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Electronic spectral studies of 2-hydroxy-5-methyl-3-nitro pyridine in various solvents

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ABSTRACT

Electronic spectra of 2-hydroxy-5-methyl-3-nitro Pyridine have been recorded in the region 185-350 nm. The effect of change of polar solvents i.e. ethanol, methanol and water on electronic transition is also explained.

Key words: Electronic spectral studies, 2-hydroxy-5-methyl-3-nitro-pyridine.

INTRODUCTION

Pyridine and their derivatives are of considerable biological importance, they have been known to act as herbicides, insecticides and plant growth regulators etc.[1-3]. The spectroscopic studies of these compounds have been motivated for its use to understand the specific biological process and in the analysis of relatively complex systems[4-5]. A systematic and complete vibrational analysis of electronic spectra of pyridine and some of its deturated analogues have been made by some previous workers[4-7]. On substitution, the π-π^* and n- π^* system of pyridine normally produce bathochromic and hysochromic shifts respectively, the vibration frequencies also get modified.

In the present work, we have measured the π-π^* and n-π^* transition of 2-hydroxy-5-methyl-3-nitro Pyridine in the region 185-350nm in liquid state using different polar solvents i.e. ethanol, methanol and water.

EXPERIMENTAL

The sample of 2-hydroxy-5-methyl-3-nitro Pyridine (abbreviated as 2,5,3-HMNP) was obtained from M/s Aldrich Chemical Co., U.S.A. Its purity was confirmed by elemental analysis and melting point determination. The ultraviolet spectra of the said molecule were recorded in different polar solvents on Beckman Spectrophotometer (model M-35). The solvents used for preparing the solutions of the said molecule were of spectroscopic grade.

RESULTS & DISCUSSIONS

The molecular structure of 2, 5, 3-HMNP is shown in Fig. -1 and its near ultraviolet spectra, in various solvents (a) ethanol, (b) methanol and (c) water are presented in Fig. -2. The electronic transitions and corresponding bands of the said molecule in electronic absorption spectra are shown in Table-1.

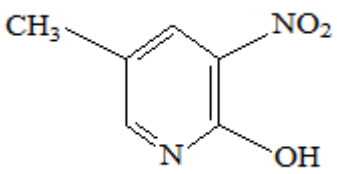

Fig-1: Molecular Structure of 2, 5, 3-HMNP

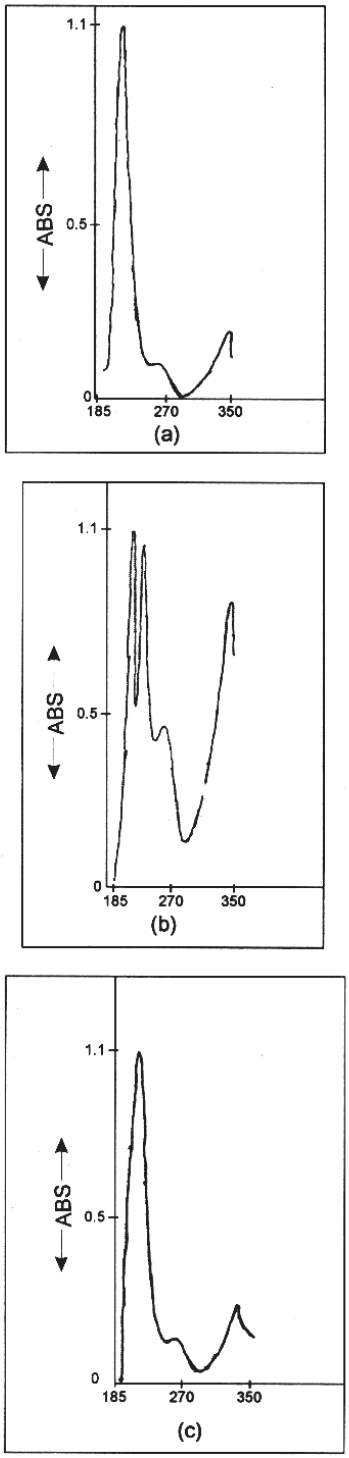

Fig. - 2: Ultraviolet absorption spectra of 2,5,3-HMNP in (a) Ethanol (b) Methanol (c) Water

