

Electronic spectral studies of 2-chloro-6-methoxypyridine in various solvents

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Abstract . The present work reports the electronic transition bands of 2-chloro-6-methoxy pyridine molecule in liquid state and the effect of α -halogen atom on the absorption intensity of the *B*-band (characteristic band of aromatic ring). The $\pi-\pi^*$ transition (*E*₁-band) has shown the usual behaviour towards the substitution and the polarity of the solvents. But the $n-\pi^*$ transition (*R*-band) has evidenced a usual behaviour towards the solvent polarity and unusual behaviour towards the substitution (*i.e.* the $n-\pi^*$ transition has shown red shift with respect to the $n-\pi^*$ system of pyridine). The halogen atom and/or ortho para directing group (having high potential for a large inductive effect) have shown a marked influence on the sp^2 electrons of the *N*-atom of the ring. As a result, the *B*-band has evidenced an unusual behaviour *i.e.* it has not shown a hyperchromic effect with increase in the polarity of the solvent.

Keywords . Ultraviolet absorption spectra, electronic absorption bands, effect of substitution and solvent polarity.

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1. Introduction

Pyridine and their derivatives are of considerable biological importance, they have been known to act as herbicides, insecticides, rodenticides and plant growth regulators [1,2] *etc.* Even then very little spectroscopic studies are reported for them in literature. Pyridine shows in addition to the usual $\pi-\pi^*$ system, a shoulder band towards the longer wavelength. This system which is symmetry allowed and polarized perpendicular to the molecular plane, has been assigned as due to $n-\pi^*$ transition by Kasha [3]. Further, a systematic and complete vibrational analysis of electronic spectra of pyridine and some of its deuterated analogues has been made by some previous workers [4-6]. On substitution, the $\pi-\pi^*$ and $n-\pi^*$ systems of pyridine normally produce bathochromic and hysochromic shifts, respectively; the vibrational frequencies also get modified. As regards the earlier studies, the spectral data of some of the mono and di-substituted pyridine are provided among others [7-11]. Srivastava and Prasad [12] have reported an unusual

red shift of the $n-\pi^*$ system for 2-chloro-3-pyridinol, 5-chloro-2-pyridinol and 6-chloro-2-pyridinol. In the present work, we have measured the $\pi-\pi^*$ and $n-\pi^*$ transitions of 2-chloro-6-methoxy pyridine (abbreviated as 2,6-CMP) in the region of 400-200 nm in liquid state using polar solvents with a view to investigate the effect of solvent and the effect of halogen and/or ortho para directing groups on the position and intensity of the electronic absorption bands.

2. Experimental procedure

The Spec. -Pure compound 2-chloro-6-methoxy pyridine was obtained from M/s Sigma Aldrich Chemicals, U.S.A. and used as such. The purity of the compound was further confirmed by boiling point (185°C) determination and elemental analysis. We have measured the $\pi-\pi^*$ and $n-\pi^*$ transitions of 2,6-CMP in a UV-VIS double beam spectrophotometer; Model Lambda-20 (Mfg. By Perkin Elmer) in the region of 400-200 nm in liquid state, using various polar solvents. The solvent used for preparing the solutions of the said compound were of spectroscopic grade.

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3. Results and discussion

The molecular structure of 2,6-CMP is shown in Figure 1 and its near ultraviolet absorption spectra (region 400-200 nm) in various solvents ((a) ethanol, (b) methanol, (c) water) are presented in Figure 2 and the electronic transitions and corresponding bands of the said molecule in electronic absorption spectra are shown in Table-2 in various solvents.

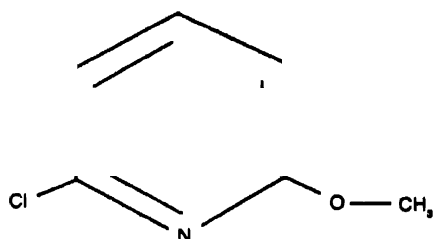


Figure 1. Molecular structure of 2-chloro-6-methoxypyridine.

