

Short Note

## 3-Cyano-4,6-diphenyl-2-(phenethylamino)pyridine

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Received: 15 April 2014 / Accepted: 17 July 2014 / Published: 6 August 2014

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**Abstract:** Novel synthesis of a 2-amino-3-cyano-2,6-diphenyl pyridine by a one-pot multi-component reaction of 1,3-diphenylpropane-1,3-dione, malononitrile and phenethylamine in the presence of *N*-hydroxybenzamide and zinc chloride has been reported. The structure of the synthesized compound was assigned on the basis of its elemental analysis, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR and mass spectral data. X-ray structure analysis confirmed unambiguously the proposed structure. The photophysical properties ( $\lambda_{Abs.}$ ,  $\lambda_{Flu.}$ ) in CH<sub>3</sub>OH, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub> and the emission spectrum of the new compound in solution and in the solid state are reported.

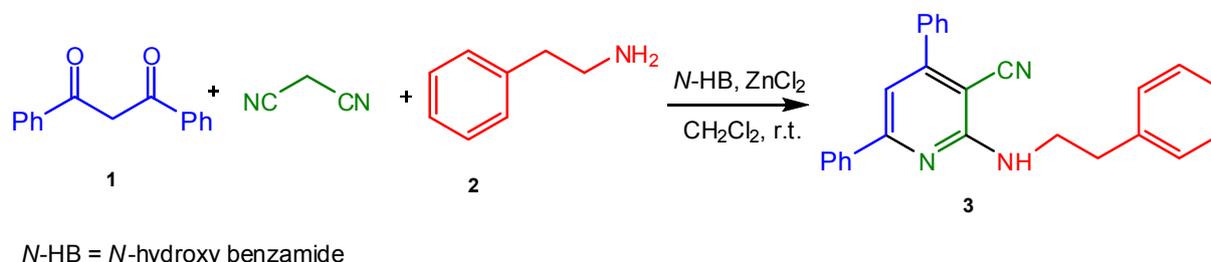
**Keywords:** 2-amino-3-cyano-4,6-diarylpyridine; fluorescence; multi-component reaction; ZnCl<sub>2</sub>; *N*-hydroxybenzamide; malononitrile

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The optoelectronic devices such as optical fibers, switches, tunable lasers and amplifiers, modulators with various applications need compounds emitting in the blue spectral region [1]. So developing a procedure for the synthesis of thermally stable, highly fluorescent materials can be urgently interesting for technology upgrading. There are some reports on using the fluorescent compounds in biochemical and medical research [2]. 2-Aminopyridine derivatives are of great

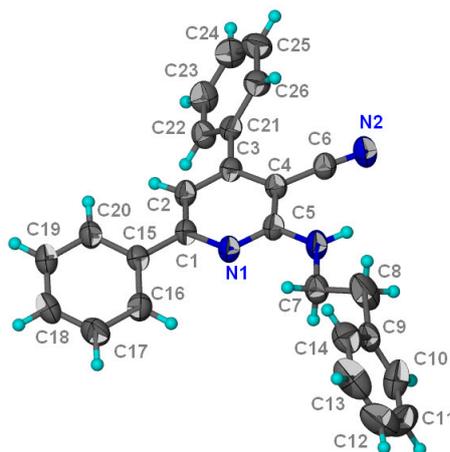
importance due to their biological activities such as cardioprotective [3], antibacterial [4], antioxidant [5], anti-inflammatory [6] and anti-HIV [7]. Sulfapyridine, an example which contains 2-aminopyridine moiety, is an old marked antibacterial drug. Therefore designing new procedures to synthesize 2-aminopyridine derivatives has attracted a lot of interest. Literature shows some reports on the synthesis of 2-amino-3-cyano-4,6-dialkylpyridines but there are few reports on diaryl ones [8–11]. Recently we have reported the synthesis of 2-amino-3-cyano-4,6-dialkyl pyridines by the one-pot multi-component reaction of 2,4-pentanedione, malononitrile and primary or secondary amines in the presence of *N*-hydroxy benzamide or *p*-toluenesulfonic acid as the acidic catalyst [12]. In continuation of our research on the synthesis of fluorescent compounds [12–14], we herein report the synthesis of 3-cyano-4,6-diphenyl-2-(phenethylamino) pyridine using *N*-hydroxybenzamide and  $\text{ZnCl}_2$  as an organic acid and Lewis acid catalysts respectively (Scheme 1).

