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by

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Solvent Effect On The Absorption Spectra of Acetylpyridines And Their N-Oxides

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SUMMARY

The electronic absorption spectra of acetylpyridines and acetylpyridine N-oxides were investigated in some organic solvents of varying polarities. The spectra indicate the presence of two absorption bands (A) and (B), the first is assigned to the local $\pi \rightarrow \pi^*$ transition and the second is assigned to $\pi \rightarrow \pi^*$ transition influenced by charge transfer (C.T.) interaction. The $n \rightarrow \pi$ was observed as a shoulder in non-polar solvents and disappeared completely in polar solvents. The C.T. nature of the band (B) is asscertained and its position is discussed in relation to molecular structure and solvent effect.

INTRODUCTION

Although few studies have previosuly appeared on the ultraviolet absorption spectra of substituted pyridines and pyridine N-oxides, the solvent effect on such spectra has received little attention. The UV spectra of pyridine N-oxides were investigated by Hriayama and Kubota[1,2] and Katritzky[3]. The absorption spectra of π -conjugated compounds containing a heteroatom, e.g. pyridine and diazines, exhibit $n \rightarrow \pi^*$ transitions as well as $\pi \rightarrow \pi^*$ transitions[4,5]. The absorption bands due to these two electronic transitions were observed with pyridine N-oxide in non-polar solvents and in vapour[6]. The present work was undertaken to establish the nature of the absorption bands of acetylpyridines and their N-oxides in the ultraviolet region and to investigate the medium effect on the band position and molar absorptivity.

EXPERIMENTAL

Materials

The 2-, 3- and 4- acetylpyridines (I, II and III) were obtained from Merck. Schuchardt. (Germany). The 2- acetylpyridine N-oxide (IV) was prepared from 2- acetylpyridine by the method of Winterfield and Zickle[7]. The 3- and 4- acetylpyridine N-oxides (V and VI) were prepared from the corresponding acetylpyridines according to the method of Kanno[8]. All the solvents were obtained from E. Merck; they were either spectroscopically pure or purified by recommended methods[9].

Spectral Measurements

The UV absorption spectra (200-400 nm) of 5×10^{-5} molar solutions of 2-, 3- and 4- acetylpyridines and their N-oxides were obtained using a PYE UNICAM SP 1750 recording spectrophotometer. The measurements were scanned in aqueous acidic and alkaline media and in organic solvents of different polarities.

RESULTS AND DISCUSSION

1. Band Assignments

The electronic absorption spectra of acetylpyridines and their N-oxides are scanned in n-hexane, cyclohexane, carbon tetrachloride, 1, 4- dioxane, chloroform, isopropanol, ethanol, methanol, water, and dimethyl formamide. The values of wavelength maxima (λ_{max}) of the bands in these spectra along with the corresponding molar absorptivities (ε_{max}) are listed in tables (1) and (2). The spectra display mainly two absorption bands (A) and (B) figs. (1) and (2). Because of the low solubility of some N-oxides in non-polar solvents as n-hexane and cyclohexane the spectra of such compounds could not be recorded quantitatively. In these cases saturated solutions were used.

The first band (A) observed in the 220-250 nm range may be assigned to $\pi \rightarrow \pi^*$ local transition within the pyridine ring; this may be accounted on the high ε values ammounting to about 10^4. The second band B at 255-326 nm range may be taken as $\pi \rightarrow \pi^*$ transition influenced

Table 1. Absorption bands of acetylpyridines in different solvents

Solvent	2-Acetylpyirdine				3-Acetylpyridine				4-Acetylpyridine			
	Band A		Band B		Band A		Band B		Band A		Band B	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
n-Hexane	225	8.58	268	4.08	228	10.12	267	2.62	222	9.50	280	3.26
Cyclohexane	228	8.50	269	4.04	229	10.84	267	3.38	222	10.92	280	3.74
CCl_4	——	——	269	6.16	——	——	268	4.04	——	——	280	3.54
1,4-Dioxane	——	——	268	4.50	——	——	265	3.80	——	——	278	3.76
Chloroform	242	3.80	270	4.20	242	4.90	269	4.16	——	——	280	3.64
Iso-propanol	230	8.20	269	4.42	230	9.80	267	3.84	221	10.32	280	3.50
Ethanol	230	9.10	269	5.02	229	a0.34	267	3.84	221	11.26	280	3.82
Methanol	230	8.00	269	4.44	228	10.44	267	4.04	215	11.28	280	3.30
DMF	——	——	270	4.48	——	——	269	3.16	——	——	280	3.60
Water	232	9.04	271	6.32	6231	11.18	268	4.68	221	8.40	282	3.48
NaOH	——	——	271	7.10	——	——	268	5.08	——	——	281	2.52
HCl	224	4.42	270	9.60	222	8.08	264	6.74	220	7.96	276	4.98