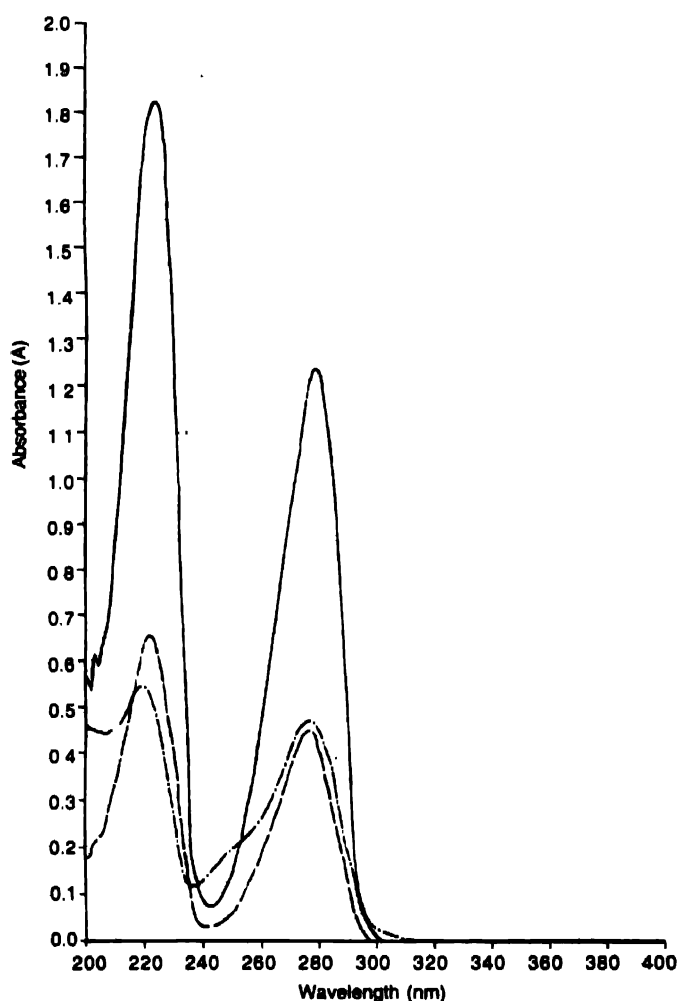


Figure 2. Near ultraviolet absorption spectra (region 400-200 cm^{-1}) in various solvents. (a) ethanol —, (b) methanol - - - and (c) water - · - ·

3.1 Bands due to $\pi - \pi^*$ transition :

The spectra of heteroaromatic compounds are on the whole similar to their corresponding hydrocarbons [13,14]. The

spectrum of pyridine is comparable with that of benzene. Benzene itself displays three electronic absorption bands [13,14] at 184 nm (ϵ , the molar absorptivity or the extinction coefficient = 60,000), at 203.5 nm ($\epsilon = 7900$) and at 256 nm ($\epsilon = 200$) due to $\pi - \pi^*$ transitions. The intense band at 180 nm results from an allowed transition [14], whereas the weaker bands at 200 and 260 nm result from forbidden transitions in the highly symmetrical benzene molecule. Different notations have been used to designate the absorption bands of benzene; these are summarized in Table 1. We shall discuss these using braude's E and B notations [14]. B -band is generally found in between 230-270 nm.

Table 1. Electronic absorption bands of benzene molecule [14].

184 nm	204 nm	256 nm	References
E_1 -band	E_2 -band	B -band	[15]
	K -band	B -band	[16]

Between benzene and pyridine, the B -band of pyridine is more intense with somewhat diminished fine structure whereas in benzene, the B -band at 256 nm displays fine structure *i.e.* the band contains multiple peaks. This transition is allowed for pyridine but forbidden for more symmetrical benzene [13,14]. The band observed at 276 nm in the study in all the three solvents are originated from $\pi - \pi^*$ transition and designated as B -band, the intense band observed at 201 nm in ethanol, and the weak shoulder band at 202 nm and at 210 nm in methanol and water, respectively are also originated from $\pi - \pi^*$ transition and designated as E_2 bands (K -bands).

3.2 Band due to $n - \pi^*$ transitions :

The weak R -band expected for an $n - \pi^*$ transition for pyridine molecule has been observed in vapour phase spectra. This band is generally swamped by the more intense B -band when the spectrum is determined in solution [14] because of intermolecular hydrogen bonding found between the N-atom of pyridine ring and the solvent molecule.

The R -bands found in this study, have originated from $n - \pi^*$ transitions due to the attachment of groups containing lone pair electrons *i.e.* $-\text{Cl}$ or $-\text{OCH}_3$ groups and occurred at 221 nm, 221 nm and 219 nm in ethanol, methanol and water, respectively.

