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The synthesis and properties of phenolic Schiff bases based on 1,8-naphthyridine

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Abstract

Two new phenolic Schiff bases **1** and **2** based on 1,8-naphthyridine were synthesized. The phenomena of ethanolic solutions of compounds **1** and **2** upon adding sodium hydroxide ethanolic solutions, and of the above solutions in air for some time have been studied by UV–vis absorption spectra. Especially, the exact structures of **1b** and **2b** have also been studied.

Keywords: Naphthyridine; Base; UV–vis

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1. Introduction

External stimulation controlling physical properties of molecules has attracted great attention in the development of molecular switches and devices [1–4]. 1,8-Naphthyridine and its derivatives have been of great interest for many people for the reason that they are potential bidentate ligands and have broad spectrum of their biological activities [5–9]. In recent years, more and more people are interested in developing multifunctional materials [10–12].

Here, we firstly report the synthesis, base-sensitive properties and the phenomena of compounds **1** and **2** in air after the addition of base (Schemes 1 and 2).

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded at room temperature on a Bruker DPX-400 spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me_4Si) for ^{1}H. Infrared spectra were recorded on a Bio-Rad FTS165 FT-IR spectrophotometer. The mass spectra were recorded on a Finnigan GC–MS 4021C spectrometer. Element analysis was carried out on Carlo Erba Corporation Model 1104 element analysis instrument. All UV–vis absorption spectra were recorded on a Hitachi U-3010 spectrometer at room temperature.

2.2. Materials

7-Amino-2,4-dimethyl-1,8-naphthyridine and 7-acetylamino-2,4-dimethy-1,8-naphthyridine were synthesized and purified following the modified procedures described before [13,14]. Selenium dioxide, 2-amino-phenol, and 4-amino-phenol were

