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TWO FACILE SYNTHETIC METHODS FOR A SCHIFF BASE FROM 4-ETHOXYANILINE AND 2-PYRIDINECARBOXALDEHYDE

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ABSTRACT

The Schiff base was acquired from the reaction between 4-ethoxyaniline and 2-pyridinecarboxaldehyde using three (3) synthetic methods: 2 hours reflux in ethanol, stirring in ethanol and in an ethanol-water (1:1 v/v) mixture at ambient temperature for an hour. The synthesis of 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base afforded dark-brown crystals with a melting point of 118-120^{o}C. The reflux reaction in ethanol gave the highest yield of 83.5% while the reaction in ethanol and in ethanol-water (1:1 v/v) mixture at ambient temperature gave 73.0% and 43.6% yield respectively. The confirmation for the formation of a new aliphatic C=N functional group was given by the IR spectrum that showed a band at 1625cm^{-1} for an aliphatic C=N group; the ^{13}C NMR spectrum that showed the presence of the imino carbon (C=N) at chemical shift 158.48ppm while the ^{1}H NMR spectral data δ(ppm) for the compound gave a one proton singlet (HC=N-) at 8.69. The spectral data were in correlation with the predicted structure of the Schiff base.

Keywords: Schiff bases, 4-ethoxyaniline-2-pyridinecarboxaldehyde, 2-pyridinecarboxaldehyde, 4-ethoxyaniline, Green synthesis, Eco-friendly solvents, ethanol-water.

INTRODUCTION

The imino functional group (HC=N-) is present in a class of compounds called imines. Schiff bases are imines that possess an organic group attached to the imino nitrogen atom. (Ibrahim *et al*., 2006). A variety of routes have been used for the synthesis of Schiff bases like reflux reactions (Uddin *et al*., 2014), stirring at ambient temperature (Umofia *et al*., 2018; Shipra *et al*., 2019), microwave irradiation (Venugopala *et al*., 2008; Bhagat *et al*., 2013; Shntaif and Rashid, 2016), ultrasonication (Li *et al*, 2001; Venkatesan *et al.*, 2011; Ahmed *et al.*, 2014), and direct fusion method (Bendale *et al.*, 2011; Abood, 2014; Mahmood and Khudhair, 2017). The conventional method for the synthesis of this compound is the reflux method and this is done in acid or alkaline medium (Qin *et al*., 2013).

Furthermore, a diverse number of solvents have been employed for the synthesis of these compounds. Most of the solvents used for their synthesis are classified as toxic solvents and these include toluene (Wang *et al*., 2008), dichloromethane (Mishra *et al*., 2012), methanol (Naeimi and Heidarnezhad, 2015), benzene (Yang and Sun, 2006), N,N-dimethyl formamide (Tomma *et al*., 2014). Some non-toxic solvents like water (Meenakshisundaram and Manickam, 2019), ethanol (Naeimi and Heidarnezhad, 2015) and, an ethanol-water mixture (Umofia *et al*., 2018; Ogbonda-Chukwu *et al*., 2021). Schiff bases have many applications like in the manufacture of

pharmaceuticals (Zhu *et al*., 2003; Saini *et al*., 2011), polymers (Rasool *et al*., 2014), dyes (Abuamer *et al*., 2014), agrochemicals (Zhu *et al*., 2003), corrosion inhibitors (Jamil *et al*., 2018), to mention but a few.

This paper focuses on the use of three diverse eco-friendly routes (solvents and techniques) for the synthesis of a new Schiff base made from 2-pyridinecarboxaldehyde and 4-ethoxyaniline to ascertain the best method for the synthesis with focus on yield obtained.

