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Short Note

4'-(*N*-(Propargyl)pyrrol-2-yl)-2,2':6',2''-terpyridine

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Abstract: A new terpyridine molecule, bearing a *N*-propargylated pyrrole, was prepared and characterized. Its synthesis was based on a Krohnke-type reaction between 2-acetylpyridine and *N*-propargylpyrrole-2-carboxaldehyde in a basic medium. An allene-containing terpyridine was also obtained as a by-product.

Keywords: alkyne derivatives; *N*-donor ligands; oligopyridines; pyrrole derivatives

1. Introduction

Owing to their ability to form a broad range of complexes with metals, 2,2':6',2''-terpyridine derivatives have been widely studied. Terpyridines and their complexes can find applications in many fields ranging from medicinal chemistry to functional materials [1,2]. In particular, terpyridine derivatives which contain an additional pyrrole heterocycle (named hereafter pyrrole-terpys) are interesting compounds because they can be deposited as thin films onto surfaces via electropolymerization [3]. The so-obtained polymeric materials can be used, for example, as an active layer in a sensor device [4]. Additionally, pyrrole-terpys can find applications in other fields such as catalysis [5] or as photosensitizers [6,7], just to name a few. Consequently, the synthesis of new pyrrole-terpys could be of interest for a broad range of scientific fields. In particular, the introduction of an alkyne moiety onto a pyrrole-terpy could be interesting since it offers the possibility to “click” the terpyridine onto various materials or biomolecules [8–10] via the Huisgen reaction [11] and allows the preparation of hetero-polymetallic complexes through complexation of both the terpyridine and alkyne parts of the molecule [12]. This paper describes the preparation and characterization of the new 4'-(*N*-(propargyl)pyrrol-2-yl)-2,2':6',2''-terpyridine **1** (Figure 1).

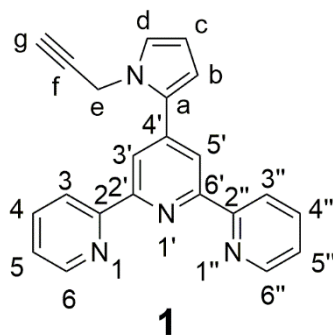


Figure 1. Structure and atom labeling of 4'-(*N*-(propargyl)pyrrol-2-yl)-2,2':6',2''-terpyridine **1**.

2. Results and Discussion

A tentative synthesis of **1** through *N*-propargylation of 4'-(pyrrol-2-yl)-2,2':6',2''-terpyridine is already reported in the literature [13]. The synthetic pathway that was explored relies on the *N*-alkylation of the pyrrole ring with propargyl bromide in a strong



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basic medium [14]. Nevertheless, this approach failed in providing **1**, and only isomeric 4'-(*N*-(propan-1,2-dienyl)pyrrol-2-yl)-2,2':6',2''-terpyridine **2** was obtained (Figure 2). This can be explained by the strong basic conditions (potassium hydroxide in dimethylsulfoxide is a superbase [15]) of the reaction which result in isomerization of the triple bond. Therefore, another synthetic strategy was developed in the present research to obtain compound **1**.

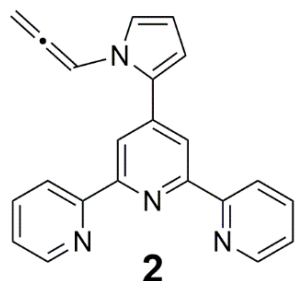


Figure 2. Structure of 4'-(*N*-(propan-1,2-dienyl)pyrrol-2-yl)-2,2':6',2''-terpyridine **2**.

Many synthetic protocols are available for the preparation of terpyridines [16–18], most of them being based on Krohnke's method [19]. Here, the reaction between 2-acetylpyridine and *N*-propargylpyrrole-2-carboxaldehyde [20] in the presence of potassium hydroxide and aqueous ammonia in ethanol [21] was selected (Figure 3).

