48. Nobuo Ikekawa*, Masao Maruyama**, and Yoshihiro Sato* : Studies on the Coal Tar Bases. VIII[1]. Ultraviolet Spectra of Methylpyridines.

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The ultraviolet absorption spectra of pyridine, three picolines, 2,6- and 2,4-lutidines, and 2,4,6-collidine are given in the litrature[2~6] and that of pentamethylpyridine has recently been reported by Karrer[7], but no corresponding examination of other methylpyridines has yet been reported. In an earlier paper of this series, the infrared absorption spectra[8] and the dissociation constants[1] of all methylpyridine isomers were shown. The present paper gives the data obtained by measuring the ultraviolet absorption spectra of these methylpyridine isomers for investigation of the spectral properties of methyl group attached to pyridine nucleus and in order to use these spectra for the qualitative and quantitative analyses of the pyridine bases.

The same pure methylpyridine samples previously reported were used and the spectra measured from 225 mμ towards the visible region in aqueous solvents containing 10% ethanol, cyclohexane, acid, or alkaline solvent. In all cases, the maximum absorption peak existed in the range of 250~280 mμ, and in general it was found that the introduction of a methyl group had a little effect on the general shape of the absorption curve of pyridine, producing only a bathochromic and hyperchromic shift by the effect of methyl group. The methyl group introduced into different position, however, did not represent the same effect on the spectra, and the position and number of methyl group have a definite relation to the absorption spectra. Although neither the shape of the curve nor the effect of methyl group on its curve was completely the same in polar and in nonpolar solvents, the methyl group in the γ-position exhibited a special character as compared with that in α- or β-position.

10% Ethanol Solution The spectra of pyridine and all methylpyridine isomers in aqueous solvent containing 10% ethanol are shown in Figs. 1~4 and their absorption maxima and molecular extinction coefficients at the maximum are summarized in Fig. 11 and Table I. As will be seen from these figures, the only band of pyridine is slit into three distinct absorption maxima, but in that of picolines, subsidiary vibrational maxima are smoothed out into a band and form one peak, as is the case of other polymethylpyridines. In general, the main peak becomes broader, the intensity stronger, and the absorption maximum shifts to a longer wave length region as the number of methyl groups introduced into pyridine nucleus increases.

The increase in the number of methyl group caused higher intensity and the order of hyperchromic effect of the methyl group was $\alpha>\beta>\gamma$. As shown in Fig. 11 and Table I, when one methyl group is introduced into the pyridine nucleus, a bathochromic effect of 5~8 mμ appears in a compound with a methyl group in α-position and 4~7 mμ in that in the β-position, but in a compound with the methyl group in the γ-position,

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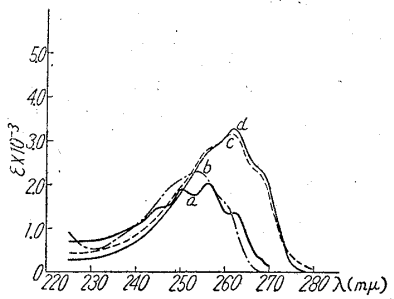
on the contrary, a hypsochromic effect of 2 to 4 mμ appears. The spectrum of pyridine exhibits the maximum peak at 256 mμ in 10% ethanol solution. The values of absorption maxima of methylpyridine spectra, calculated from the effect of methyl groups on the assumption that the introduction of a methyl group into pyridine nucleus causes a shift of +6.5, +5, and −3.5 mμ in α-, β-, and γ-substitution, respectively, agree remarkably well with the observed values as shown in Table I. These results apparently indicate that the adjacent methyl groups have no interaction between them.

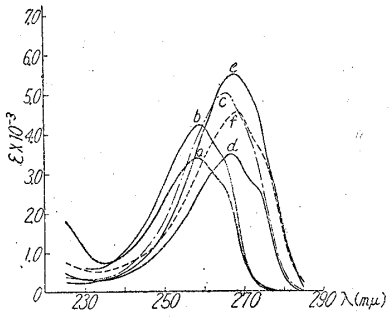
The intensity of 3,4,5-collidine at absorption maximum is lower than that of 2,4,6-collidine, and that of 2,3,4,5-tetramethylpyridine is likewise lower than that of 2,3,4,6- and 2,3,5,6-tetramethylpyridines. The assumption that the hyperchromic effect of α-position may be more intense than that of β-position appears more probable from these results than the idea that the interaction of adjacent methyl groups is capable of diminishing the intensity of the absorption.

