

Fluro-Chemical Response of Organic Drug 2-(Methylamino)Pyridine in Different Media

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ABSTRACT

This paper reports on the excited state intermolecular proton transfer (ESIPT) of 2-(Methylamino) Pyridine (2MAP) in different solvent media. The Absorption and Fluorescence data along with the change in pH of the solvent shows a huge possibility of ESIPT

Keywords : ESIPT, Methylamino, Pyridine

I. INTRODUCTION

Excited state intermolecular and intramolecular proton transfer (ESIPT) is an interesting phenomenon that has been studied for a long time [1–11]. It is a well known that in an excited state, a molecule can undergo structural changes and can assume a different geometry due to significant charge redistribution [12], thereby greatly changing the excited state's properties. Weller [1] established that when the acid and base moiety of the same molecule becomes stronger in the excited state, an excited state proton transfer can ensue. The formation of tautomers or zwitterions during ESIPT is manifested by a large, Stokes-shifted, fluorescence band [2]. Kasha [13] first showed that intramolecular proton transfer in an excited state is facilitated by preexisting, intramolecular hydrogen bonding in the ground state. ESIPT can be used in a variety of applications, such as in energy data storage devices and optical switching [14–17], Raman filters and hard scintillation counters [18], polymer photostabilizers [19,20] and triplet quenchers [21]. Many groups [22–24] are studying different fluorescing molecules in order to systematize and control their

emissive property due to their interesting and useful applications.

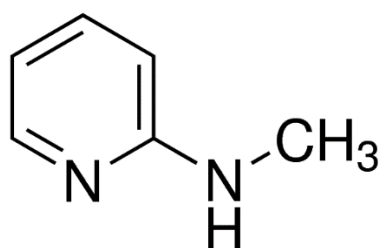
2-(Methylamino) Pyridine (2MAP) [Scheme-I] is potentially a good reagent for Intermolecular Proton Transfer. The two amino tautomers with nearly isoenergetic conformation around the C–N(HCH₃) bond for 2MAP change into N-2(1H)-pyridinylidenemethanamine as the methyl-imino tautomers by intramolecular hydrogen-atom (or proton) transfer. By introducing an electron withdrawing group, both a structural change and a change in either the basicity or acidity of the groups could occur in the excited state in order to facilitate ESIPT in 2-(Methylamino)Pyridine (2MAP). Our work also helped to establish the mechanistic details of ESIPT in 2MAP by using steady-state absorption and emission spectroscopy.

II. EXPERIMENTAL

2MAP was purchased from the Aldrich chemical company and was recrystallized before use. Ethyl Hydroxide (EtOH), acetonitrile (ACN), Hexane

(Hx) triethylamine (TEA) and H₂SO₄ were obtained from Merck Specialties Pvt. Ltd. (India) and were used after checking their emission in the region of interest. Water was used after triple distillation.

A Shimadzu UV-vis absorption spectrophotometer (model UV- 2401PC) was used to take the absorption spectra. The emission spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. For the emission measurements, the sample concentration was maintained at 10⁻⁵ M in each case in order to avoid aggregation.



Scheme-I

III. RESULT AND DISCUSSION

The absorption spectra of 2MAP were investigated in various protic, aprotic, hydrocarbon, polar and nonpolar solvents. In all solvents, 2MAP exhibited two bands around 235 nm (high intensity) and 305 nm (small intensity).

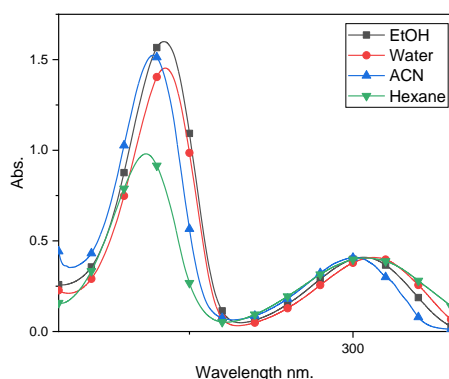


Figure-1

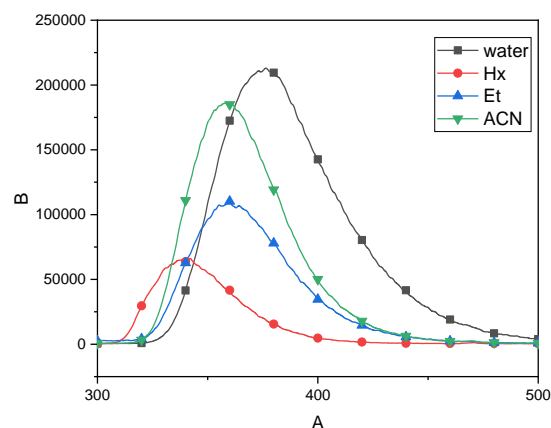


Figure-2

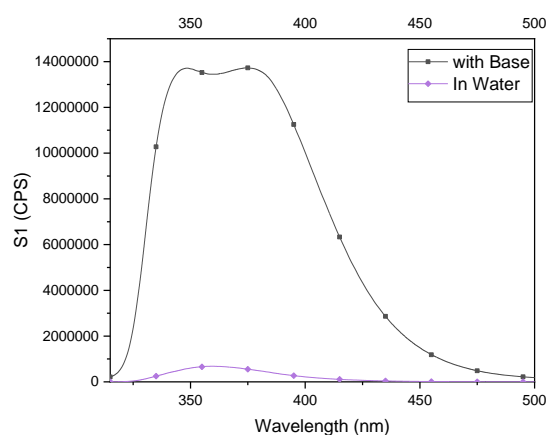


Figure-3

The absorption spectra of 2MAP was taken with the solvent Hexane (Hx), Ethyl Hydroxide (EtOH), Acetonitrile (ACN) and Water (Wat) (Figure-1). It clearly shows a sharp peak at around 235 nm with a shoulder at around 305nm. The spectra get slightly red shifted in presence of polar solvents which indicates the possibility of ESIPT of 2MAP.

The emission spectra of 2MAP was taken with the solvent Hexane (Hx), Ethyl Hydroxide (EtOH), Acetonitrile (ACN) and Water (Wat) (Figure-2). The emission spectra got red shifted as we proceed from a non-polar solvent to a more polar ones. This is probably due to the presence of hydrogen atom attached with the nitrogen atom with a weak hydrogen bonding. And this proton may be removed

to the solvent with the increase of solvent polarity, enhancing the possibility of ESIPT.

There is no such change in either absorption or emission intensity and/or band position if we decrease the pH under 7. But increase in pH above 7 results a huge increase in intensity of emission spectra of aqueous 2MAP (Figure-3). This may be due to the presence of more negative ions in basic solution which favours the ESIPT.

IV. CONCLUSION

We can conclude that our molecule 2MAP is a potential member for showing Excited State Intermolecular Proton Transfer phenomena in solutions which is a polar one and this phenomena pushes us to study more about this molecule.

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