MATERIALS AND METHODS

Materials

The chemicals used for this research were synthesis grade chemicals purchased from Sigma-Aldrich. Melting point were determined with a melting point apparatus and was uncorrected. Thin Layer Chromatography (TLC) was carried out using Merck pre-coated silica gel plates (10 x 10 cm), the R_f value obtained using ethyl acetate as the mobile phase and the spot located and visualized using an ultraviolet lamp at 256 nm. The IR spectrum of the sample was recorded on Fourier Transform Infrared spectrometer, Carry 630 Agilent Technologies in the range of 650-4000 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectrum of the sample was recorded on a JEOL Eclipse 400 NMR spectrophotometer by JEOL (Pleasanton, USA) using DMSO-d_6.

Methods

Synthesis in ethanol at reflux temperature:

The reactants were dissolved separately in 20 ml ethanol in 50 ml beaker and then poured into a flat bottom flask (150 ml). The reaction mixture was stirred under reflux at 80 ^0C for 1 hr followed by the addition of few drops of concentrated hydrochloric acid. The reaction mixture was then stirred for one more hour.

Synthesis in ethanol at room temperature:

The reactants were dissolved separately in 20 ml ethanol in a 50 ml beaker and then poured into a flat bottom flask (150 ml). The reaction mixture was stirred at room temperature for 30 min. A few drops of concentrated hydrochloric acid (HCl) was added to the mixture with further stirring for another 30 min.

Synthesis in ethanol-water (1:1 v/v) at room temperature:

The reactants were dissolved separately in 20 ml ethanol in a 50 ml beaker and then poured into a flat bottom flask (150 ml). The reaction mixture was stirred at room temperature for 30 min followed by the addition of a few drops of concentrated hydrochloric acid (HCl). The mixture was further stirred for another 30 min.

Synthesis of 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base:

4-ethoxyaniline (0.01 mol, 1.37 g, 1.29 ml) and 2-pyridinecarboxaldehyde (0.01 mol, 1.07 g, 0.95 ml) were reacted using the methods above. The reaction was monitored to completion using thin layer chromatography (TLC) (ethyl acetate). The resulting dark-brown reaction mixture was extracted using water and dichloromethane. The dark-brown oil that formed was then triturated using diethyl ether to give dark-brown crystals. The solid product was recrystallized using ethanol and hexane, filtered and air-dried.

The reaction equation for the synthesis of the Schiff base obtained from 4-ethoxyaniline and 2-pyridinecarboxaldehyde is illustrated in fig. 1 below.

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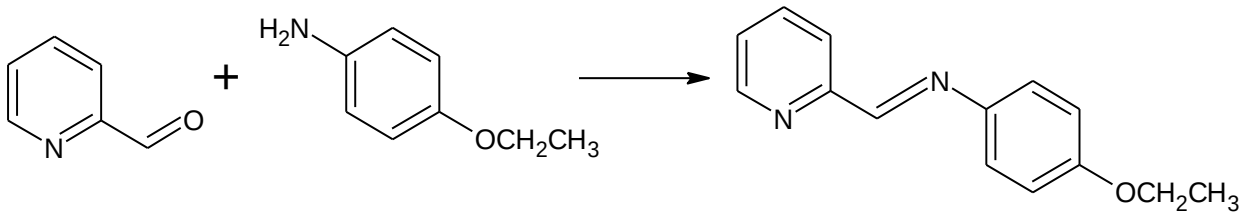

2-pyridinecarboxaldehyde 4-Ethoxyaniline 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base

Figure 1: Reaction equation for the synthesis of 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base

RESULTS AND DISCUSSION

The synthesis of the new 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base was achieved using three (3) different methods; the conventional method (stirring in ethanol under reflux for 2 hours) and stirring in ethanol and in an ethanol-water (1:1 v/v) mixture at room temperature for an hour (new routes). The work-up technique was tedious for the 3 methods but it was done to ensure the purity of the compound. The conventional method gave the highest yield of the product (83.5%) while one of the new methods which involved stirring in ethanol at ambient temperature produced a relatively high yield of 73.0%. The physicochemical and spectral studies proved that the three methods gave the same Schiff base.

Rf: 0.73, m.p: 118 - 120^{o}C, yield: 83.5%, 73.0%, 43.6% (for method 1, 2 and 3 respectively).