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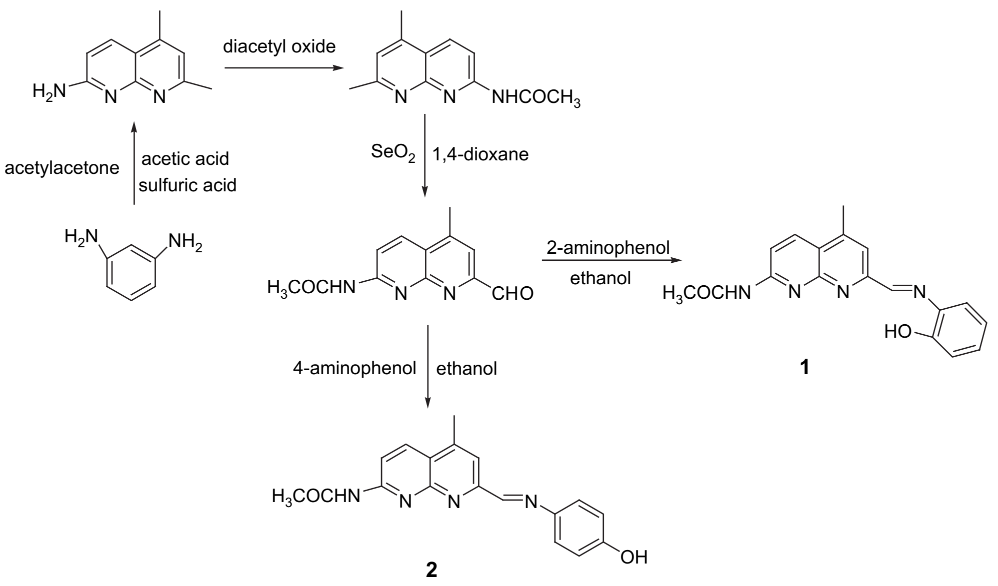
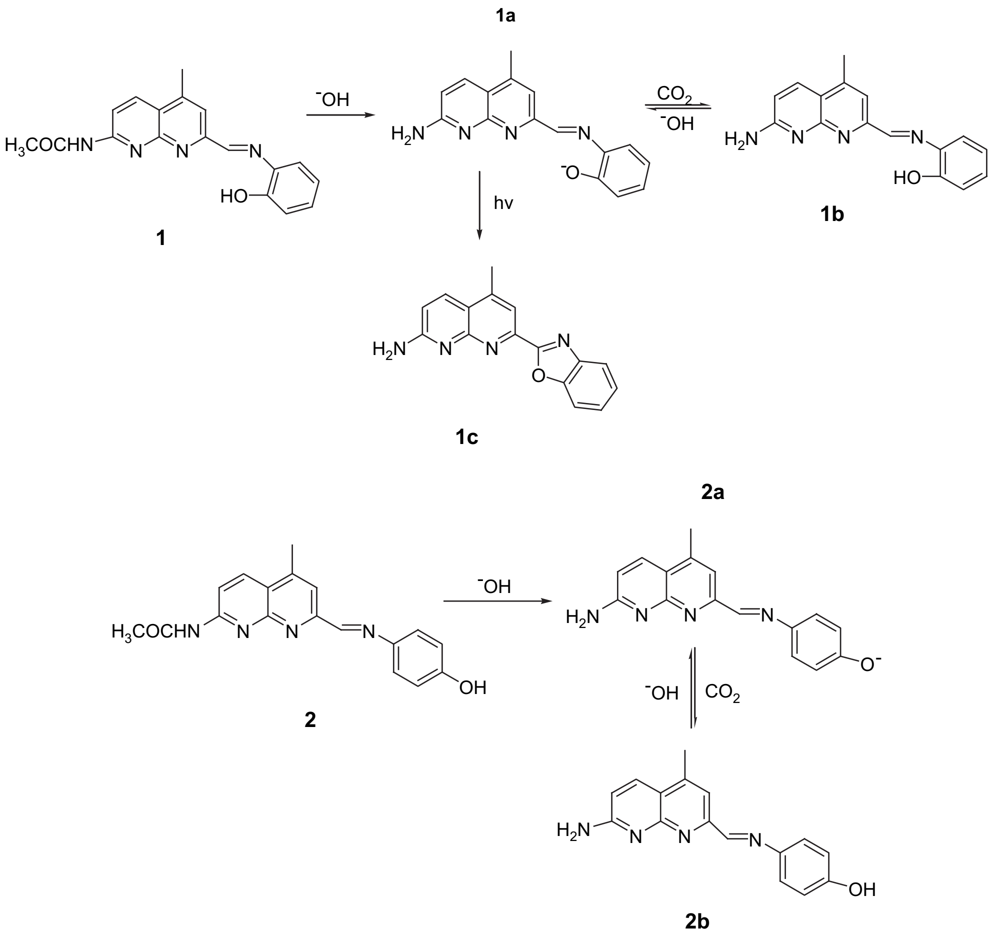


Scheme 1.



Scheme 2.

purchased from Beijing chemical reagents company. Ethanol and 1,4-dioxane, were purified according to the method reported before use [15].

2.3. Synthetic procedures

2.3.1. 7-Acetamidyl-4-methyl-1,8-naphthyridine-2-aldehyde [16,17]

7-Acetamidyl-2,4-dimethyl-1,8-naphthyridine (4 g, 0.0186 mol) and selenium dioxide (2.5 g, 0.0225 mol) were added in 200 ml 1,4-dioxane, and the reaction mixture was refluxed for 4 h with stirring under nitrogen. The mixture was filtered while hot, and the crude product was obtained from the concentration in vacuum. The final product was obtained by column chromatography over silica gel column using dichloromethane/ethanol (30:1) as eluent (1.49 g, 35%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm): 2.34–2.37 (3H, s), 2.83–2.87 (3H, s), 7.87 (1H, s), 8.38–8.40 (1H, m), 8.65–8.67 (2H, d), 10.19 (1H, s). IR (KBr) ν_{max} (cm^{-1}): 3398, 3193, 3133, 3060, 2923, 2840, 1701, 1612, 1587, 1570, 1504, 1397, 1343, 1306, 1234, 1143, 997, 807, 761. MS, *m/z* (%): 229 (M$^+$) (100%), 214, 186, 173, 160, 144, 131. Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.85; H, 4.86; N, 18.31.

