Ultraviolet Absorption Spectra of 4-Chloro- and Bromo-pyridine N-Oxides

By Norisuke HATA

(Received August 23, 1955)

Introduction

In a previous paper[1], we have reported the ultraviolet absorption spectrum of pyridine N-oxide in solution and in vapor phase, where we observed a weak absorption system due to an $n-\pi^*$ electronic transition, and discussed the effect of proton-donors on this absorption.

In the present investigation we measured the ultraviolet absorption spectra of 4-chloro- and bromo-pyridine N-oxides in various solvents.

In each of these substances we obtained a weak absorption at about 330 mμ and a strong absorption at about 290 mμ. The weak absorption is regarded as due to the $n-\pi^*$ electronic transition, considering the solvent effect and the oscillator strength.

Experimental

4-Chloro- and bromo-pyridine N-oxides used in this experiment were prepared by the method described by Ochiai[2] and purified by recrystallisation from acetone several times. Melting points of 4-chloro- and bromo-pyridine N-oxides were 169.5°C and 143.5°C, respectively.

The solvents used were carbon tetrachloride, ethanol and water, which were purified by the methods described in "Organic Solvents"[3]. The spectra were measured with a Shimadzu Quartz Spectrophotometer Model QB-50, using a fused quartz cell of 1 cm. thickness. Measurements were limited to the region of wave-length shorter than 390 mμ.

Results and Discussion

Figs. 1 and 2 show the absorption curves of 4-chloro- and bromo-pyridine N-oxides, respectively, in various solvents. In the case of carbon tetrachloride solution, it appears that there are two absorption regions between 26000 cm^{-1}, and 44000 cm^{-1}, one of which is the weak absorption at about 30000 cm^{-1} (referred to as Transition I) and the other the strong absorption at about 34000 cm^{-1} (Transition II). When either ethanol or water is used as the solvent, the Transition I is not observed and the absorption maximum of the Transition II is remarkably shifted toward the shorter wave-length.

Even in water solution, however, the spectrum of 4-bromopyridine N-oxide shows a weak absorption at about 32,000 cm^{-1}. This weak absorption may be due to another transition different from the Transition I mentioned above, and the Transition I ob-

---

[1] M. Ito and N. Hata, This Bulletin, 28, 260 (1955).

[2] E. Ochiai, *J. Org. Chem.*, 18, 534 (1953).

[3] A. Weissberger and E. Proskauer, "Organic Solvents", Oxford (1935).

served in carbon tetrachloride solution may also overlap with this third transition.

The nature of spectra of these compounds may be explained in the same way as that of pyridine N-oxide reported by Ito and Hata⁽¹⁾.

4-Chloro or bromo-pyridine N-oxides molecules have two pairs of $2p$ non-bonding electrons on the oxygen atom, one of which is in conjugation with the π-electron system of the pyridine ring and the other remains as a non-bonding pair just as in the pyridine N-oxide molecule. According to our previous interpretation for pyridine N-oxide, the longer-wave weak absorption is ascribed to the transition of one of the oxygen non-bonding electrons to the lowest unoccupied orbitals (n-π^* transition), while the shorter-wave strong absorption is ascribed to the π-π^* transition, from the consideration of the solvent effect, the oscillator strength and the features in the vapor spectrum.

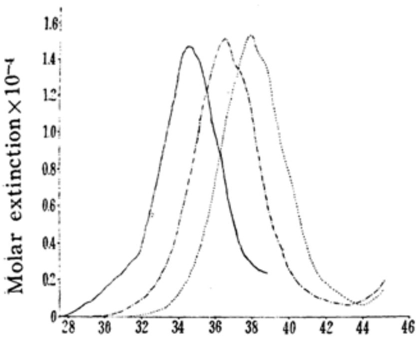


Fig. 1. Absorption curve of 4-chloropyridine N-oxide.
——— Carbon tetrachloride solution
– – – – Ethanol solution
- - - - - - Water solution

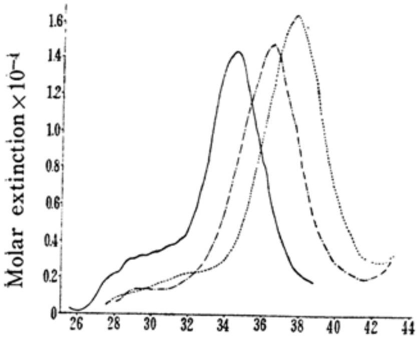


Fig. 2. Absorption curve of 4-bromopyridine N-oxide.
——— Carbon tetrachloride solution
– – – – Ethanol solution
- - - - - - Water solution

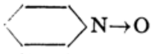
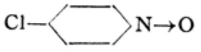
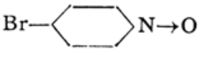
4-Chloro- and bromo-pyridine N-oxides may also have the weak n-π^* and the strong π-π^* transition. From the curves of Figs. 1 and 2, we see that the weak absorption (Transition I) completely disappears in ethanol or water solution.†

The disappearance of the Transition I in the ethanol and water solutions shows that it is due to the n-π^* electronic transition, since with these solvents of proton-donor character the oxygen non-bonding electron is largely stabilized in energy as a result of hydrogen bond formation.

