difference peaks are near the disordered water molecules, R1[I > 2σ(I)] = 0.0802, wR2(all data) = 0.2255, Δρ<sub>max</sub> = 0.70 eÅ<sup>-3</sup>. The poor quality of the data is probably due to the disordered water molecules that could be moving within the molecular channels (several attempts were made to obtain better data).

**Spectroscopic and analytical data of compound 3.** Yellow solid. mp 255-257 °C (AcOEt). HRMS found M<sup>+</sup> 339.1233; C<sub>19</sub>H<sub>13</sub>N<sub>7</sub> requires 339.1232. ν<sub>max</sub> (KBr) (cm<sup>-1</sup>) 1618, 1561, 1547, 1377, 776. λ<sub>max</sub> (nm) (log ε) 232.0 (5.35), 285.5 (5.33), 374.5 (4.12). <sup>1</sup>H NMR δ 8.87 (ddd, J<sub>1</sub>= 4.71, J<sub>2</sub>= 1.68, J<sub>3</sub>= 0.93Hz, 1H), 8.81 (ddd, J<sub>1</sub>= 7.89, J<sub>2</sub>= 1.71, J<sub>3</sub>= 0.93 Hz, 1H), 8.77 (ddd, J<sub>1</sub>= 4.71, J<sub>2</sub>= 1.71, J<sub>3</sub>= 0.75 Hz, 1H), 8.65 (d, J= 9.6Hz, 1H), 8.49 (ddd, J<sub>1</sub>= 7.89, J<sub>2</sub>= 1.68, J<sub>3</sub>= 0.75Hz, 1H), 7.97-7.86 (m, 2H), 7.51 (d, J= 9.6Hz, 1H), 7.48-7.40 (m, 2H), 2.64 (s, 3H). <sup>13</sup>C

NMR  $\delta$  163.75 (C), 161.40 (C), 155.65 (C), 153.68 (C), 150.33 (CH), 149.38 (C), 148.89 (CH), 137.59 (CH), 137.59 (C), 137.19 (CH), 131.50 (C), 125.87 (CH), 125.59 (CH), 125.12 (CH), 125.00 (CH), 122.80 (CH), 117.00 (CH), 113.51 (C), 10.36 (CH<sub>3</sub>). MS m/z (%), 339 (13), 311 (100), 206 (10).

## Supplementary Section

Supplementary information available: X-ray Crystallography data in the form of Crystallographic information files (CIF).<sup>7</sup>

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