*2.3.2. (E)-2-(2-Hydroxyphenylimino)-4-methyl-7-acetamidyl-1,8-naphthyridine (**1**) [18]*

7-Acetamidyl-4-methyl-1,8-naphthyridine-2-aldehyde (2.29 g, 0.01 mol) and 2-aminophenol (1.20 g, 0.011 mol) were mixed in 50 ml ethanol and the mixture was refluxed for 2 h under nitrogen atmosphere. After concentration of the solvent, the product was recrystallized from ethanol (2.07 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm): 2.31–2.33 (3H, s), 2.80 (3H, s), 6.95–6.98 (1H, m), 7.05–7.07 (1H, d), 7.28–7.32 (1H, m), 7.43–7.45 (1H, d), 8.16 (1H, s), 8.40 (1H, s), 8.43–8.45 (1H, m), 8.56–8.58 (1H, m), 8.95 (1H, s), 10.20 (1H, s). IR (KBr) ν_{max} (cm^{-1}): 3411, 1704, 1614, 1592, 1513, 1485, 1410, 1334, 1229, 806, 749. MS, *m/z* (%): 320 (M$^+$) (100%), 277, 249, 185, 159, 158. Anal. Calcd for $C_{18}H_{16}N_4O_2$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.55; H, 4.88; N, 17.56.

*2.3.3. (E)-2-(4-Hydroxyphenylimino)-4-methyl-7-acetamidyl-1,8-naphthyridine (**2**)*

The synthetic method of compound **2** is similar as that of compound **1**. Yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm): 2.31 (3H, s), 2.79 (3H, s), 6.92–6.70 (2H, m), 7.33–7.52 (2H, d), 8.20 (1H, s), 8.40 (1H, s), 8.44–8.46 (1H, m), 8.64–8.67 (1H, d), 8.75 (1H, s), 10.20 (1H, s). IR (KBr) ν_{max} (cm^{-1}): 3449, 1687, 1607, 1579, 1510, 1408, 1310, 1266, 834. MS, *m/z* (%): 320 (M$^+$) (100%), 277, 278, 250, 249, 185, 159. Anal. Calcd for $C_{18}H_{16}N_4O_2$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.57; H, 4.95; N, 17.53.

2.4. Absorption measurements

Ethanolic solution of compound **1** was obtained as 1.0×10^{-4} M, and each 2 ml of above solution was added in 5 ml tube. In addition, a 1.0×10^{-2} M ethanolic solution of sodium hydroxide was obtained and appropriate amount of the above sodium hydroxide solution was added in the tubes containing compound **1** ethanolic solution. The mixture was diluted as 2.0×10^{-5} M for compound **1** with ethanol. For compound **2**, the method is similar as that of compound **1**.

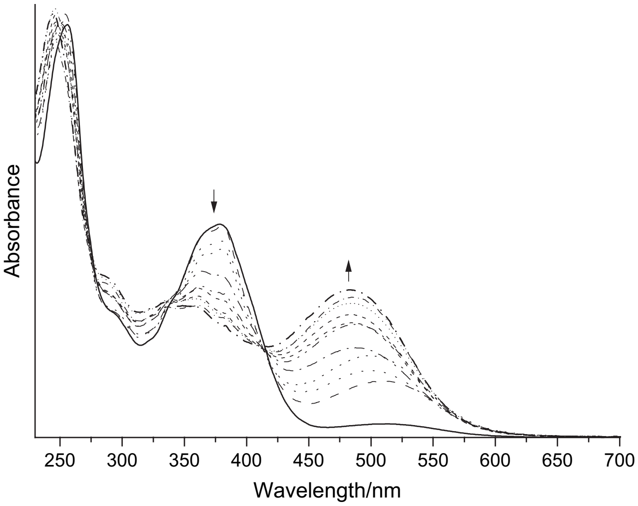


Fig. 1. Absorption spectra of (*E*)-2-(2-hydroxyphenylimino)-4-methyl-7-acetamidyl-1,8-naphthyridine ethanolic solution upon adding sodium hydroxide ethanolic solution (0–30 equal).