$\varepsilon_{max} = \varepsilon \times 10^{-3}$; λ_{max} = nm; ——— not observed

Table 2: Absorption bands of acetylpyridine N-oxides in different solvents

Solvent	2-Acetylpyridine N-oxide				3-Acetylpyridine N-oxide				4-Acetylpyridine N-oxide			
	Band A		Band B		Band A		Band B		Band A		Band B	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
n-Hexane	236	29.00	286	13.00	234	S	280	S	234	22.16	320	39.43
Cyclohexane	237	32.00	285	17.00	240	13.23	290	6.47	235	S	320	S
CCl_4	244	21.00	282	23.00	250	S	291	S	——	——	326	17.78
1,4-Dioxane	——	——	283	21.80	236	23.50	287	13.19	235	3.69	322	20.52
Chloroform	243	20.80	281	22.80	242	10.34	283	15.05	242	5.59	315	24.44
Iso-propanol	234	23.84	274	15.54	231	26.85	273	14.55	229	14.05	305	24.14
Ethanol	233	35.40	273	24.00	231	21.03	272	11.52	228	12.34	303	20.69
Methanol	232	25.32	271	18.30	230	31.64	270	16.22	227	15.10	300	26.00
DMF	——	——	282	24.80	——	——	285	12.83	——	——	320	16.90
Water	230	26.16	262	17.80	228	55.20	262	24.16	221	9.08	290	16.30
NaOH	——	——	255	35.00	——	——	258	44.04	——	——	290	12.10
HCl	228	31.48	264	20.16	226	33.90	261	12.06	221	8.40	280	12.86

$\varepsilon_{max} = \epsilon \times 10^{-3}$; λ_{max} = nm; —— not observed; S = saturated solution

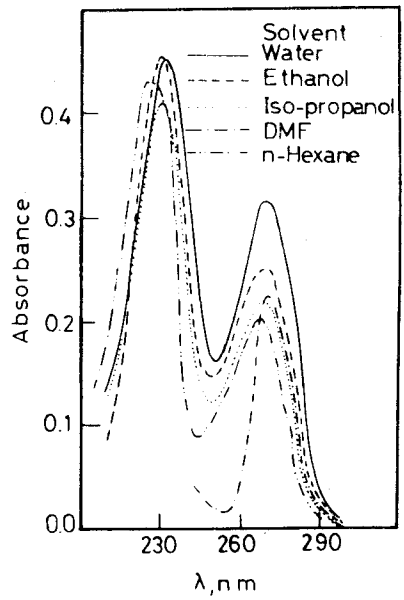


Fig. 1: Electronic absorption spectra of 2- acetylpyridine in different solvents.

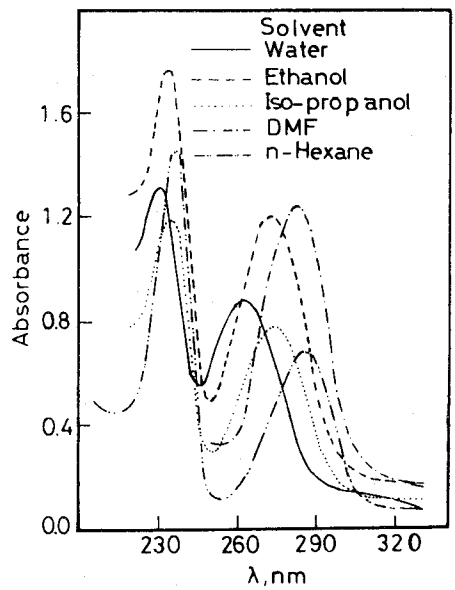
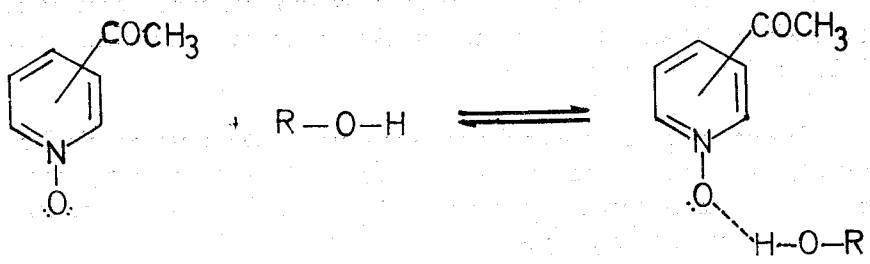