Cyclohexane Solution The ultraviolet absorption spectra of the pyridines in cyclohexane are shown in Figs. 5~8. The absorption curves have more inflexions in this



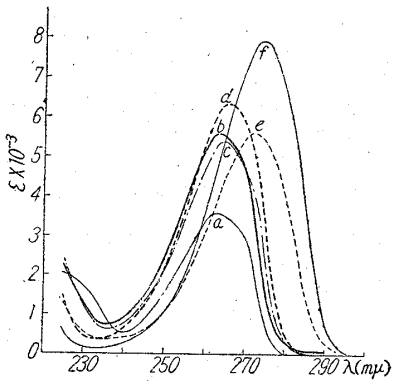
a Pyridine
b 4-Methylpyridine
c 2- 〃
d 3- 〃

Fig. 1. Ultraviolet Spectra of Pyridine and Picolines (in 10% ethanol)



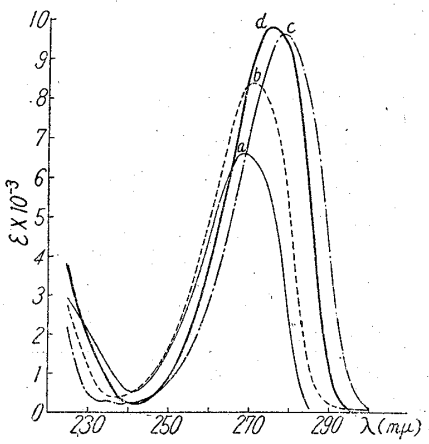
a 3,4-Dimethylpyridine
b 2,4- 〃
c 2,3- 〃
d 3,5- 〃
e 2,6- 〃
f 2,5- 〃

Fig. 2. Ultraviolet Spectra of Dimethylpyridines (in 10% ethanol)



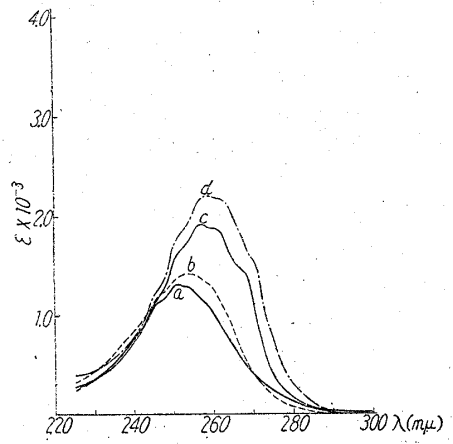
a 3,4,5-Trimethylpyridine
b 2,3,4- 〃
c 2,4,5- 〃
d 2,4,6- 〃
e 2,3,5- 〃
f 2,3,6- 〃

Fig. 3. Ultraviolet Spectra of Trimethylpyridines (in 10% ethanol)



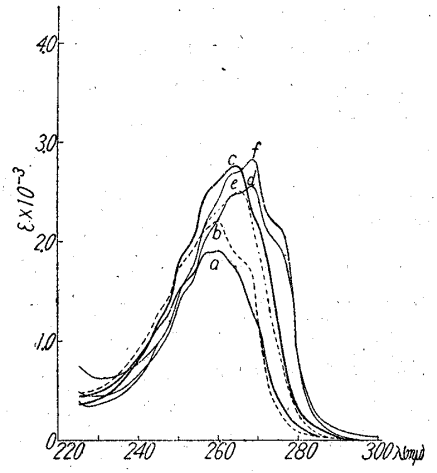
a 2,3,4,5-Tetramethylpyridine
b 2,3,4,6- 〃
c 2,3,5,6- 〃
d Pentamethylpyridine

Fig. 4. Ultraviolet Spectra of Tetramethylpyridines and Pentamethylpyridine (in 10% ethanol)



