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Synthesis, optical, and thermal properties of conjugated, bispyridyl and tetrapyridyl compounds by Knoevenagel reaction

Pradip K. Bhowmik,* Alexi K. Nedeltchev and Haesook Han

Department of Chemistry, University of Nevada Las Vegas, 4505 Maryland Parkway, Box 454003, Las Vegas, NV 89154, USA

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Abstract—A series of conjugated, bispyridyl and tetrapyridyl compounds were synthesized from either terephthalaldehyde or isophthalaldehyde and activated pyridyl compounds by Knoevenagel reaction on heating in acetic anhydride in presence of acetic acid and their optical and thermal properties were examined. All of them exhibited photoluminescence in chloroform, tetrahydrofuran, and dimethyl sulfoxide as well as in solid state. In solid state, their emission spectra exhibited bathochromic shifts when compared with those in less or more polar solvents. Some compounds emitted UV light both in polar solvents and in the solid state; other compounds emitted UV light in polar solvents, but emitted visible light in the solid state.

The Knoevenagel reaction, when applied to activated methyl derivatives of pyridine or other nitrogen heterocycles, directly leads to arylene–vinylene–heteroarylene structures, which constitute the basic structural elements of entirely π-conjugated molecules. They are essentially an interesting class of organic molecules, which have many applications in the field of supramolecular chemistry via hydrogen-bonding and in optoelectronic devices.[1–5]

Although other organic reactions like Heck and Wittig reactions yield similar structures, but the Knoevenagel reaction has the advantage of being a simple and easy reaction to perform, since water is the only other product. There are no unstable reactive intermediates involved or other special chemical reagents necessary for this reaction yielding the desired reaction products, all of these elements make this reaction environmentally friendly. Furthermore, the reaction products of this reaction are usually *trans*-alkenes, since it is a thermal condensation reaction and occurs at relatively high temperature. In contrast, Wittig reaction produces a mixture of *cis*/*trans*-alkenes. This Knoevenagel reaction can be usually catalyzed with either organometallic or base or acid catalysts.

In this Letter, we report a facile synthetic approach to a series of conjugated, bispyridyl and tetrapyridyl compounds, **1**–**5**, via Knoevenagel reaction (Scheme 1), which was carried in acetic anhydride in the presence of acetic acid.[6] Their chemical structures were characterized by ^{1}H ^{13}C NMR spectra and elemental analyses. Their optical and thermal properties were studied with the aim of understanding the structure–physical property relationships and developing novel organic materials.

We synthesized compound **1** in moderate yield (57%) by Knoevenagel reaction.[6] It was previously synthesized from γ-picoline and terephthalaldehyde on heating by using $ZnCl_2$ as a catalyst in a sealed tube at 210–215 °C for 50 h in 60% yield (mp 262–263 °C).[7] It was also prepared by the reaction of 2 equiv of deprotonated γ-picoline, prepared by the addition of appropriate amount of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at low temperature, with terephthalaldehyde, followed by dehydration of the intermediate dialcohol with $POCl_3$ in anhydrous pyridine with a yield of 60%.[8] Lu et al.[4] reported the mp of **1** as 265 °C as determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Unfortunately, no detailed synthetic procedure for this compound was available. Recently, Lin et al.[5] reported the synthesis of **1**

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* Corresponding author. Tel.: +1 702 895 0885; fax: +1 702 895 4072; e-mail: pradip.bhowmik@unlv.edu

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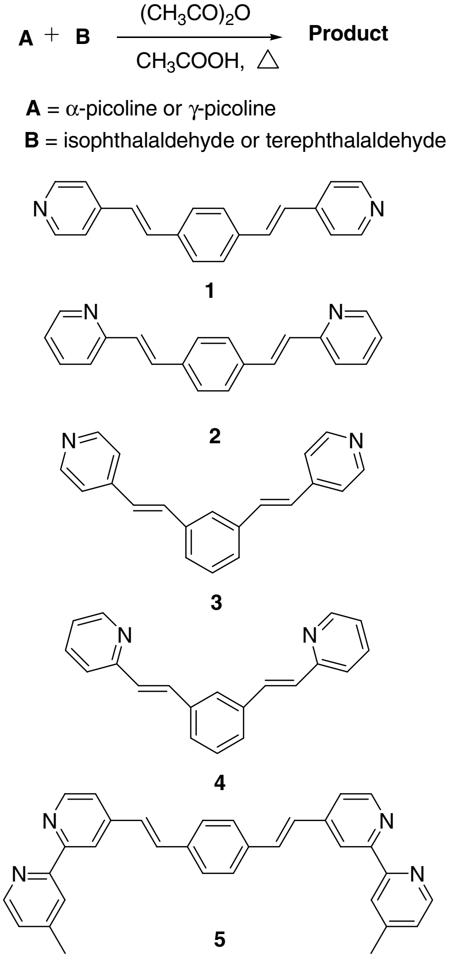