4. Effect of substitution on electronic transitions

An auxochrome (*i.e.* a saturated group with non-bonded electrons *e.g.* $-\text{OR}$, $-\text{OH}$, $-\text{NH}_2$ and $-\text{Cl}$ etc) attached to chromophore (a covalently unsaturated group responsible for electronic absorption, *e.g.* aromatic ring, $-\text{C}=\text{C}-$, $-\text{C}\equiv\text{C}-$ etc) alters both the wavelength and the intensity of the absorption [13]. Auxochromic substitution on the aromatic ring shift

B -band to longer wavelength, frequently with intensification of the B -band and loss of its fine structure because of $n-\pi^*$ conjugation [14]. Generally, the B -band occurred in between 230-270 nm) and displays a fine structure *i.e.* the band contain multiple peaks. In the present investigation, B -bands observed at 276 nm in all the three solvents *i.e.* ethanol, methanol and water, have large intensity without a fine structure. Auxochrom on the aromatic ring forms the E_2 -band in the near Ultraviolet region [14], although in many cases, it dose not appear at wavelengths > 210 nm. In auxochromic substitution, the heteroatom with the lone pair of electrons, shares these electrons with the π -electron system of the ring facilitating the $\pi-\pi^*$ transition and thus causing a red shift of the E_2 -band. A bathochromically displaced E_2 -band is considered responsible for the intense fine structured bands of polynuclear aromatics. In auxochromic substitution, the E -bands are formed and the B -band shifts to longer wavelength with frequently increase in intensity. In this present study, a sharp intense band observed at 201 nm in ethanol, and weak shoulder band, at 202 nm and 210 nm in methanol and water, respectively are designated as E_2 -bands. The occurrence of E_2 -bands below or at 210 nm is due to the shift of $n-\pi^*$ transition towards the longer wavelength.

The auxochromic groups present on aromatic ring are responsible for $n-\pi^*$ transition due to the presence of non-bonding electrons (*i.e.* lone pair electrons) available on the auxochromic group. In 2,6-CMP molecule (*i.e.* di-substituted molecule), the additive effect of two auxochromic groups is responsible for $n-\pi$ conjugation. The -Cl group has three lone pair of electrons to that of -OCH₃ group in which O-atom has only two lone pair of electrons. Furthermore, the -Cl group is highly electro-negative and have much more negative inductive effect in comparison to that of -OCH₃ group; also the size of -Cl group is much lower than that of -OCH₃ group. As a result of which valence shell electrons of -Cl group contribute large

nuclear charge in comparison to that of -OCH₃ group. Hence the lone pair electrons present on O-atom of the -OCH₃ group in this work, are largely responsible for the $n-\pi$ conjugation. In conjugated systems, the energy separation between the groups at the excited states is reduced and the system absorbs at longer wavelengths with an increased intensity [13] (*i.e.* B -band is intense and at longer wavelength). Moreover, due to lowering of the energy gap, the $n-\pi^*$ transition (due to the presence of the heteroatom) *i.e.* the R -band also undergoes a red-shift [12] with a little change in intensity [13]. The shift in absorption results from a combination of inductive and resonance effects (Figure 3). In this investigation, an unusual feature has been found: a red shift has been observed with respect to the $n-\pi^*$ system of pyridine due to $n-\pi^*$ transition of non-bonding electrons of the O-atom of the methoxy group. This is further confirmed by the Infrared and Raman spectra of this (2,6-CMP) molecule showing the presence of C-O bond (somewhat stiffened by resonance). The R -band (due to the additive effect of two auxochromic substitutions) shifts to longer wavelengths at 222, 221 and 219 nm in ethanol, methanol and water, respectively.

5. Effect of solvents on electronic transitions

An increase in the solvent polarity does not affect either the position or the intensity of the B -band of benzene, but produces a hyperchromic effect (an increase in absorption intensity) for pyridine and its homologs [13, 14]. This effect is assigned to the hydrogen bonding through the lone pair of electrons of the nitrogen atom [13, 14]. In 2,6-CMP molecule, hyperchromic effect is not observed with an increase in solvent polarity because of the presence of α -halogen atom (-Cl) which has high negative inductive effect (-I) and influence the sp^2 electrons of the N-atom of the ring. As a result, it makes the lone pair electrons of N-atom of the ring less available for H-bonding. The negative