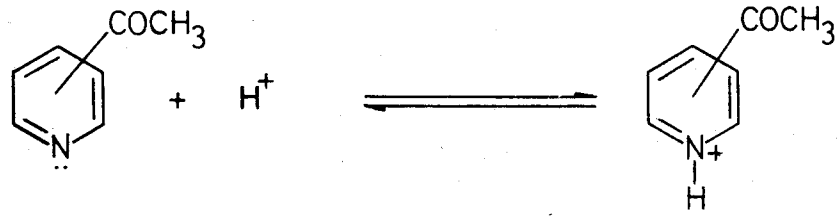
Fig. 2: Electronic absorption spectra of 2- acetylpyridine N-oxide in different solvents.

by intramolecular charge transfer interaction. This is substantiated by the fact that pyridine has only one band at 257 nm and the pyridine N-oxide has only one band at 265 nm in ethanol[6] and by determination of charge transfer energy. Generally, the λ_{max} of the band B has the order: 4- Acetyl > 3-Acetyl $\simeq$ 2-Acetyl, indicating the higher conjugation in the 4-acetyl derivatives than for 3- and 2- acetyl derivatives[3].

The weak band due to $n \rightarrow \pi^*$ transition appeared in case of the N-oxides as a very weak shoulder in the region 340-370 nm especially in non-polar solvents which is in agreement with the previous studies [4,5,6]. On going from non-polar to polar solvents, the two bands were blue shifted and the shoulder disappeares completely. In other words, these compounds show a solvent effect in the opposite direction of most reported transitions[10]. However, such spectral behaviour in pyridine N-oxides may be explained as follows. Pyridine N-oxide molecule has two pairs of 2p non-bonding electrons on the oxygen atom, one of which is considered to be in conjugation with the π-electron system of the pyridine ring, and the other remains as a nonbonding pair. When proton-donor solvents are used, the oxygen non-bonding orbital is largely stabilized in energy as a result of the formation of hydrogen bond[2] with



solvent molecules. As a result, the $n \rightarrow \pi^*$ absorption disappears completely in polar solvents. On the other hand, since the π- electron system will be purturbed (due to the formation of such hydrogen bond), the $\pi \rightarrow \pi^*$ absorption will shift to shorter wavelength[6]. This is in agreement with our observation, and furthermore, the more polar the solvent the greater was the blue shift. On the other hand, the spectra of acetylpyridines aremore or less, little affected by solvents. Appreciable shifts to shorter wavelength were observed only in 1N HCl solution in which the protonated pyridinium ion species are formed according to:



2. Effect of solvent

The absorption spectra in various solvents are influenced by solvation and/or dielectric effects of the solvents. To verify whether the band shift is due to change in solvation energy or pure dielectric effects, the relation given by Gati and Szalay[11] was applied in the form:

$$\triangle\bar{\nu} = \{(a-b)\left(\frac{n^2-1}{2n^2+1}\right)\} + b\ \frac{D-1}{D+1}$$

in which (n) and (D) are the refractive index and dielectric constant of the medium, (a) and (b) are constants having the values 4858 cm^{-1} and 1217 cm^{-1} respectively.

