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2-*N*-ANILINOPYRIDINE AND 2-*N*-PIPERIDINOPYRIDINE: FLUORESCENCE PROPERTIES

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ABSTRACT

2-Chloropyridine, which was obtained commercially, was used as the precursor for the preparation of 2-*N*-piperidinopyridine and 2-*N*-anilinopyridine. Fluorescence studies were carried out in various solvents, in capped and uncapped condition. 2-*N*-Piperidinopyridine showed the highest fluorescence peak in ethanol for both conditions. The fluorescence peak of 2-*N*-piperidinopyridine was observed at 372 nm, when excited at 258 nm for capped sample, where the uncapped sample showed fluorescence peak at 372 nm, when excited at 293 nm. Similar results were obtained with capped and uncapped samples of 2-*N*-anilinopyridine; whereby fluorescence peak was observed at 383 nm when excited at 277 nm for capped condition, and fluorescence peak at 335 nm when excited at 384 nm for uncapped condition. The fluorescence peaks of 2-*N*-anilinopyridine were recorded at higher wavelengths to 2-*N*-piperidinopyridine.

Key words : 2-N-Anilinopyridine 2-Piperidinopyridine, Fluorescence.

INTRODUCTION

The pyridine ring systems are very widely distributed in nature, especially in the plant kingdom. Many important alkaloids are pyridine derivatives[1]. The pyridine ring plays a key role in several biological processes such as the oxidation/reduction coenzyme nicotine adenine dinucleotide (NAPP). The vitamin niacin is required for its biosynthesis[2].

The first pyridine was obtained by isolation from bone oil and from coal tar by Anderson[3]. The cyclic nature of pyridine was suggested by Korner and Dewar, in 1869 as a hexagonal structure having alternate double and single bonds[4].

The pyridine ring can be synthesized using two main synthetic routes, namely Hantzsch synthesis and Guareshi synthesis. The most important pyridine synthesis is by

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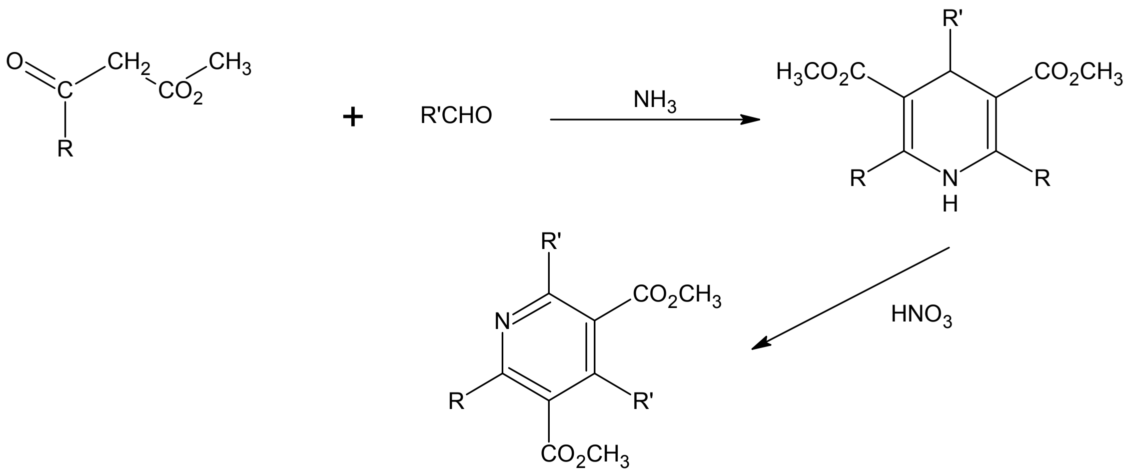
using Hantzsch method, which involved the condensation of two molecules of β-keto ester with an aldehyde and ammonia as shown in Scheme 1. However in this work, 2-chloropyridine was obtained commercially.



Scheme 1

The fluorescence characteristic of pyridine or other heterocycles are not extensively studied, even though a wide variety of heterocylic compounds are known to be fluorescent[4].

This work involves synthesizing various pyridine derivatives followed by the study of their fluorescence characteristics in various solvents. However, this paper will only report on the fluorescence characteristics of 2-*N*-anilinopyridine and 2-*N*-piperidinopyride.