Scheme 1. Compounds **1**–**5** synthesized via Knoevenagel reaction.

from *p*-xylene in three steps: *N*-bromosuccinimide (NBS) bromination, formation of phosphonium salt and Wittig reaction with γ-picoline. The yield of NBS bromination product was not given, since it was used for the subsequent step without any purification. However, compound **1** was purified by column chromatography over silica gel (eluent: ethyl acetate/hexane = 5:1). The yields for the second and third steps were 46% and 16%, respectively. Thus, the yield and purity of this compound via Knoevenagel reaction were far superior to the methods described in the literature,[4,5,7,8] since this reaction is simple to carry out in a single-step without any special reagents or anhydrous solvents or any uncommon pieces of glassware.

Similarly, compound **2** was also prepared by Knoevenagel reaction and it was found that the yield was low (28%) for 24 h reaction time when compared with the yield of **1**. However, when the reaction was carried out for a long reaction time of 48 h, the yield increased to 46%. No attempts were made for the optimization of the conditions for this reaction. Since the Witting reaction produced low yield (56%) of **2**,[7] Hasegawa et al.[9] reported a method wherein this compound was prepared via Knoevenagel reaction by heating to reflux a mixture of terephthalaldehyde (1.0 equiv) and α-picoline (2.0 equiv) in benzoic anhydride for 8 h with a yield of 75%. Recently, Lin et al.[5] also reported the synthesis of **2** from *p*-xylene in three steps: *N*-bromosuccinimide (NBS) bromination, formation of phosphonium salt and Wittig reaction with α-picoline. The yield of NBS bromination product was not given, since it was used for the subsequent step without purification. However, the compound **2** was also purified by column chromatography on silica gel (eluent: ethyl acetate/hexane = 5:1). The yields for the second and third steps were 46% and 17%, respectively. In this regard, our method was slightly inferior to that of Hasegawa et al.[9] with regard to yield but superior to that of Lin et al. (single-step vs sequential three-step).[5]

Compounds **3** and **4** were prepared via Knoevenagel condensation reaction of γ-picoline and α-picoline with isophthalaldehyde under identical conditions with those of compounds **1** and **2** with yields of 28% and 39%, respectively.[6] The compound **5** was also prepared in a single step procedure by using this reaction with a poor yield of 6%. It was previously prepared in two steps from the reaction of 1 equiv of deprotonated 4,4′-dimethyl 2,2′-bipyridine, which was again prepared by the addition of 1 equiv of LDA in THF at low temperature, with 0.5 equiv terephthalaldehyde, followed by dehydration of the intermediate dialcohol with $POCl_3$ in anhydrous pyridine. Unfortunately, no information regarding the overall yield for the synthesis of **5** is available.[10]

Since all of the compounds, **1**–**5**, contained chromophores, they were examined for their optical properties by UV–vis absorption and photoluminescence spectra. The optical properties of compounds **1** and **2** both in dimethyl sulfoxide (DMSO) solutions and in the solid state including their photoreactivity have been studied extensively by Ebied et al.[11–14] and others.[5] In $CHCl_3$ solution of compound **1** at 6.80×10^{-8} M showed a major λ_{em} at 401 along with a shoulder peak at 383 nm when excited at 343 nm. Similarly, it exhibited λ_{em} at 398 along with a shoulder peak at 381 nm at identical concentration in THF, when excited at 345 nm. As expected, in highly polar solvent like DMSO at identical concentration both the λ_{em} peak (408 nm) and shoulder peak (390 nm), when excited at 345 nm, were slightly shifted bathochromically because of the more polar excited state than the ground state. In the solid state, it exhibited λ_{em} at 433 nm when excited at 250 nm. At other excitation wavelengths, it showed not only a major λ_{em} peak at ca. 433 nm but also a shoulder peak in the range of 544–549 nm. This shoulder peak is related to the excimer emission that originates from the excited state molecular aggregation in the solid state.

Compound **2** at 6.86×10^{-8} M in $CHCl_3$ solution showed two λ_{em} peaks at 386 and 405 nm when excited at 345 nm. Similarly, it exhibited λ_{em} peaks at 382 and 402 nm at identical concentration in THF. As expected, in highly polar solvent like DMSO at identical concentration both the λ_{em} peaks (388 and 407 nm) were slightly shifted bathochromically because of the more polar excited state than the ground state. In the solid state, it exhibited λ_{em} peaks at 435 and 461 nm when ex-