One of the properties of the solvent which shows a reasonable degree of correlation with the transition energy is the static dielectric constant (D) or more precisely a function f(D)[12] or Φ (D)[12] which lead to a linear relationship, where:

$$f(D) = \frac{2(D-1)}{2D+1} \text{ and } \Phi\ (D) = \frac{D-1}{D+2}$$

The plots of (D–1) /(D+1), f (D) and Φ (D) against the wave number ($\bar{\nu}_{max}$ in cm^{-1}) are shown in Fig. (3) for the N-oxide derivatives. These plots are linear in the solvents of moderate polarity. This may be explained on the basis that the dielectric constant is the main factor affecting the band shift in such solvents. However, in the highly polar solvents (e.g.

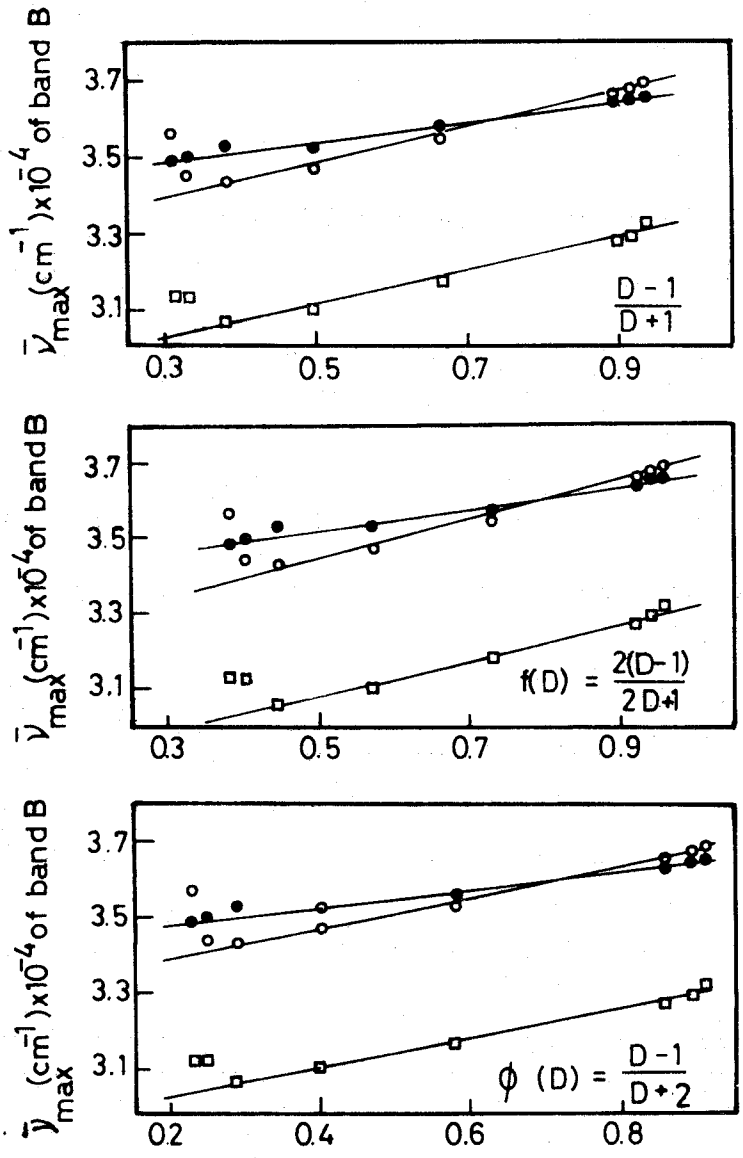


Fig. 3: Effect of solvent-polarity on the absorption of (a) 2-acetylpyridine N-oxide, (b) 3-acetylpyridine N-oxide, and (c) 4-acetylpyridine N-oxide.

●—●— (a)
○—○— (b)
□—□— (c)

water and dimethyl-formamide), there is a deviation from linearity. This may be attributed to formation of strong hydrogen bonding between the solute and the solvent molecules leading to high solvolysis which may overcome the dielectric effect of such solvents.