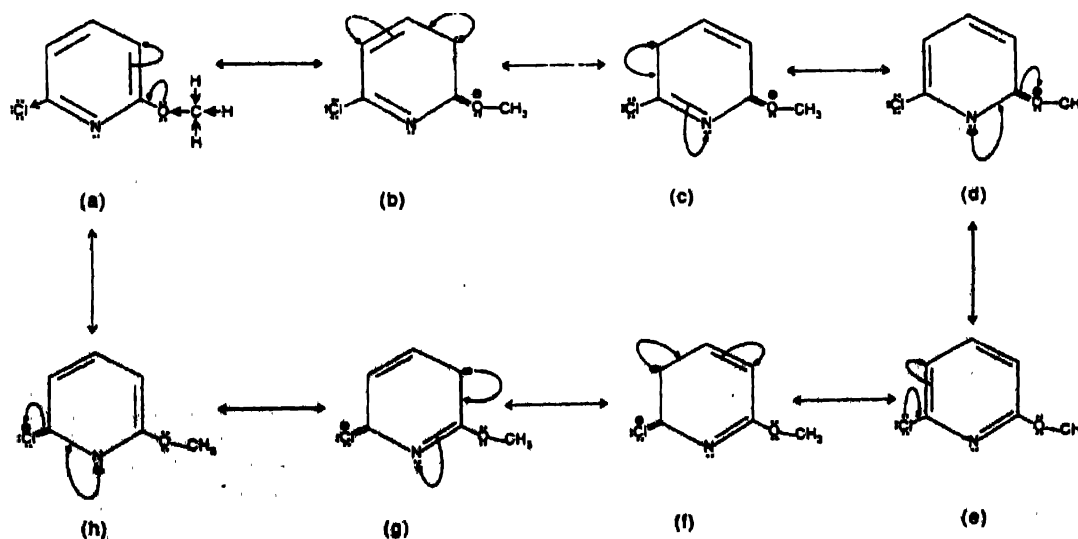


Figure 3. The combined inductive and mesomeric (resonance) effects of chloro and methoxy groups, responsible for shift in $n-\pi^*$ and $\pi-\pi^*$ transitions.

inductive effect of chloro group becomes much greater as the solvent polarity increases by the dipole-dipole interaction between the solute and solvent particles. As the solvent polarity decreases, the negative inductive effect of $-Cl$ group also decreases, as a result, the lone pair electrons of N-atom of the ring are readily available for intermolecular H-bonding to result in the increase in absorption intensity of the B-band in less polar solvent than in more polar solvent.

The R-band shows a blue-shift on increasing the polarity of the solvent [13]. When the non-bonding electrons of oxygen atom of the methoxy group (as discuss above that the lone pair electrons of O-atom of the methoxy are largely responsible for $n-\pi^*$ transition) coordinate with a hydroxylic solvent [17,18], the net energy of lone pair electrons is lowered. Thus, the distance to π^* (antibonding π orbital)-level will be higher and as a result in polar solvent, the $n-\pi^*$ transition (R-band) will be of higher energy *i.e.* of lower wavelength (blue shift), which is shown in Figure 4. In this work, the blue-shift has been observed by $n-\pi^*$ transition (R-band) as the polarity of the solvent increased *i.e.* ethanol \rightarrow methanol \rightarrow water [19] (Table 2). The amount of blue-shift has been used as a measure of the strength of the H-bonding.

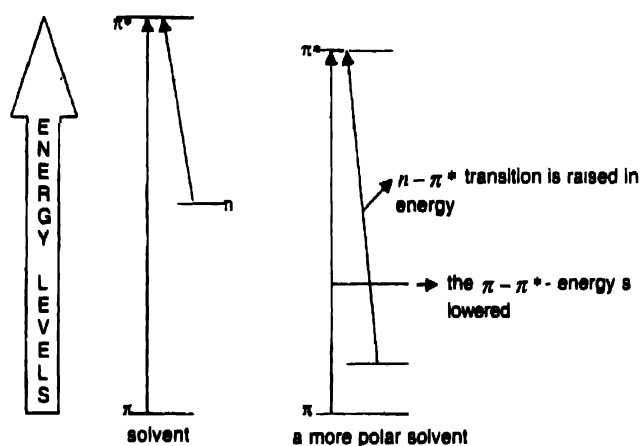


Figure 4. Solvent effects on $n-\pi^*$ and $\pi-\pi^*$ transitions.

The K-band (so called E_2 -band) *i.e.* the $\pi-\pi^*$ transition, on the other hand, has shifted to the longer wavelength *i.e.* red-shifted (lower energy) in a more polar solvent [13]. The polar excited state of the $\pi-\pi^*$ transition is stabilized by H-bonding in more polar solvent. This lowers the distance between π and π^* levels with a subsequent lowering in the energy or raising the wavelength of the transition shown in Figure 4. We have observed the red shift by the $\pi-\pi^*$ transition (E_2 -band) as the polarity of the solvent has increased from ethanol to water [19] (Table-2).

Table 2. Effect of solvent on electronic absorption bands / transitions of 2-chloro-6-methoxypyridine. (All values are in nanometer).

Solvents	$\pi-\pi^*$ transition (B-band)/nm	$n-\pi^*$ transition (R-band)/nm	$\pi-\pi^*$ transition (K-band or E-band)/nm
Water	276	219	210
Methanol	276	221	202
Ethanol	276	222	201

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