**Scheme 1.** Synthesis of 3-cyano-4,6-diphenyl-2-(phenethylamino)pyridine **3**.



Structure **3** was assigned on the basis of its elemental analysis,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , IR and mass spectral data. The light yellow crystals of **3** were obtained by crystallization from ethyl acetate/*n*-hexane: 1/3 and its X-ray structure was determined to confirm unambiguously its structure. [15] (Figure 1).

**Figure 1.** X-ray crystal structure of **3**.



Compound **3** has shown fluorescence activity in the blue region in solution and solid phase. The photophysical data for this compound including  $\lambda_{\text{Abs.}}$  (nm),  $\lambda_{\text{Flu.}}$  (nm) have been measured for 0.00002 M solutions in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  (Table 1). The fluorescence emission spectrum of compound **3** solutions in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}$  is shown in Figure 2.

**Table 1.** Photophysical data: electronic absorption (*Abs.*) and fluorescence (*Flu.*) of **3**.

Comp	CH <sub>3</sub> OH		CH <sub>3</sub> CN		CH <sub>2</sub> Cl <sub>2</sub>	
	$\lambda_{Abs}$	$\lambda_{Flu}$	$\lambda_{Abs}$	$\lambda_{Flu}$	$\lambda_{Abs}$	$\lambda_{Flu}$
<b>3</b>	300	404	300	403	320	401

