Ultraviolet Absorption Spectra of Three Isomeric Pyridinemethanols and Their N-Oxides

By Norisuke HATA

(Received June 27, 1957)

In recent years, the ultraviolet absorption spectra of pyridine derivatives were investigated by various workers[1-3], and several studies were also made for pyridine *N*-oxides[4-6]. However, the ultraviolet absorption spectra of hydroxymethyl, aldehyde, and carboxyl derivatives of pyridine were not studied in detail, although these compounds are important in the fields of organic and biological chemistry.

In the present investigation, the author measured the ultraviolet absorption spectra of three isomeric pyridinemethanols and their *N*-oxides in various solvents, and discussed the solvent effects on their spectra and also the effects of introduction of a hydroxymethyl group on the absorption spectra of pyridine and pyridine *N*-oxide.

Experimental

The synthesis of 2-, 3- and 4-pyridinemethanols were carried out by methods given in the literature and these compounds were purified several times by recrystallization or vacuum distillation.

2-Pyridinemethanol[7]: b. p. 100°∼3°C/5 mmHg.
3-Pyridinemethanol[8]: b. p. 144°∼5°C/20 mmHg.
4-Pyridinemethanol[7]: m. p. 176°∼7°C (from butanol).

The syntheses of 2-, 3- and 4-pyridinemethanol *N*-oxides were done by treating the corresponding pyridinemethanol with aqueous hydrogen peroxide in glacial acetic acid and they were purified by recrystallization from ethyl acetate several times[9].

2-Pyridinemethanol *N*-oxide: m. p. 141°C. 3-Pyridinemethanol *N*-oxide: m. p. 93°∼4°C. 4-Pyridinemethanol *N*-oxide: m. p. 125°C.

Solvents used in the spectral measurements were purified[10] *n*-hexane, carbon tetrachloride, ethanol and water.

The ultraviolet absorption spectra were measured with a SHIMADZU Quartz Spectrophotometer Type QB-50, using a fused quartz cell of 1 cm. thickness.

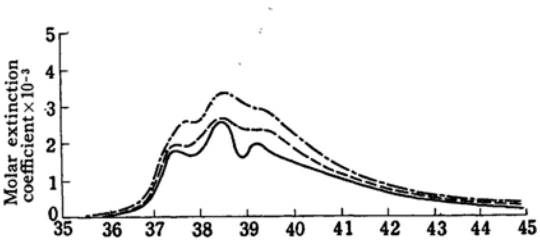


Fig. 1. Absorption curves of 2-pyridinemethanol.
—— *n*-Hexane.
— — — Ethanol.
-·-·- Water.

---

1) H. Sponer and H. Stückeln, *J. Chem. Phys.*, **14**, 101 (1946); J. H. Rush and H. Sponer, ibid., **20**, 1847 (1952); W. K. Miller et al., *J. Am. Chem. Soc.*, **72**, 1629 (1950).

2) R. J. L. Andon et al., *Trans. Faraday Soc.*, **50**, 918 (1954); N. Ikekawa et al., *Pharm. Bull.*, **2**. 209 (1954).

3) H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

4) H. Hirayama and T. Kubota, *Annual Reports of Shionogi Research Laboratory*, **2**, 47 (1952); T. Kubota, *J. Pharm. Soc. Japan* (*Yakugaku Zassi*), **73**, 140 (1953); **74**, 831 (1954); H. H. Jaffe, *J. Am. Chem. Soc.*, **77**, 4451 (1955).

5) N. Ikekawa and Y. Sato, *Pharm. Bull.*, **2** ,400 (1954).

6) M. Ito and N. Hata, This Bulletin, **28**, 260 (1955); N. Hata, ibid., **29**, 82 (1956).

7) V. Boekelheide and W. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).

8) R. G. Jones and E. C. Kornfeld, ibid., **73**, 107 (1951).

9) The synthesis was performed by Mr. S. Furukawa of our laboratory, to whom the author's thanks are due. For the details, see S. Furukawa, *J. Pharm. Soc. Japan* (*Yakugaku Zassi*), in press.

10) A. Weissberger and E. S. Proskauer, "Organic Solvents", 2nd, Ed. (1955).