3. The absorption band having C.T. nature

In the case of acetylpyridines, since the acetyl group is an electron withdrawing group, an intramolecular charge transfer (C.T.) may be expected from the ring to the C = O group. In the acetylpyridine N-oxides under investigation, the N-O group can participate as a donor beside the pyridine ring, then an intramolecular charge transfer may also be expected in this case from the N-O group to the carbonyl group. To verify this opinion (i.e. whether the band B is a charge transfer band or not) the observed charge transfer energy (E_{CT} in eV) obtained from λ_{max} is compared with that calculated. The equation used for the calculation of the energy due to intramolecular charge transfer is given by[13]:

$$E_{CT} = I_P - (E_A + C)$$

where:

E_{CT} = energy of the charge transfer.

I_P = ionisation potential of the donor system.(9.2 eV for pyridine)[14]

E_A = electron affinity of the acceptor system (-1.4 eV for C = O group)[15].

C = energy of the coulombic force between the negative charge and the positive hole left behind (5.7 eV).

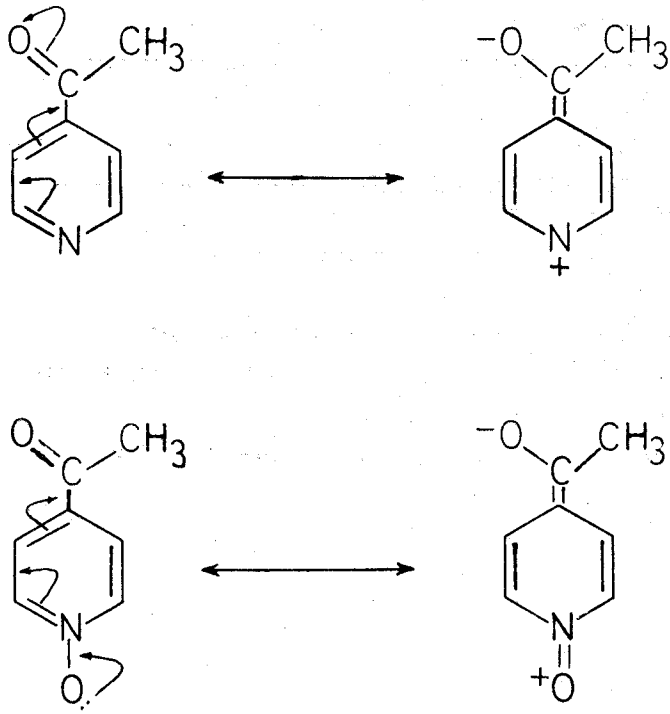
The values of E_{CT} for the compounds calculated using the above equation is 4.9 eV. On substracting the value corresponding to the shift to lower energy due to conjugation with a double bond ($E_{CT(b)} - Ec\pi_{(j)}$) amounting to 0.39 eV, the resulting value (4.51 eV) is in agreement with those calculated from λ_{max} using the relation $E = hc/\lambda$, especially in polar solvents table (3).

Table 3. Values of charge transfer energy (E_{CT} in eV) for acetylpyridines and their N-oxides.*

Solvent	Pyridines			Pyridine N-oxides		
	2	3	4	2	3	4
n-Hexane	4.64	4.64	4.44	4.34	4.44	3.88
Cyclohexane	4.64	4.65	4.44	4.36	4.28	3.88
CCl_4	4.62	4.64	4.44	4.41	4.27	3.81
1,4–Dioxane	4.64	4.69	4.47	4.39	4.33	3.86
Chloroform	4.60	5.62	4.44	4.42	4.39	3.94
Iso-propanol	4.62	4.65	4.44	4.63	4.55	4.07
Ethanol	4.62	4.65	4.44	4.55	4.57	4.10
Methanol	4.62	4.65	4.44	4.58	4.60	4.14
DMF	4.60	4.62	4.44	4.41	4.36	3.88
Water	4.58	4.64	4.41	4.74	4.74	4.28
NaOH	4.58	4.64	4.42	4.87	4.82	4.28
HCl	4.60	4.71	4.50	4.71	4.76	4.30

*The calculated E_{CT} = 4.51 eV.

The charge transfer interaction may be represented as:



The results of charge transfer energy indicate that the values generally follow the sequence:

$$4\text{- Acetyl} < 3\text{- Acetyl} \leq 2\text{-Acetyl}$$

This may be explained by the higher conjugation in the 4-substituents facilitating the charge transfer interaction which is in agreement with the fact that the charge transfer energy "E_{CT}" is inversely proportional to the distance between the donor and acceptor sites[16].

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