EXPERIMENTAL

Synthesis

2- *N*-Anilinopyridine

2-Chloropyridine (1.0 mL) was added to aniline (1.0 mL) and refluxed for 7 hours. The mixture was cooled and evaporated. Water (10 mL) was added to the slurry and the pH was adjusted to 7. The slurry was extracted with ether (3 x 10 mL) and washed with water and dried over anhydrous sodium sulphate. Evaporation of ether gave dusty pink solid, which was purified using preparative thin layer chromatography in ethyl acetate: hexane (6 : 1) yield : 23%, M. pt: 119^o - 126^o C, IR (cm^{-1}): 1590, 1460, 1380; ^1H NMR ($CDCl_3$) δ: 8.14, d, 1H (H_6), 7.43, m, 1H (NH), 7.25, m, 4H (H_2, H_3, H_5, H_6), 6.99, m, 1H (H_4), 6.82, d, 1H (H_3), 6.66, t, 2H (H_4, H_5); M^+: 169.000 required: 169.2194

2-*N*-Piperidinopyridine

Piperidine (4.0 mL) was added to 2-chloropyridine (0.431 mL)[5, 6] and the mixture was refluxed for 6 hours. The mixture was evaporated off. Water (10 mL) was added to the slurry and the pH was adjusted to 7. The slurry was extracted with ether (3 x 10 mL). The ethereal layer was washed with water and dried over anhydrous sodium sulphate. Evaporation of ether gave yellow brownish liquid, which was purified with preparative thin layer chromatography using hexane: ethyl acetate (1 : 10)

yield : 23%, IR (cm^{-1}): 1590, 1480, 1250; ^1H NMR ($CDCl_3$) δ 8.14, d, 1H (H_6), 7.41, t, 1H (H_3), 6.62, d, 1H (H_5), 6.52, t, 1H (H_4), 3.48, s, 4H (H_2, H_6), 1.67, s, 6H (H_3, H_4, H_5); M^+: 162.000 required: 162.2473

Spectroscopic analysis

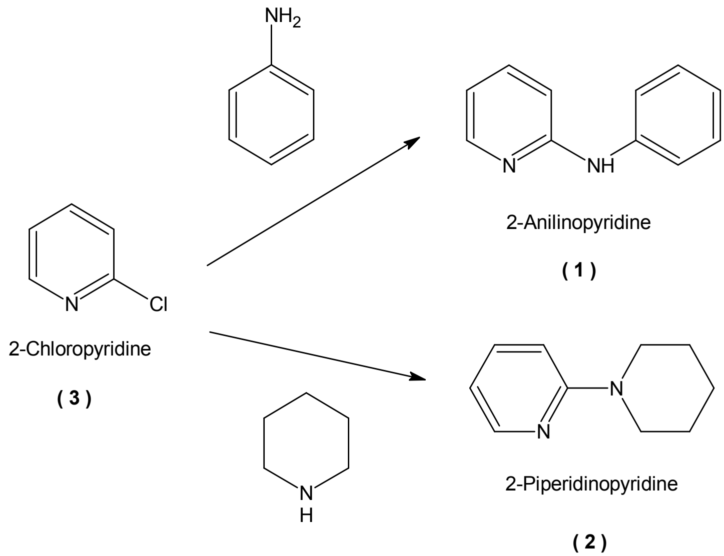
All solvents were redistilled before use. Melting points were determined with electrothermal melting point apparatus and were not corrected. Infrared spectra were recorded using Perkin Elmer 298 Infrared Spectrometer and FTIR Perkin-Elmer 1600 Series. ^1H and ^{13}C NMR spectra were recorded on a Joel JNM-LA400 FT and Joel-EX90A FT NMR systems spectrometer. Mass spectrum was recorded using GCMS Hewlett-Packard HP 6890 Series with mass selective indicator.

Fluorescence studies

2-*N*-Anilinopyridine and 2 *N*-piperidinopyridine with the same concentration were prepared in ethanol, tetrahydrofuran, ethyl acetate and acetonitrile. The fluorescence measurement was carried out in a quartz cell, using Fluorescence spectrometer Model F-2000 Hitachi at room temperature.

RESULTS AND DISCUSSION

2-*N*-Anilinopyridine **(1)** and 2-*N*-piperidinopyridine **(2)** were obtained, when commercially available 2-chloropyridine **(3)** was reacted with aniline and piperidine respectively, as shown in Scheme 2. The structures of both compounds were confirmed by infrared, ^1H NMR and mass spectra, and recorded in the experimental section.



Scheme 2

2-Chloropyridine showed fluorescence weak peak in acetonitrile and tetrahydrofuran where as no fluorescence peak was observed in ethanol, ethyl acetate and chloroform. Fluorescence peak of 2-chloropyridine was recorded at 438 nm, when exited at 378 nm in tetrahydrofuran.

