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Short Note

4′-(3,5-Dimethoxy-4-propargyloxyphenyl)-2,2′:6′,2″-terpyridine

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Abstract: The preparation and characterization of a new terpyridine molecule containing an acetylenic moiety is described. Part of this molecule, unknown in the literature, is obtained from a biomass-derived synthon that is formed from the naturally occurring syringaldehyde 4-hydroxy-3,5-dimethoxybenzaldehyde. The title compound was fully characterized by NMR spectroscopy (^{1}H and ^{13}C), as well as by high-resolution mass spectrometry and infrared spectroscopy.

Keywords: alkyne derivatives; heterocycles; ligand; oligopyridines

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1. Introduction

Terpyridines and their metal complexes are assemblies which find a broad range of applications in many fields [1,2]. Amongst this class of compounds, 2,2′:6′,2″-terpyridines, which are further functionalized with an internal or terminal alkyne, are particularly interesting, since they can be used to prepare functional materials (Figure 1).

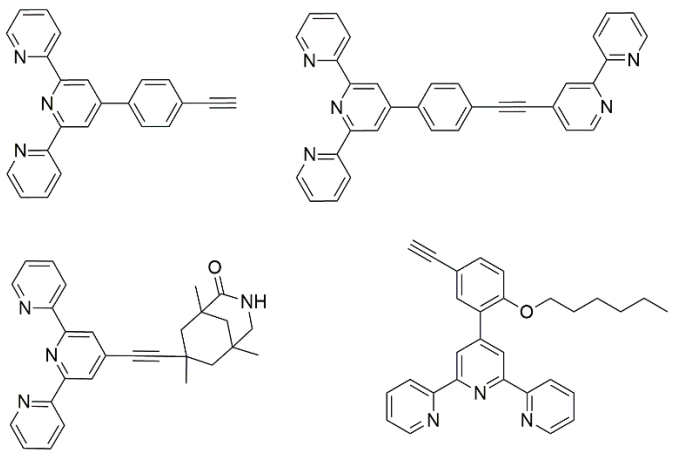

Figure 1. Selected examples of terpyridine molecules containing an alkyne moiety.

For example, these alkynyl *N*-heterocycles were used to prepare electrochromic materials [3], biological probes [4], supramolecular assemblies [5], catalysts and photocatalysts [6,7] or metal-containing polymers [8,9], to name a few. Furthermore, the ethynyl fragment can be used to attach terpyridine scaffolds onto various molecules, such amino acids [10], nucleosides [11] or aromatics [12]. Finally, the ability of both the terpyridine fragment and the alkyne moiety to complex metals allows the preparation of polymetallic complexes with interesting properties [13–17]. Because of all the above-mentioned points, the preparation of new terpyridine derivatives containing an alkyne function is still of interest.

This paper describes the preparation of the hitherto unknown terpyridine 1 (Figure 2), which features an acetylenic part that is connected to the terpyridine framework via a dimethoxyphenyl linker. The latter is introduced into the molecular scaffold from a

biomass-derived synthon, for instance, Syringaldehyde, which can be obtained from various renewable resources [18]. The use of biomass-derived aldehydes, such as furfural derivatives or 3,4,5-trimethoxybenzaldehyde, for the preparation of terpyridines has been already reported [19–22]. This approach of using reagents from renewable resources instead of using petroleum-based ones is envisioned to make chemical processes more sustainable. For instance, this agrees to principle 7 of green chemistry (use of renewable feedstocks) [23]. This paper also presents the characterization of this new potentially ditopic ligand 1 by different analytical techniques such as proton and carbon NMR, mass spectrometry and infrared spectroscopy.

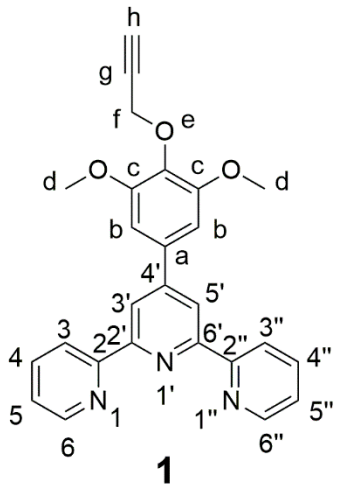

Figure 2. Structure and atoms labelling of compound **1**.

2. Results and Discussion

2.1. Synthesis

Most of the protocols for the synthesis of terpyridine derivatives [24–26] are based on the Kröhnke pyridine synthesis [27]. In the present case, the method of Wang and Hanan was used [28], starting from 2-acetylpyridine and 3,5-dimethoxy-4-propargyloxybenzaldehyde (**2**), as depicted in Figure 3. The acetylenic aldehyde **2** was synthesized from the reaction between syringaldehyde and propargyl bromide [29].

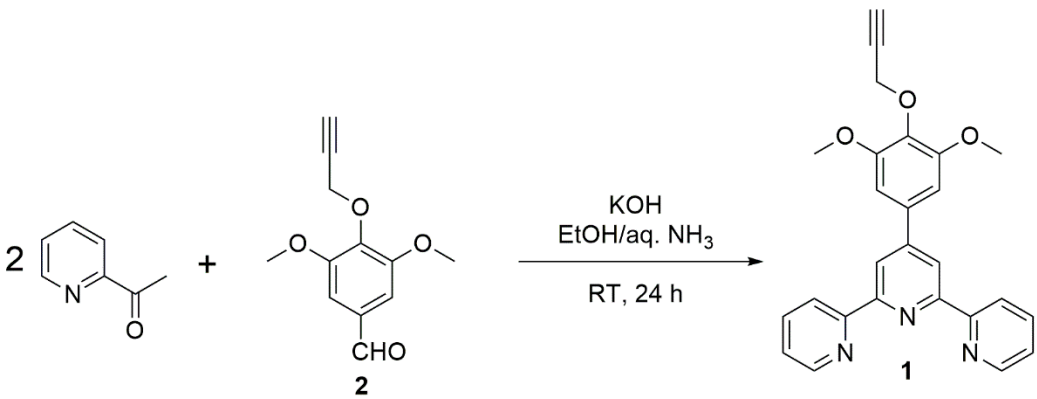

Figure 3. Reaction scheme.