Electronic spectra

In case of N-Heterocyclic compounds the bands observed at 256, 258 and 260mm in ethanol, methanol and water are corresponds to $A_1 \rightarrow B_1$ transition which is derived from $A_{1g} \rightarrow B_{1u}$ transition. According to Yadav et. al.[7] the bands observed at 210 and 200nm corresponds to $A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow A_{1u}$ transitions respectively. According to Yadav *et al.*[5] in pyridines n-π^* transitions correspond to out-of-plane transition while π-π^* and n-σ^* transitions to in-plane transitions. In view of this, the n-π^* transition at 346nm in ethanol and 348nm in both methanol and water have been taken to represent to out-of-plane bending while the π-π^* transition bands at 256nm in ethanol, 258, 226nm in methanol and 260nm in water have been taken to represent in-plane transitions in 2, 5, 3-HMNP. Dyer[8], suggested that in compound which contains non bonding electrons and group such as, -OH, -OR, etc. there occurs a band below 210nm which correspond to n-σ^* transition. In view of this, the bands observed at 209nm in ethanol and 210nm in water and methanol have been taken to represent n-σ^* transitions.

Effects of solvents and substitutions

According to W.west[9], the effect of changing the solvent system up on the position of the bands in an absorption spectrum may often be used to classify the bands as π-π^*, n-π^* or n-σ^*. Usually, the solvents used in such a study are non polar one such as hexane and polar or more commonly a hydroxylic such as alcohol or water. If a band shifts to shorter wavelength upon a change of solvent it is called a blue shift band if it shift to higher wavelength then it is called a red shift band. For a non polar solute under going a π-π^* transition, the shift of a band upon a change from a non polar to polar depends upon the difference in the polarization red shifts in the two solvents[10]. Since the shifts is larger in polar solvents than in non polar solvents a red shift will be observed.

A red shift has been observed in π-π^* and n-σ^* transitions in the said compound with increase the polarity of the solvents (ethanol $\rightarrow$ methanol $\rightarrow$ water) as shown in Table -1 and Fig. -2 respectively. The blue shift is due to the stabilization of the ground state by the hydrogen bonding in ethanol, methanol and water and increase in transition energy.

Table - 1: Solvent effect on electronic transition of 2, 5, 3-HMNP (All values are in nm)

Solvent	DC[+]	RI[++]	n-π*	π-π_I*	π-π_{II}*	n-σ*
Ethanol	25.0	1.3773	346	256	-	209
Methanol	32.0	1.3362	348	258	226	210
Water	80.5	1.3380	348	260	-	210

[+] Dielectric Constant
[++]Refractive Index

This energy is required to weaken or break the hydrogen bond[11]. During the present investigation, the n-π* transition is red shifted in the compound 2,5,3-HMNP with increasing solvent polarity which is contrary to the behaviour usually observed for π-π* transitions.

An auxochrome (*i.e.* a saturated group with non bonding electrons *e.g.* -OR, -OH, etc.) attached to a chromphore (a covalent unsaturated group responsible for electronic absorptions *e.g.* aromatic ring, -C = C-, -C ≡ C, etc.) alters both the wavelength and intensity of the absorption. Auxochromic substitution on the aromatic ring shifts π-π* transition towards longer wavelength[10-12].

The auxochromic group present on aromatic ring is responsible for n-π* transition due to presence of non bonding electrons (*i.e.* lone pair of electrons) available on the auxochromic group[10]. In 2,5,3-HMNP molecule –OH group is responsible for n-π* conjugation. In this investigation an unusual feature has been found, *i.e.* a red shift has been observed with respect to the n-π* transitions of non bonding electrons of the O-atom of the hydroxyl group. Further more, greater the dielectric constant of the solute greater will be the degree of solvation[7-11]. Also as the solvent polarity increases the attraction between solute and solvent molecule will also increases and hence the system will be more stable. This explains the red shift observed in π-π* and n-σ* in the said molecule on going from ethanol → methanol → water solvent.

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