IR (KBr, cm^{-1}): 1625 (C=N), 1584 (aromatic C=C stretch), 2981 (aromatic C-H stretch), 1505 (aromatic C=N stretch), 1114 (aliphatic C-C stretch), 1021 (aromatic C-O stretch), 2825 (aliphatic C-H stretch).

^{1}H δ(ppm) 6.98-8.62, m (8H) (Ar-H), 8.69, s (1H) (HC=N-), 4.05, q (2H) and 1.34, t (3H) (OCH_2CH_3). ^{13}C NMR (δppm); 158.68 (C=N, imino), 154.98 and 150.18 (C-N of aromatic pyridine moiety), 121.44 – 137.53 (aromatic carbons), 158.48 (aromatic C-O), 63.88 (aliphatic C-O), 15.22 (aliphatic C).

The results obtained from the spectral analyses established that the structure of the compound was as anticipated. The results are also in tandem with the findings of Bhagat *et al*. (2013); Shipra *et al*.(2019); Sachdeva et al. (2014) and Ahmed *et al*. (2014) The presence of the imino group (C=N) peak at 1625cm^{-1} and the absence of the amino and carbonyl group peaks at 3400-3250cm^{-1} and 1740-1720cm^{-1} respectively, suggested the formation of the new 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base.

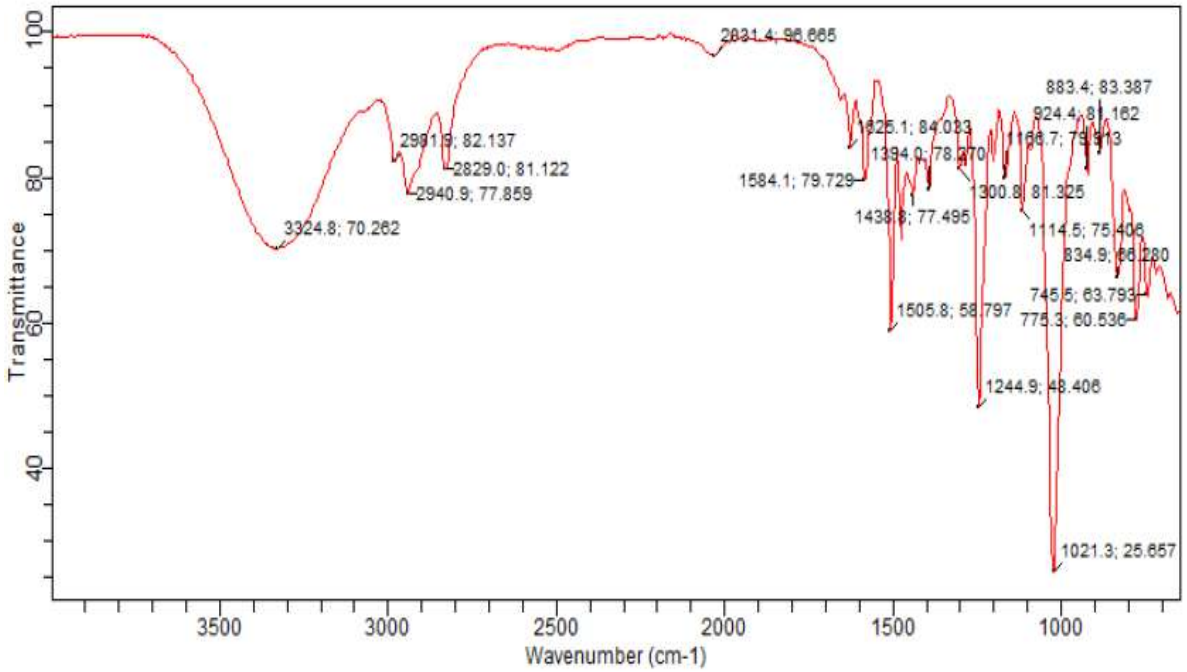

Figure 2: IR Spectrum of 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base

Additionally, the ^{1}H NMR result revealed the presence of the imino proton at 8.69 ppm and the ^{13}C NMR presented the imino (C=N) peak at 158.68 ppm as a result of the deshielding effect of the imino nitrogen atom.