Tables 1 and 2 show the fluorescence characteristic 2-*N*-anilinopyridine and 2-*N*-piperidinopyridine in various solvents. Table 1 shows that 2-*N*-anilinopyridine showed the highest fluorescence intensity in tetrahydrofuran, followed by ethyl acetate for both capped and uncapped samples. The high fluorescence intensity recorded in tetrahydrofuran may be to the formation of a complex with the solvent through hydrogen-bonding as suggested in Fig. 1.

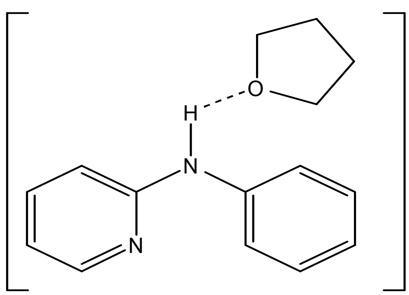


Fig. 1

This complex may enhance the $\pi \rightarrow \pi^*$ transition in the excited state, resulting in high fluorescence intensity. However, detailed study on the effect of tetrahydrofuran on the fluorescence of diazines system is still undergoing before any concrete conclusion can be made.

Table 1. Fluorescence characteristics of 2-*N*-anilinopyridine in various solvents (M = 6.126×10^{-6})

Condition	Solvent	Excitation wavelength(nm)	Fluorescence wavelength/nm	Intensity(I)
Capped	Ethyl acetate	283	358	14.55
	Tetrahydrofuran	282	366	18.27
Uncapped	Ethanol	347	384	0.042
	Acetonitrile	335	384	0.673
	Ethyl acetate	336	371	0.402
	Tetrahydrofuran	339	368	0.993

Fig. 2 shows the fluorescence spectra of 2-*N*-anilinopyridine in tetrahydrofuran and ethyl acetate for capped samples.

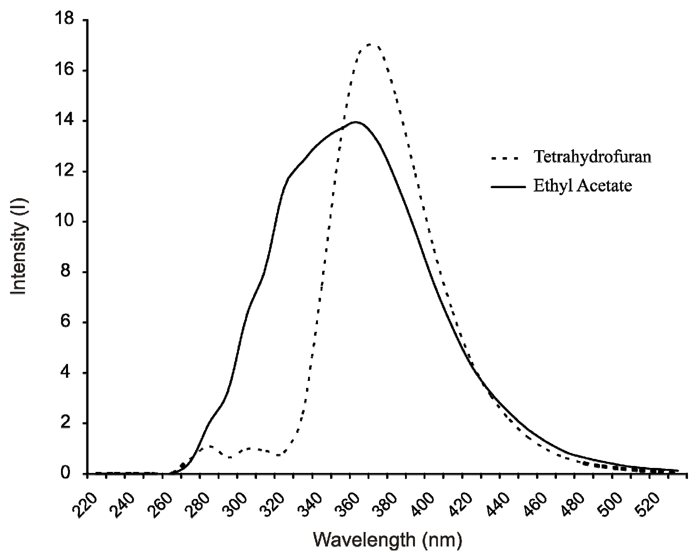


Fig. 2: Fluorescence spectrum of 2-N-anilinopyridine in various solvents

The fluorescence intensity of 2-*N*-anilinopyridine in ethyl acetate was recorded as 14.55, excited at 283 nm and fluoresced at 358 nm. As observed in 2-*N*-anilinopyridine in tetrahydrofuran, it is believed that a complex may also formed with ethyl acetate, as shown in Fig. 3

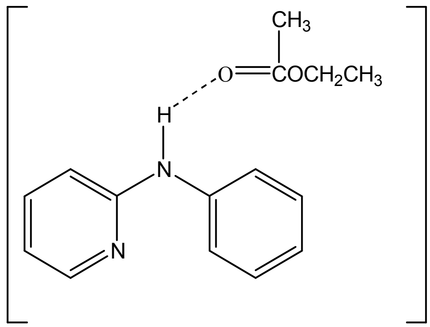


Fig. 3

The lower intensity of 2-*N*-anilinopyridine in ethyl acetate as compared to tetrahydrofuran is probably due to complex formed in ethyl acetate which is less rigid than the complex formed in tetrahydrofuran. The $-CH_3$ and $O-CH_2CH_3$ group of ethyl acetate may increase the vibrational amplitude of the complex, and energy absorbed is thus dissipated as heat and as a result, low fluorescence intensity was observed.