The strong Transition II (π-π^* electronic transition) is remarkably shifted toward the shorter wave-length in ethanol and water solutions compared with carbon tetrachloride solution. These shifts are caused by the perturbation due to the hydrogen bond formation with ethanol or water. The absorption maxima and the molar extinction coefficients of Transition II of 4-chloro- and bromo-pyridine N-oxides in various solvents are given in Table I, together with that of the pyridine N-oxide.

TABLE I

ABSORPTION MAXIMA AND MOLAR EXTINCTION OF $\pi-\pi^*$ ABSORPTION (TRANSITION II)

Solvent	Carbon tetrachloride		Ethanol		Water	
Compound	$\lambda_{max.}$	$\varepsilon_{max.}\times10^{-4}$	$\lambda_{max.}$	$\varepsilon_{max.}\times10^{-4}$	$\lambda_{max.}$	$\varepsilon_{max.}\times10^{-4}$
	281	0.97	265	1.34	255	1.22
	289	1.48	265	1.34	255	1.54
	291	1.44	278	1.48	266	1.64

Next, in order to estimate the extent of contributions to the absorption by the n-π^* and π-π^* transitions respectively, peak analysis was made for carbon tetrachloride solution, and the oscillator strengths of the n-π^* and π-π^* transitions were calculated from the following equation⁽⁴⁾, as for the pyridine N-oxide reported in our previous paper⁽¹⁾,

---

† However, 4-bromopyridine N-oxide has another absorption near 32000 cm^{-1} as previously stated, even in the water and ethanol solution.

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

$$f=4.32\times 10^{9}\int \epsilon d\nu .$$

Figs. 3 and 4 represent the peak analysis of the absorption curves of 4-chloro-and bromo-pyridine N-oxides, respectively. For 4-bromopyridine N-oxide, the π-π^* curve is extended in the exponential manner as the continuation of the normal absorption in the region where Transition I and the unknown transition mentioned above are not appreciable. The numerical results are given in Table II. As seen in this table, the ratios of oscillator strengths of n-π^* and π-π^* transitions are in the order of 10^{-2} for 4-chloro- and bromo-pyridine N-oxides, as well as for the pyridine and pyridine N-oxide. This also supports our assignment of the n-π^* and π-π^* electronic transitions assumed in this paper.

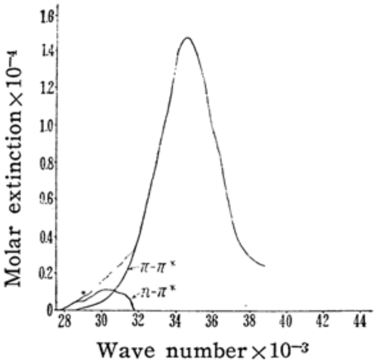


Fig. 3. Peak analysis of the absorption of 4-chloropyridine N-oxide in carbon tetrachloride solution.

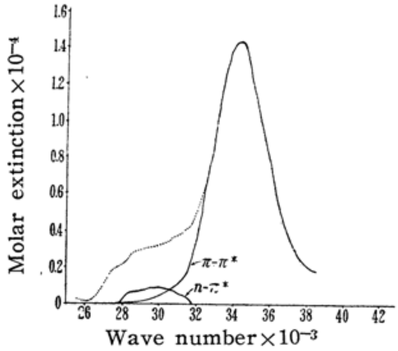
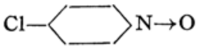
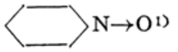
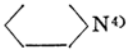


Fig. 4. Peak analysis of the absorption of 4-bromopyridine N-oxide in carbon tetrachloride solution.

TABLE II
OSCILLATOR STRENGTH OF $n-\pi^*$ AND $\pi-\pi^*$ TRANSITIONS

Compound	$f_{n-\pi^*}$	$f_{\pi-\pi^*}$	$f_{n-\pi^*}/f_{\pi-\pi^*}$
	0.0059	0.205	0.029
	0.0063	0.249	0.025
	0.012	0.173	0.079
	0.003	0.041	0.073

Summary

The solution spectra of 4-chloro- and bromo-pyridine N-oxides were measured in various solvents, in each of which were observed two absorption regions, one weak and the other strong.

The weak one was assigned to the transition involving the excitation of an oxygen non-bonding electron and the strong one to the transition involving the excitation of a π-electron.

In conclusion the author wishes to express his hearty thanks to Prof. S. Imanishi of Kyushu University for his kind guidance and valuable suggestions, and also to Prof. G. Kobayashi and Assistant Prof. E. Suenaga of Nagasaki University for their helpful advice. My thanks are also due to Mr. R. Tsuji and Miss. H. Yoshitomi for their assistance in the course of this work.

Faculty of Pharmacy, Nagasaki University, Nagasaki