The reaction was carried out for 24 h and afforded **1** in 52% yield as a faint yellow solid. The product was of >98% purity as determined by quantitative ^{1}H NMR [30]. Only a single product was observed by TLC and NMR (vide infra). No isomerization of the triple bond to an allene occurred, in contrast to what has been reported for the preparation of another terminal alkyne-containing terpyridine, namely 4′-(*N*-(propargyl)pyrrol-2-yl)-2,2′:6′,2″-terpyridine, using the same protocol [31].

2.2. Characterization

The product was first characterized by ^{1}H and ^{13}C NMR spectroscopy (Supplementary Materials). The proton spectrum exhibits characteristic signals for a terpyridine compound. In the present case, the singlet for protons 3′ and 5′ is merged with the doublet for protons 3 and 3″ (Supplementary Materials). The signal for the acetylenic proton appears as a triplet centered at 2.46 ppm (J = 2.4 Hz), due to coupling with the propargylic O-CH_2- (doublet, δ = 4.81 ppm, J = 2.4 Hz) through the triple bound. The ^{13}C NMR spectrum exhibits 16 peaks, as expected for the structure (due to the symmetry of both the terpyridine and phenyl parts of the molecule, thus limiting the number of equivalent carbons).

The infrared spectrum recorded in attenuated total reflectance (ATR) mode features the ≡C-H and the C≡C stretching vibrations at 3300 and 2166 cm^{-1}, respectively.

The composition was further confirmed by HR-MS indicating a measured m/z of 424.16521, which is coherent with the calculated mass for the molecular ion $[C_{26}H_{21}N_3O_3 + H]^+$ (m/z = 424.16557).

3. Materials and Methods

All reagents were purchased from commercial suppliers and used as received. Aldehyde **2** (3,5-dimethoxy-4-propargyloxybenzaldehyde) was prepared by a method adapted from the literature [29] (Supplementary Materials). ^{1}H and ^{13}C NMR spectra were recorded on a Brucker AC 400 (Bruker, Wissembourg, France) spectrometer at 400 and 100 MHz, respectively, using $CDCl_3$ as a solvent. The infrared spectrum was recorded on a Vertex 70 spectrometer (Bruker, Wissembourg, France) in ATR mode. The melting point was recorded with a Stuart SMP 10 melting point apparatus (Bibby Sterilin, Stone, UK) and was uncorrected. HR-MS was recorded at Sayence SATT, Dijon, France.

4′-(3,5-Dimethoxy-4-propargyloxyphenyl)-2,2′:6′,2″-terpyridine: To a solution of 2-acetylpyridine (5.50 g, 45.4 mmol) in ethanol (115 mL), 3,5-dimethoxy-4-propargyloxybenzaldehyde (5.00 g, 22.7 mmol), 85% potassium hydroxide pellets (3.50 g, 53.0 mmol) and 25% aqueous ammonia solution (66 mL) were successively added. The reaction mixture was stirred at room temperature for 24 h. The precipitated solid was collected by filtration, washed with ice-cold 50% ethanol until the filtrate was colorless, then dried under vacuum over phosphorus pentoxide to afford **1** as a faint yellow solid (5.10 g, 52%); mp = 224 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.74 (d, 2H H6, 6″, J = 4.2 Hz), 8.67 (m, 4H, H3, 3″, 3′, 5′), 7.89 (td, 2H, H4, 4″, J = 7.7 Hz, J = 1.6 Hz), 7.37 (ddd, 2H, H5, 5″, J = 7.5 Hz, J = 4.9 Hz, J = 1.0 Hz), 7.06 (s, 2H, Hb), 4.81 (d, 2H, Hf, J = 2.4 Hz), 3.99 (s, 6H, Hd), 2.46 (t, 1H, Hh, J = 2.4 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz), δ (ppm): 156.1, 155.8, 153.9, 150.6, 149.0, 137.0, 136.4, 135.2, 123.9, 121.5, 119.0, 104.7, 79.3, 75.0, 60.0, 56.6. HR-MS: calc. for $[C_{26}H_{21}N_3O_3 + H]^+$ 424.16557, found 424.16521. IR (ATR) ν_{max} (cm^{-1}): 3299.7, 2951.9, 2929.3, 2836.8.

4. Conclusions

The new ditopic terpyridine ligand 4′-(3,5-dimethoxy-4-propargyloxyphenyl)-2,2′:6′,2″-terpyridine was prepared and characterized. The use of this compound to construct functional materials by exploiting the complexing ability of both the terpyridine and alkyne coordination sites toward various metal fragment is currently under investigation. Results will be reported in due course.

Supplementary Materials: The following are available online. Synthetic protocol for the preparation of aldehyde **2**; ^{1}H, ^{13}C and ATR-IR spectra; HR-MS full report.

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