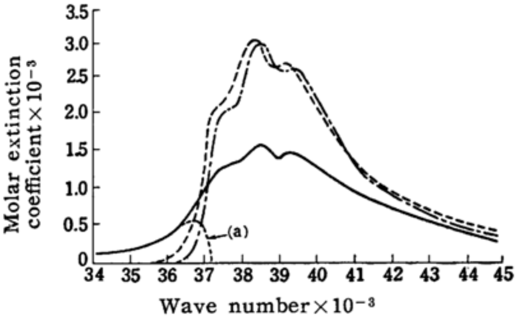


Fig. 2. Absorption curves of 3-pyridinemethanol.
——— n-Hexane.
– – – Ethanol.
–·–·– Water.
(a)··· n-π^* Absorption curve separated by peak analysis. (c. f., refs. 3 and 6).

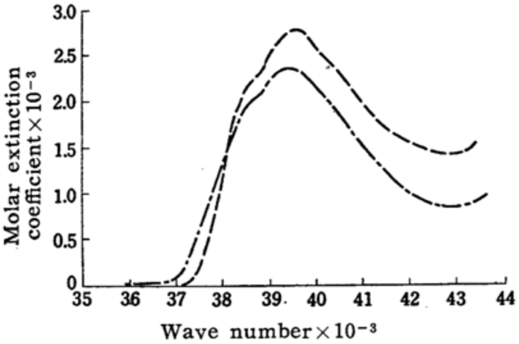


Fig. 3. Absorption curves of 4-pyridinemethanol.
– – – Ethanol.
–·–·– Water.

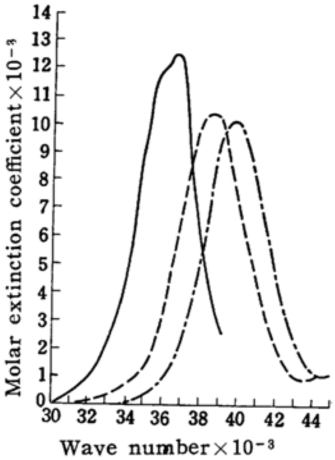


Fig. 4. Absorption curves of 2-pyridinemethanol N-oxide.
——— Carbon tetrachloride.
– – – Ethanol.
–·–·– Water.

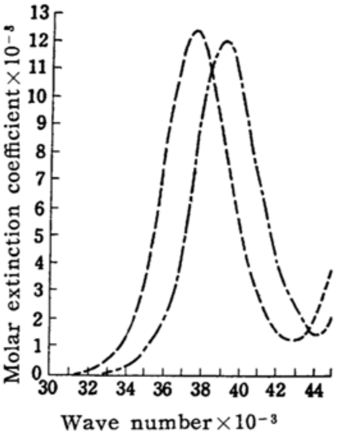


Fig. 5. Absorption curves of 3-pyridinemethanol N-oxide.
– – – Ethanol.
–·–·– Water.

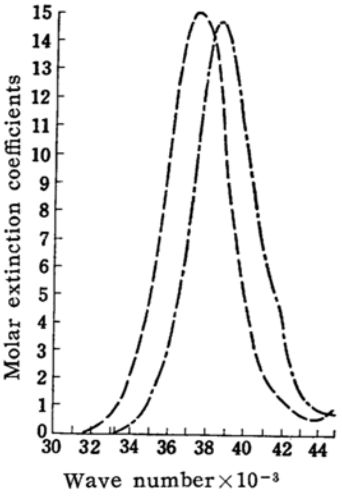


Fig. 6. Absorption curves of 4-pyridinemethanol N-oxide.
– – – Ethanol.
–·–·– Water.

Results and Discussion

Figs. 1 to 6 show the absorption curves of three isomeric pyridinemethanols and their N-oxides in various solvents. The observed values of maximum wavelength, wave number, molar extinction coefficient, and oscillator sterength[11] are listed in Table I.