3. Results and discussion

Addition of sodium hydroxide (0.01 M) ethanolic solution to the ethanolic solution of **1** produces decrease of the band at 378 nm ($\varepsilon_{max}/10^4 = 1.36$ M^{-1} cm^{-1}) with a concomitant increase of a new one at 482 nm ($\varepsilon_{max}/10^4 = 0.94$ M^{-1} cm^{-1}), which are ascribed to **1a** (Fig. 1). Comparing the absorption spectra of **1a** with that of **1**, it is found that the longest band

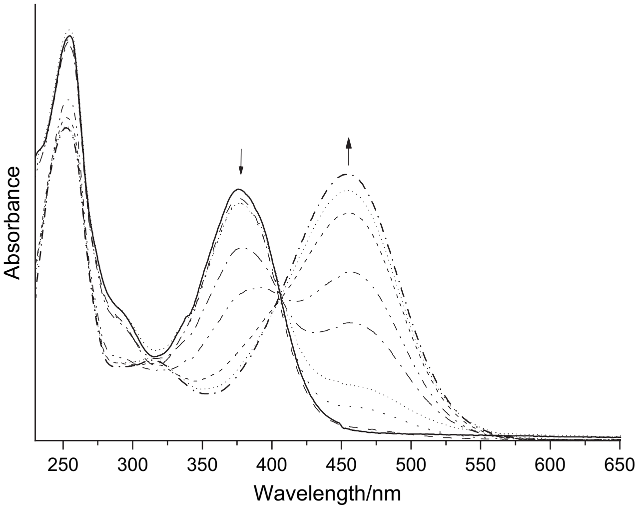


Fig. 2. Absorption spectra of (*E*)-2-(4-hydroxyphenylimino)-4-methyl-7-acetamidyl-1,8-naphthyridine ethanolic solution upon adding sodium hydroxide ethanolic solution (0–30 equal).

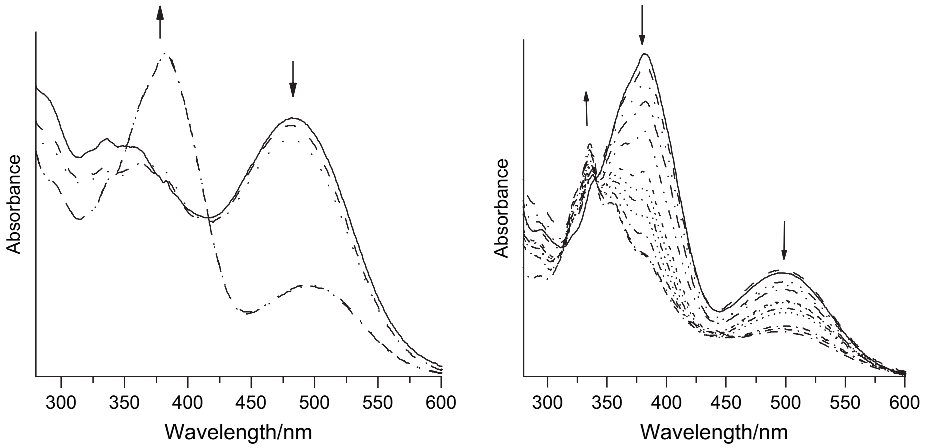


Fig. 3. Absorption spectra of (*E*)-2-(2-hydroxyphenylimino)-4-methyl-7-acetamidyl-1,8-naphthyridine ethanolic solution after adding sodium hydroxide ethanolic solution (left: the first period of time; right: the second time).

of **1a** is red-shifted as much as 104 nm ($\Delta\lambda_{max} = 482 - 378$ nm), which results from deprotonation of phenol and the change from -acetamidyl to -amino. As far as compound **2** is concerned, the similar phenomenon (Fig. 2) is detected when sodium hydroxide ethanolic solution (0.01 M) was added to the ethanolic solution of compound **2** ($\lambda_{max} = 376$ nm, $\varepsilon_{max}/10^4 = 1.73\ M^{-1}\,cm^{-1}$). Red-shift is 80 nm ($\Delta\lambda_{max} = 456 - 376$ nm). The attribution of the significant red-shift is the same as that of compound **1**.