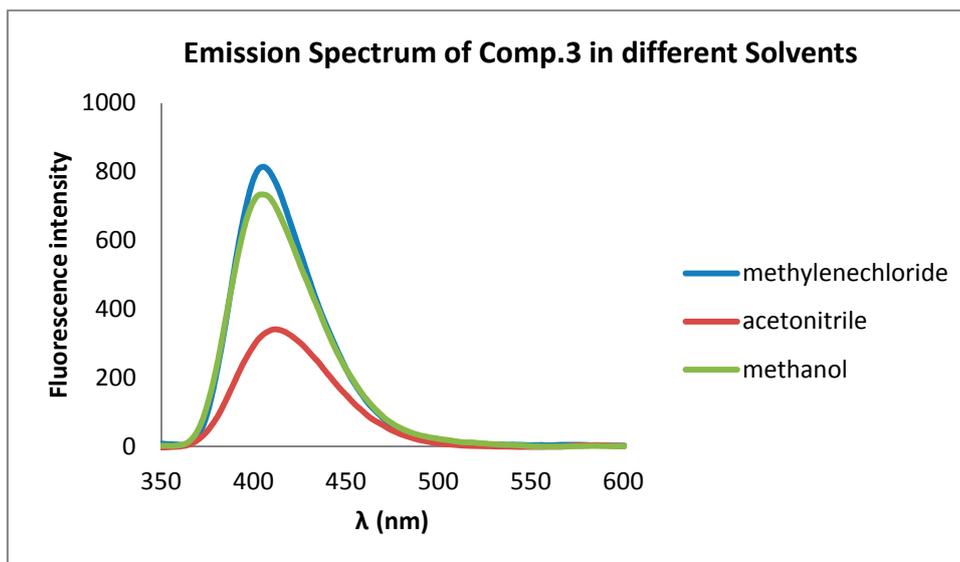
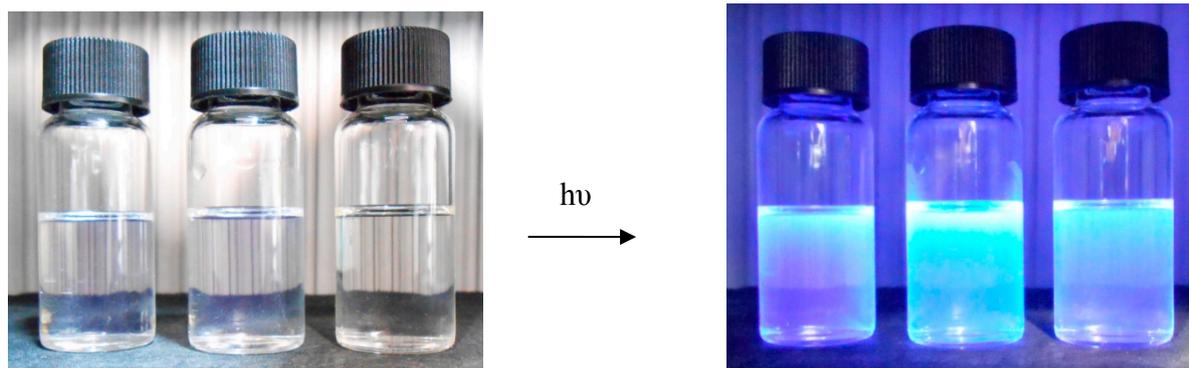
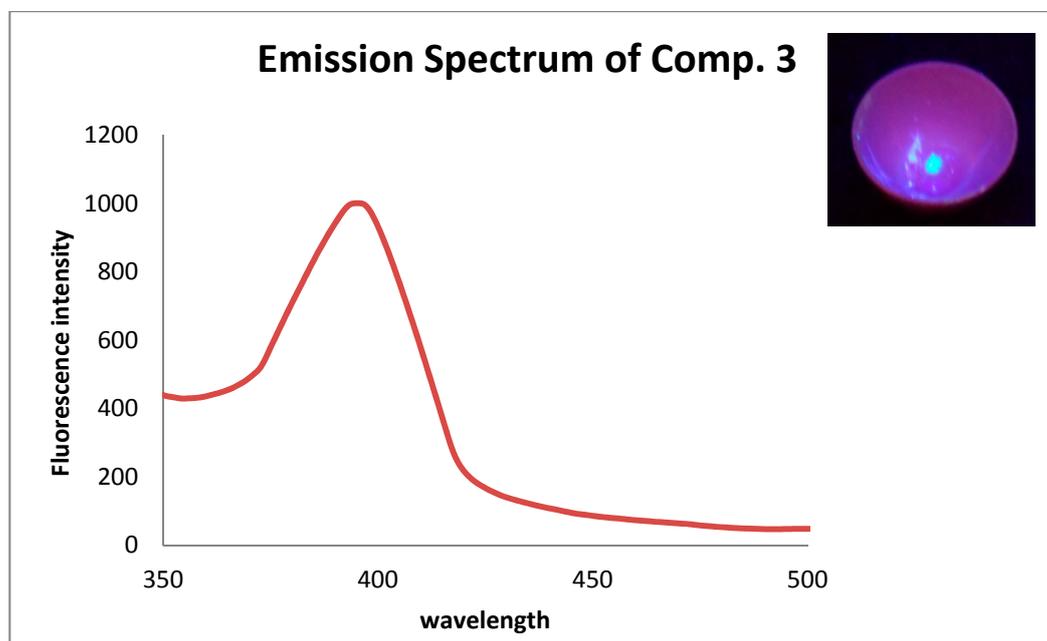
**Figure 2.** The fluorescence emission spectrum of compound **3** solutions in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN and CH<sub>3</sub>OH.

Figure 3 shows photographs of compound **3** solutions in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN and CH<sub>3</sub>OH (a): under visible light and (b): under a UV lamp with  $\lambda = 366$  nm (Philips TL8W/08F8T5/BLC).

**Figure 3.** Photographs of solutions of **3** from left to right in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>CN respectively.