(1) Effect of Solvent *a*) *Pyridinemethanols.* — These compounds show the absorption bands ($\varepsilon = 2000 \sim 5000$) with some vibrational structure in the region between 35000 cm.$^{-1}$ and 44000 cm.$^{-1}$ like correspond-

---

[11] The calculations of the oscillator strengths were made according to the method described in Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

ing three isomeric picolines. On account of the wavelength of the absorption region, the absorption intensity, and the solvent effect, this absorption is regarded to be due to a $\pi-\pi^*$ transition corresponding to an A_1-B_1 type in pyridine.

In 2-pyridinemethanol, the absorption maximum at about 38450 cm.$^{-1}$ does not essentially shift in solvents such as *n*-hexane, ethanol and water, but the intensity increases in the above order of solvents. $n-\pi^*$ Absorption due to the excitation of a non-bonding electron localized on the nitrogen atom as observed in 2-picoline was not observed in this compound.

The absorption spectrum of 3-pyridinemethanol shows a solvent effect similar to that of 2-pyridinemethanol, but when *n*-hexane is used as solvent, a shoulder absorption is observed near 36400 cm.$^{-1}$. This is regarded to be due to an $n-\pi^*$ transition like that observed in 3-picoline. This assignment is supported by the facts that when ethanol or water, acting as a proton donor to the nitrogen atom of a pyridine nucleus, is used as solvent, this absorption completely disappears and the ratio of oscillator strength between this absorption and the $\pi-\pi^*$ absorption near 39100 cm.$^{-1}$ is in the order of 10^{-2}. In ethanolic or aqueous solution, however, the intensity of the $\pi-\pi^*$ absorption increases remarkably. This fact may be considered to be due to the overlap with the $n-\pi^*$ absorption displaced to shorter wavelength as a result of the hydrogen bond formation between the nitrogen atom of ethanol or water, since the non-bonding electron of nitrogen is largely stabilized in energy as a result of such a hydrogen bond formation.

The solvent effect for 4-pyridinemethanol absorption differs somewhat from other pyridine derivatives and is similar to that of pyridine. That is, $\pi-\pi^*$ absorption of 4-pyridinemethanol shifts to red and the intensity dereases by changing the solvent from ethanol to water.

In the spectra of 2-, 3- and 4-pyridinemethanols mentioned above, the $n-\pi^*$ absorption is observed only for 3-pyridine methanol in *n*-hexane. The explanation for this fact is qualitatively given as follows. If a hydrogen atom of the methyl group were replaced by a hydroxyl group, the inductive effect of methyl group would decrease to some extent. Therefore, the binding energy of a non-bonding electron localized on the nitrogen atom in 2-pyridinemethanol would increase compared with that of 2-picoline. Such an increase in binding energy causes the $n-\pi^*$ absorption shift to the spectral region of the $\pi-\pi^*$ transition or further. On the other hand, the inductive effect of of hydroxymethyl group for the nitrogen atom of 3-pyridinemethanol is negligible. Consequently, the $n-\pi^*$ absorption is observed in *n*-hexane solution as a shoulder absorption like pyridine. However, the $n-\pi^*$ absorption is not observed in ethanolic or aqueous solution, because the $n-\pi^*$ absorption which is displaced to shorter wavelength by the hydrogen bonding between the solute and the solvent falls in the spectral region of $\pi-\pi^*$ transition.

In 4-pyridinemethanol, it is presumed that the $n-\pi^*$ absorption occurs in the region at about 34500cm.$^{-1}$, because this compound is insoluble in non-polar solvents.

b) *Pyridinemethanol N-oxides.*—The solvent effects for the strong absorption bands of pyridinemethanol *N*-oxides appearing at 31000 cm.$^{-1}$ to 43000 cm.$^{-1}$ are noticeably different from those of pyridinemethanols mentioned above. As is seen from Figs. 4~6, the absorption of these compounds shows a greater blue shift when the solvent is changed from carbon tetrachloride to ethanol and water, just as does the absorption of pyridine *N*-oxide[4,6]. This phenomenon is considered to be due to the formation of a hydrogen bond between N—O group and R—OH of the solvent acting as a proton donor, a phenomenon similar to that found in pyridine *N*-oxide.

(2) Effect of Hydroxymethyl Group.—Since several pyridinemethanols and their *N*-oxides are insoluble in non-polar solvents, the effect of hydroxymethyl substitution on pyridine or pyridine *N*-oxide absorption is discussed in relation to the spectra in ethanolic solution.