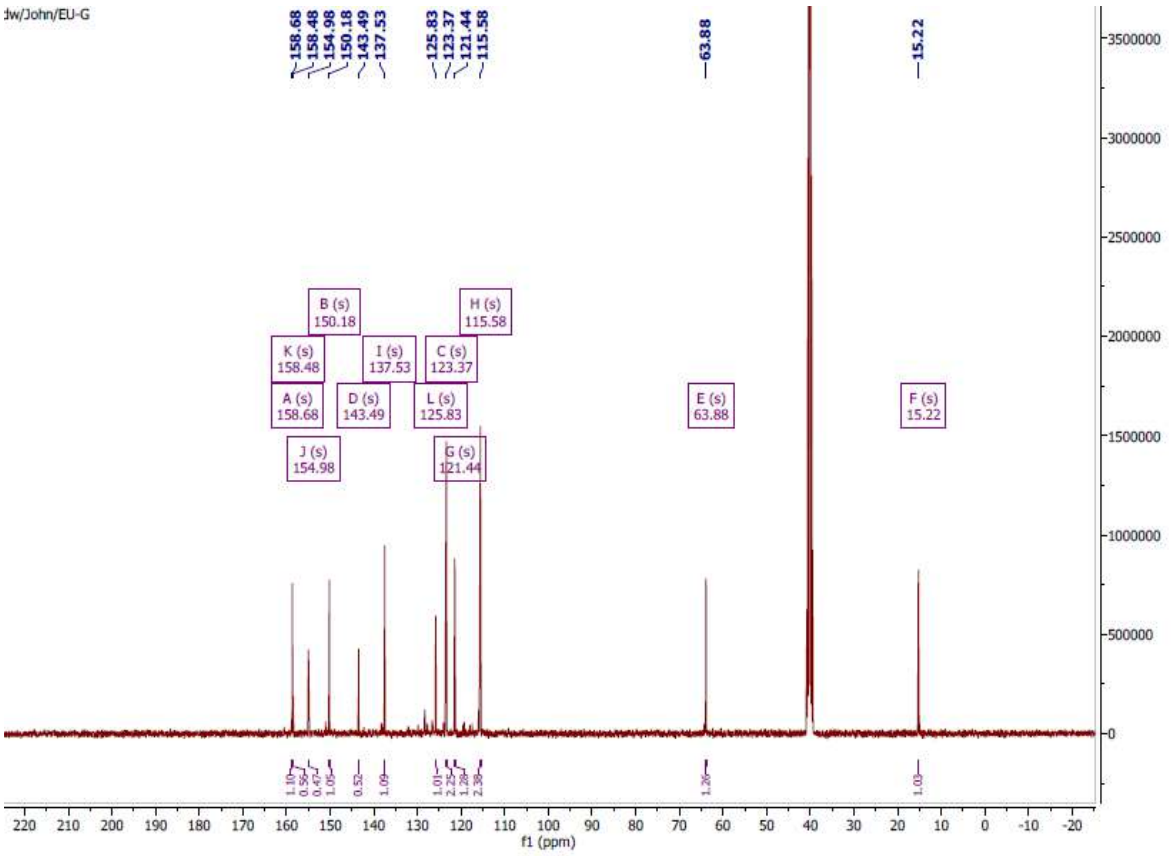

Figure 3: ^{13}C NMR Spectrum of 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base