The emission spectrum of compound **3** has been determined. The sample is prepared as the following: a solution of compound **3** (0.5 mL) in CHCl<sub>3</sub> ( $10^{-8}$  mol L<sup>-1</sup>) was first coated on a quartz glass sheet and dried at room temperature, then placed in a 1 cm length quartz cell. The excitation and emission slits were adjusted on 3 nm. The fluorescence emission intensity of compound **3** after excitation in 300 nm is shown in Figure 4. The photo in the top right of Figure 4 has been taken under a UV lamp with  $\lambda = 366$  nm (Philips TL8W/08F8T5/BLC), only to show the fluorescence property of compound **3** in solid state. It seems the title compound can achieve a good chance among the optoelectronic devices.

**Figure 4.** The fluorescence emission spectrum of compound **3** after excitation in 300 nm. The photo in the top right has been taken under a UV lamp with  $\lambda = 366$  nm (Philips TL8W/08F8T5/BLC).



## Experimental

Elemental analysis for C, H and N was performed using a Thermo Finnigan Flash EA1112 instrument.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were determined on a Bruker 250 spectrometer. IR spectra were measured on a Bruker EQUINOX 55 spectrophotometer with the ATR method. Mass spectra were recorded on a Finnigan-MAT 8430 spectrometer. Photophysical data measurements were made by a luminescence PERKIN ELMER LS 50B spectrometer.

*3-Cyano-(2-phenethylamino)-4,6-diphenyl pyridine (3)*. To a magnetically stirred solution of 1,3-diphenylpropane-1,3-dione (0.224 g, 1 mmol) and  $\text{ZnCl}_2$  (10 mol %) in 10 mL  $\text{CH}_2\text{Cl}_2$ , malononitrile (0.066 g, 1 mmol), phenethyl amine (0.12 mL, 1 mmol) and *N*-hydroxy benzamide (50 mol %, 0.68 g) were added in a one-pot manner. The solution was stirred at room temperature for 10 h. The reaction progress was monitored by IR. When one of the CN absorptions ( $2228\text{ cm}^{-1}$ ) in IR spectrum of the reaction mixture had disappeared, the solvent was removed under reduced pressure and the product was purified using column chromatography (silica gel, ethyl acetate/*n*-hexane: 1/5). The crystals of product were obtained (0.27 g, 72% yield) as yellow crystals. Melting point:  $148\text{ }^\circ\text{C}$ .

## Structural Characterization

IR,  $\nu_{\text{max}}$ : 3353, 2211,  $1550\text{ cm}^{-1}$ ;  $\delta_{\text{H}}$  (250 MHz,  $\text{CDCl}_3$ ): 3.08 (2H, t,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 3.96 (2H, q,  $J = 6.7$  Hz,  $\text{CH}_2\text{-N}$ ), 5.51-5.55 (1H, br s, NH), 7.19 (1H, s, CH of pyridine ring), 7.26-7.42, 7.50-7.59, 7.64-7.68, 8.12-8.15 (15H, 4m, Ph protons) ppm;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ): 35.93 ( $\text{CH}_2$ ), 43.25 ( $\text{CH}_2\text{-N}$ ), 109.61 (CN), 117.41 (CH of pyridine), 126.60, 127.39, 128.76, 128.78, 128.94, 129.73, 130.17, 137.34, 138.34, 139.17, 155.08, 159.06 (aromatic carbons) ppm; MS:  $m/z = 375$  ( $\text{M}^+$ ), 298, 272, 255, 221, 195,

120, 91, 77, 75, 43; Anal. Calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>: C, 83.17; H, 5.64; N, 11.19; Found: C, 83.20; H, 5.69; N, 11.23.

### Acknowledgments

Support of this study by the Research Council at the University of Tehran is gratefully acknowledged.

### Author Contributions

All the authors equally contributed to the research. ZI and HS did the experiments. KA performed the spectroscopic data. SWN performed the X-ray structure. AZ wrote the paper.

### Conflicts of Interest

The authors declare no conflict of interest.

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15. Crystallographic data for the structure of compound **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. 983903. CCDC 983903 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.com.ac.uk/data\\_request/cif](http://www.ccdc.com.ac.uk/data_request/cif). (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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