As seen from Table I and Fig. 7, the absorption at about 38900 cm.$^{-1}$ of pyridine shifts to the shorter wavelength in 4-pyridinemethanol and to the longer wavelength in 2- or 3-pyridinemethanol. This tendency is similar to those in picoline[2] or monohalogeno-pyridines[3]. Such a shift of absorption maxima caused by substituting a group for hydrogen of pyridine nucleus is in agreement with the results of the molecular orbital calculations by Tsubomura[12] who discussed the electron migration effect from the substituent to the conjugated system of pyridine ring. The

---

[12] H. Tsubomura, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 293 (1957).

Table I

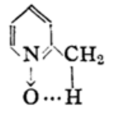
WAVE LENGTH, WAVE NUMBER, MOLAR EXTINCTION COEFFICIENT, AND OSCILLATOR STRENGTH OF THREE ISOMERIC PYRIDINEMETHANOLS AND THEIR *N*-OXIDES

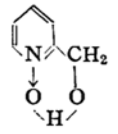
Compound	Solvent	Wave length (mμ)	Wave number (cm.$^{-1}$)	Molar extinction coefficient	Oscillator strength
2-Pyridinemethanol	n-Hexane	267	37430	1850	0.032
		260	38450	2600	
		255.5	39100	1950	
	Ethanol	266.5	37500	1850	0.046
		260	38450	2700	
	Water	265	37700	2600	0.056
		259.5	38500	3400	
3-Pyridinemethanol	n-Hexane	260	38400	1650	0.0043
		255.5	39100	1500	
		275s†	36350	400	0.00036
	Ethanol	261	38350	3000	0.0056
		256	39100	2700	
	Water	259.5	38500	2980	
		254	39300	2700	0.0050
4-Pyridinemethanol	Ethanol	253	39570	2760	0.040
	Water	253.5	39450	2340	0.035
2-Pyridinemethanol *N*-oxide	CCl_4	276	36240	12600	0.210
	Ethanol	259	38580	10500	0.204
	Water	252	39600	10300	0.201
3-Pyridinemethanol *N*-oxide	Ethanol	264	37800	12400	0.239
	Water	254	39300	12000	0.234
4-Pyridinemethanol *N*-oxide	Ethanol	266	37600	15000	0.285
	Water	257	38800	14800	0.279

† denotes the shoulder absorption ($n-\pi^*$)

smaller shift of absorption maximum to the shorter wavelength in 2-, 3- and 4-pyridinemethanols compared with the corresponding picolines may be considered to be due to the decrease in hyperconjugative power of the methyl group. The decrease in shift is caused by the replacement of a hydrogen atom in the methyl introdution group with a hydroxyl group.

In pyridinemethanol *N*-oxides, the absorption at 38000 cm.$^{-1}$ shifts to the longer wavelength by the substitution of hydroxymethyl group at 3- or 4-position and to the shorter wavelength by substitution at 2-position. A similar tendency of shift is found in picoline *N*-oxides5). Previously, Ikekawa and Sato5) have reported that the absorption maximum of pyridine *N*-oxide shifted to blue by the introduction of 2-methyl group. For the cause of this shift they attributed the formation of a weak intramolecular hydrogen bond between the oxygen atom of N—O group and the hydrogen atom of 2-methyl group as shown in (A), which hindered the resonance of pyridine *N*-oxide. In the present work the blue shift caused by the introduction of 2-hydroxymethyl group was also observed. If the formation of a weak intramolecular hydrogen bond is assumed to 2-pyridinemethanol *N*-oxide as one of the main factors for such a blue shift phenomenon, the electron migration from the oxygen atom of N—O group to the pyridine ring may be prevented by the increase in its electronegativity caused by the formation of the intramolecular hydrogen bond as shown in (B). Therefore, the maximum wavelength of 2-pyridinemethanol *N*-oxide may be close to that of pyridine. As is seen from Fig. 7 and Table I, the ethanol solution of 2-pyridinemethanol *N*-oxide has a similar


(A)


(B)