When the ethanolic solutions of compounds **1a** and **2a** are in air for a moment, great difference can be seen from the recorded absorption spectra (Figs. 3 and 4). As to compound **1a**, for the first period of time, a new band at 384 nm appeared along with the decrease of the original band at 482 nm. During the second period, unexpected band at 336 nm increased with the decrease of bands at 482 nm and 384 nm. While for compound **2a**, there is only a new band at 379 nm appearing with the decrease of band at 456 nm ($\varepsilon_{max}/10^4 = 1.83\ M^{-1}\,cm^{-1}$).

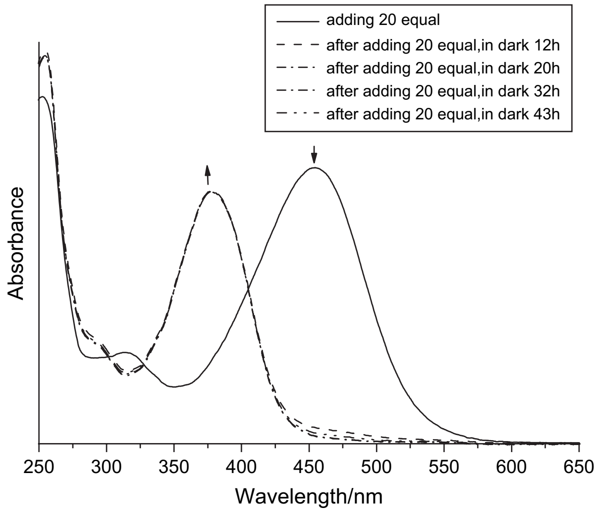


Fig. 4. Absorption spectra of (*E*)-2-(4-hydroxyphenylimino)-4-methyl-7-acetamidyl-1,8-naphthyridine ethanolic solution upon and after adding sodium hydroxide ethanolic solution.

Comparing the phenomena of both compounds **1a** and **2a**, it is easy to see that there is a similar process happening in the ethanolic solutions of compounds **1a** and **2a** in air, which can be concluded from the similar new bands each at 384 nm and 379 nm. We attribute both new bands to compounds **1b** and **2b**. To confirm the veracity of our attribution, we aerate carbon dioxide to the ethanolic solutions of compounds **1a** and **2a**, and the same results as that in air are obtained. The exact structures of compounds **1b** and **2b** are characterized by MS and ^{1}H NMR [19,20]. The absorption band at 336 nm for the ethanolic solution of compound **1a** in air is ascribed to compound **1c** [18,21–23].

4. Conclusion

In summary, two novel base-sensitive compounds have been synthesized. The phenomena of ethanolic solutions of compounds **1** and **2** upon adding sodium hydroxide ethanolic solution, and of the above solutions in air for some time have been studied by UV–vis absorption spectra. Especially, the exact structures of **1b** and **2b** have also been characterized. Although the exact structure of **1c** has not been characterized, this unexpected phenomenon still makes people put attention to the research of this field.

Acknowledgements

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[19] (*E*)-2-(4-Hydroxyphenylimino)-4-methyl-7-amino-1,8-naphthyridine (**1c**): ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H(ppm): 2.80 (3H, s), 4.50 (2H, s), 6.96–6.99 (1H, m), 7.06–7.08 (1H, d), 7.29–7.31 (1H, m), 7.42–7.44 (1H, d), 8.16 (1H, s), 8.44–8.46 (1H, m), 7.35 (1H, s), 8.10–8.12 (1H, d), 10.20 (1H, s). MS, *m*/*z* (%): 278 (M^+) (100%), 276, 275, 185, 172, 120.

[20] (*E*)-2-(4-Hydroxyphenylimino)-4-methyl-7-amino-1,8-naphthyridine (**2c**): ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H(ppm): 2.76 (3H, s), 4.51 (2H, s), 6.94–6.70 (2H, m), 7.33–7.36 (2H, d), 8.20 (1H, s), 8.43–8.45 (1H, m), 8.15 (1H, s), 8.17–8.20 (1H, d), 10.20 (1H, s). MS, *m*/*z* (%): 278 (M^+) (100%), 276, 275, 186, 171, 120.

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