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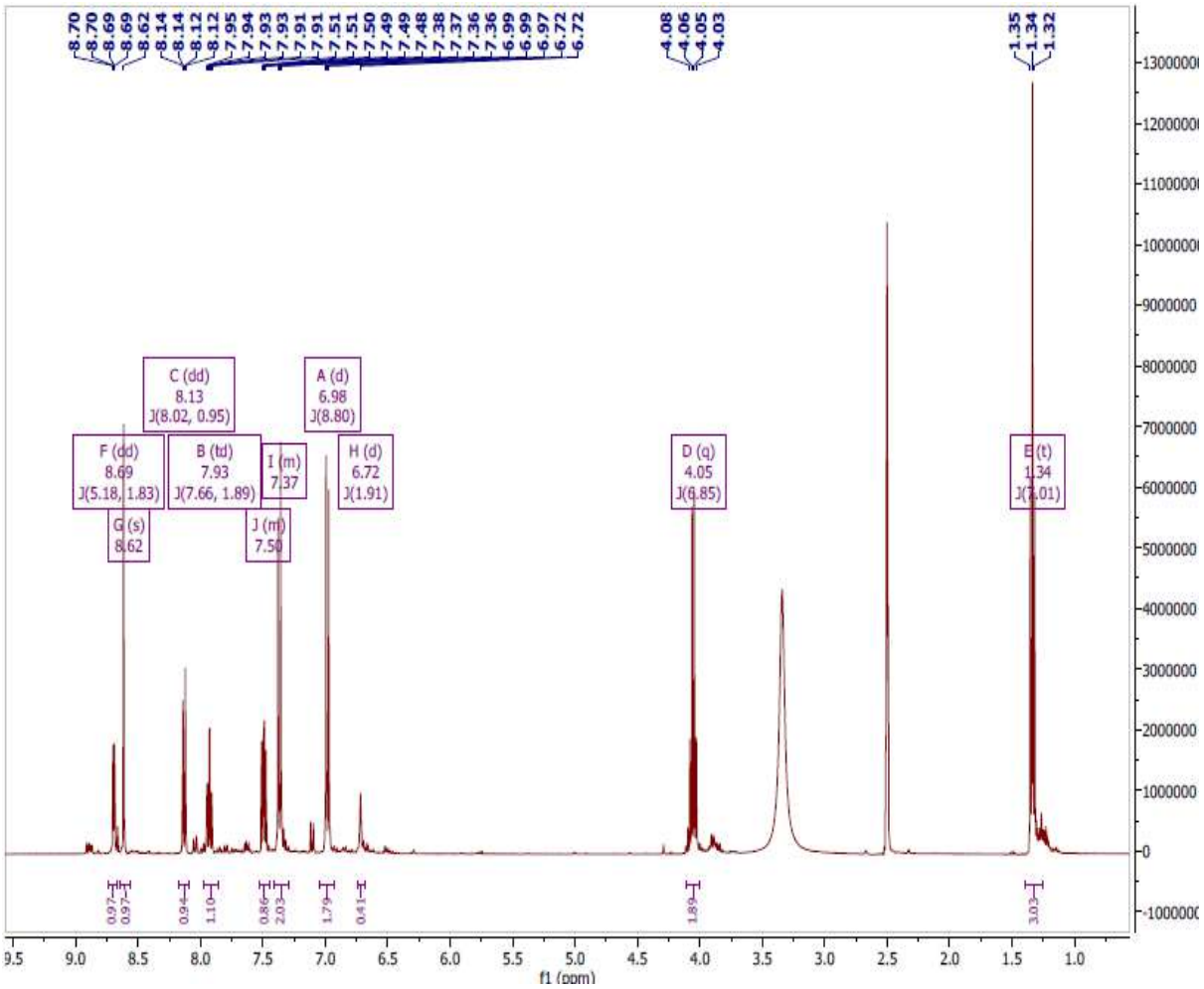

Figure 4: ^{1}H NMR Spectrum of 4-ethoxyaniline-2-pyridinecarboxaldehyde Schiff base

CONCLUSION

The results from this study verify that the Schiff base 4-ethoxyaniline-2-pyridinecarboxaldehyde can be synthesized using only eco-friendly solvents. Furthermore, this research has shown that this compound can be produced at a very high yield using the reflux method with ethanol as a solvent.

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