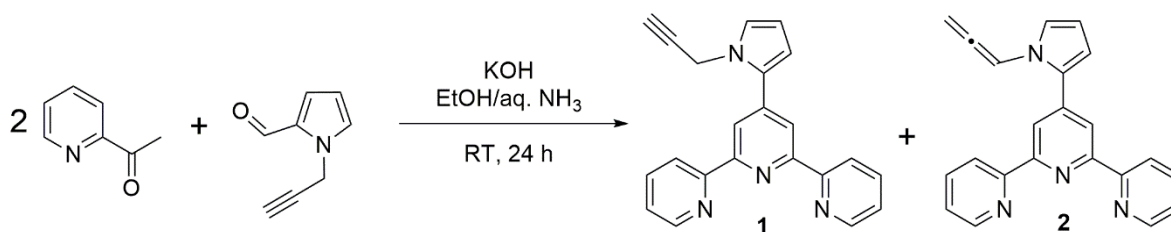


Figure 3. Reaction scheme.

Although the reaction is also conducted in a basic medium, it was expected that the basicity of potassium hydroxide would be lower in the present solvent system (aqueous ethanol) than in dimethylsulfoxide (*vide supra*), thus minimizing the formation of compound **2**. In fact, after 24 h of reaction, a mixture of **1** and **2** was obtained. The two products were separated by flash chromatography over neutral alumina (Figure 4). The main product was the awaited terpyridine **1** which was obtained in 9.4% yield, while compound **2** was obtained in 2.8% yield.

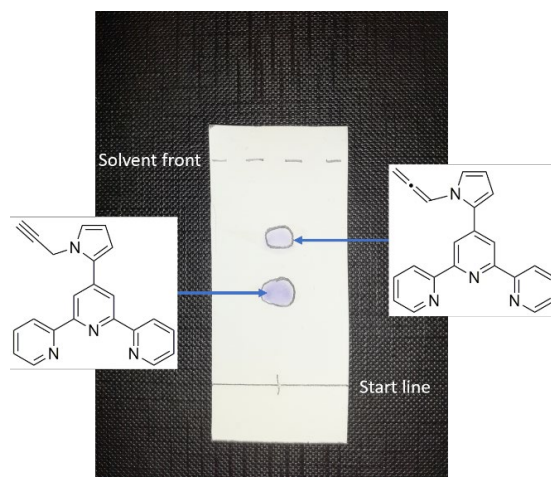


Figure 4. TLC onto alumina (cyclohexane/ethyl acetate 9:1 *v/v*) of the crude mixture after staining with an aqueous solution of Mohr's salt.

v/v). This afforded compound **1** as a white solid (1.11 g; 9.4%) Mp = 136 °C together with compound **2** (0.33 g; 2.8%) as a white solid Mp = 128 °C.

Compound **1**: ¹H-NMR (CDCl₃, 400 MHz), δ (ppm): 8.71 (m, 2H H₆, 6''), 8.65 (d, 2H, H₃, 3'', J = 8.0 Hz), 8.57 (s, 2H, H_{3'}, 5'), 7.87 (td, 2H, H₄, 4'', J = 7.6 Hz, J = 1.8 Hz), 7.34 (ddd, 2H, H₅, 5'', J = 7.5 Hz, J = 4.8 Hz, J = 1.1 Hz), 7.07 (dd, 1H, H_d, J = 2.7 Hz, J = 1.8 Hz), 6.62 (dd, 1H, H_b, J = 3.7 Hz, J = 1.8 Hz), 6.32 (dd, 1H, H_c, J = 3.7 Hz, J = 2.9 Hz), 4.91 (d, 2H, H_e, J = 2.6 Hz), 2.45 (t, 1H, H_g, J = 2.6 Hz). ¹³C-NMR (CDCl₃, 100 MHz), δ (ppm): 156.2, 155.8, 149.2, 142.1, 136.8, 132.1, 124.5, 123.8, 121.3, 119.6, 111.9, 109.4, 78.4, 73.9, 37.5. HR-MS: calc. for [C₂₂H₁₆N₄ + H]⁺ 337.14477, found 337.14436. IR (KBr disc): ν_{\max} (cm⁻¹): 3174, 3049, 3013, 2114.

Compound **2**: The physical and spectroscopic properties agree with those reported in the literature [13].

4. Conclusions

The new terpyridine ligand 4'-(N-(propargyl)pyrrol-2-yl)-2,2':6',2''-terpyridine was prepared and characterized. Future work will emphasize incorporating this ligand into new complexes and functional materials.

Supplementary Materials: ¹H- and ¹³C- NMR, IR spectra and HR-MS (full report) of terpyridine **1**.

Author Contributions: J.H. conceived and carried out the experiments, analyzed data and prepared the manuscript. L.G. analyzed data and contributed to the manuscript preparation. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data from this study are available in this paper and in its Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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