Table 2. Fluorescence characteristics of 2-*N*-piperidinopyridine in various solvents ($M = 6.126 \times 10^{-6}$)

Condition	Solvent	Excitation wavelength (nm)	Fluorescence Wavelength (nm)	Intensity (I)
Capped	Ethanol	258	372	10.30
	Ethyl acetate	263	358	9.31
	Tetrahydrofuran	260	362	11.88
Uncapped	Ethanol	293	372	0.893
	Acetonitrile	334	371	1.972
	Ethyl acetate	298	364	0.782
	Tetrahydrofuran	303	364	0.944

The fluorescence characteristics of 2-*N*-piperidinopyridine is shown in Table 3. Fig. 4 shows the fluorescence spectra of 2-*N*-piperidinopyridine in various solvents.

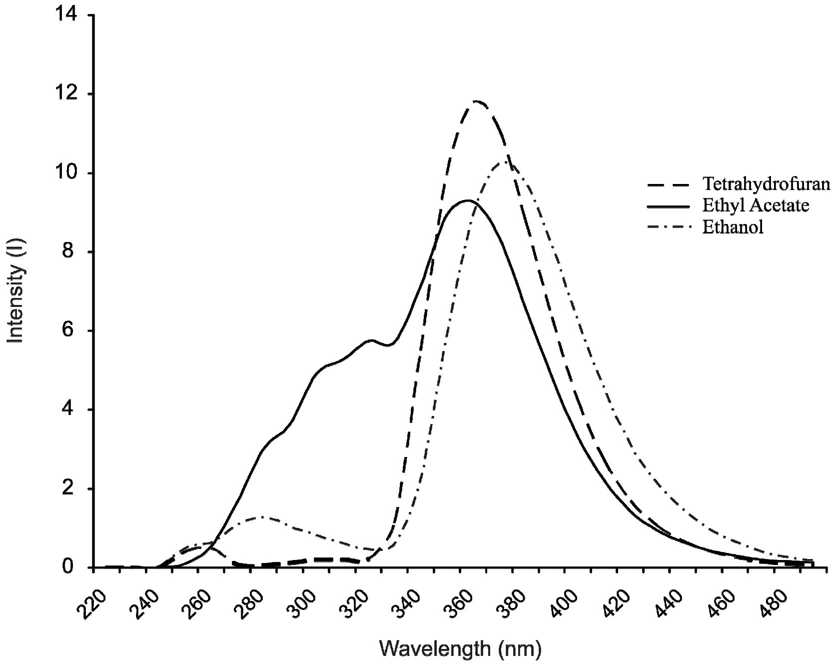


Fig. 4: Fluorescence spectrum of 2-*N*-piperidinopyridine in various solvents.

2-*N*-Piperidinopyridine showed almost the same fluorescence intensity in tetrahydrofuran and ethanol, (Table 2). It is believed that the fluorescence intensity of 2-*N*-piperidinopyridine in ethanol is also due to H-bonding capability of ethanol; thus forming a complex with the compound under study. Similar phenomenon was observed with pyrimidine system studied earlier[5].

In general, it can be seen from Tables 1 and 2 that 2-*N*-anilinopyridine fluoresced at higher wavelength compared to 2-*N*-piperidinopyridine. The fluorescence peak of 2-*N*-anilinopyridine recorded at higher wavelengths in all solvents is probably due to the increase in the degree of conjugation in the 2-*N*-anilinopyridine as compared to 2-*N*-piperidinopyridine. The same phenomena were observed with purine derivatives studied earlier[7]. The increase in the degree of conjugation is also reflected in the high fluorescence intensity observed in 2-*N*-anilinopyridine as compared to 2-*N*-piperidinopyridine.

The fluorescence studies of both compounds in various solvents were carried in capped and uncapped conditions. In general, the fluorescence intensity of capped samples is higher than the uncapped samples (Tables 1 and 2). The low fluorescence intensity for uncapped sample is believed to be due to the unlimited amount of oxygen in the quartz cell, and therefore, quenched the fluorescence intensity of the compounds[8]. Oxygen, which has an unusually large diffusion coefficient, and on prolong exposure of the solution to the atmosphere could result in large quantity of oxygen diffusing into solution[9]. Similar results were obtained with other heterocycles studied.

CONCLUSION

2-*N*-Anilinopyridine showed the highest fluorescence peak in tetrahydrofuran, while 2-*N*-piperidinopyridine showed the highest fluorescence peak in ethanol and tetrahydrofuran. The fluorescence intensity of capped sample is higher than uncapped sample.

ACKNOWLEDGEMENTS

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