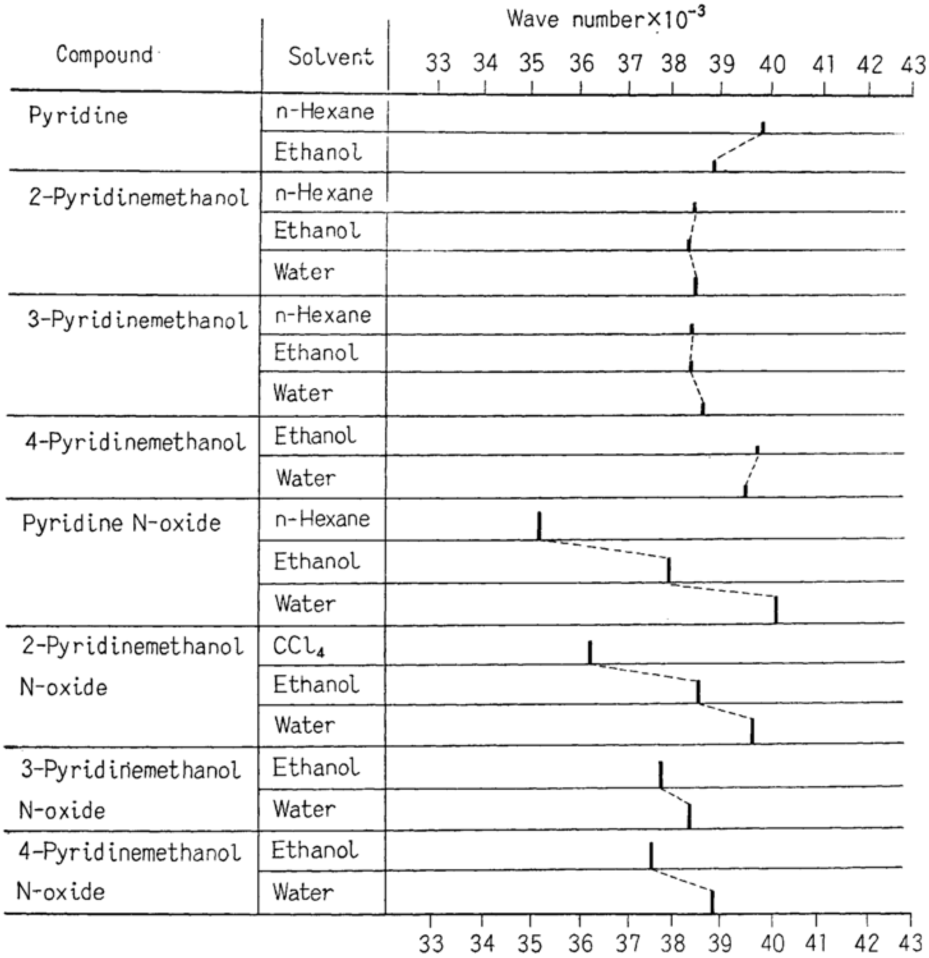


Fig. 7. Schematic expression of absorption spectra of three isomeric pyridinemethanols and their *N*-oxides.

value of the maximum wavelength with pyridine, while in 3- or 4-pyridinemethanol *N*-oxide its maximum wavelength differs remarkably from that of pyridine. These facts also support the intramolecular hydrogen bond formation in 2-pyridinemethanol.

Summary

The ultraviolet absorption spectra of three isomeric pyridinemethanols and their *N*-oxides were measured in various solvents. $n-\pi^*$ Absorption was observed as the shoulder absorption only in n-hexane solution of 3-pyridinemethanol, for which a qualitative discussion was made.

It was also found that the substituiton of a hydroxymethyl group in 4-position of pyridine or 2-position of pyridine *N*-oxide caused the blue shift. To explain this fact the presence of a weak intramolecular hydrogen bond in 2-pyridinemethanol *N*-oxide was assumed.

In conclusion, the author wishes to express his hearty thanks to Professor S. Imanishi of Kyushu University for his kind guidance and encouragement. Thanks are also due to Dr. E. Suenaga of Nagasaki University for his helpful advice.

Faculty of Pharmacy, Nagasaki
University, Nagasaki