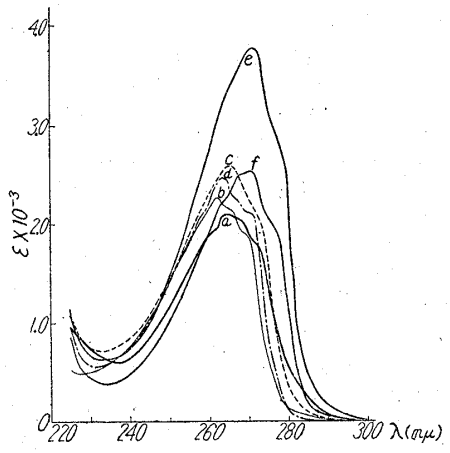
a Pyridine
b 4-Methylpyridine
c 3- //
d 2- //

Fig. 5. Ultraviolet Spectra of Pyridine and Picolines (in cyclohexane)



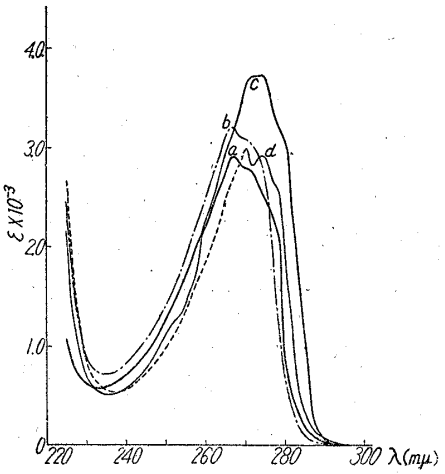
a 3,4-Dimethylrypidine
b 2,4- //
c 2,3- //
d 3,5- //
e 2,6- //
f 2,5- //

Fig. 6. Ultraviolet Spectra of Dimethylpyridines (in cyclohexane)



a 3,4,5-Trimethylpyridine
b 2,3,4- //
c 2,4,5- //
d 2,4,6- //
e 2,3,5- //
f 2,3,6- //

Fig. 7. Ultraviolet Spectra of Trimethylpyridines (in cyclohexane)



a 2,3,4,5-Tetramethylpyridine
b 2,3,4,6- //
c 2,3,5,6- //
d Pentamethylpyridine

Fig. 8. Ultraviolet Spectra of Tetramethyl- and Pentamethylpyridine (in cyclohexane)

solution than in a polar solution. As shown in Fig. 11 and Table I, the main peak of methylpyridine shifts generally to the shorter wave length region and its intensity is lower than that in a polar solution. The absorption maximum of methylpyridine possessing a methyl group in the γ-position is shorter in its wave length and lower in intensity than that which does not possess it in the γ-position, as observed in a polar solution.

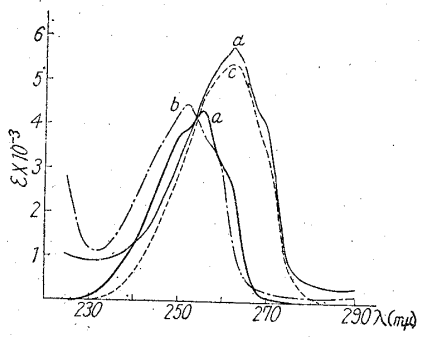
The absorption maximum shifts to a longer wave length region when a methyl group is introduced into the α- or β-position of the pyridine ring, and a similar tendency is observed in the case of that in the γ-position of pyridine and picoline, but when methyl is introduced into the γ-position of di-, tri-, and tetramethylpyridines, absorption maximum

shifts to a shorter wave length region, as in the spectra in a polar solution.

Acid and Alkaline Solution The absorption spectra of pyridine and picolines in 0.2*N* sulfuric acid and 0.1*N* sodium hydroxide solution containing 1% ethanol are shown in Figs. 9 and 10. In these solutions, absorption curves of di-, tri-, tetra-, and pentamethylpyridines are almost similar in shape to those in a 10% ethanol solution. The absorption maxima and intensity are shown in Table I. Generally, the absorption maximum of methylpyridines (excluding some substances) in the alkaline solution shifts slightly to a shorter wave length region and to a lower intensity, and in the acid solution, it shifts slightly to a longer wave length and to a higher intensity——approximately twice that in the alkaline solution——than those in a neutral solution.

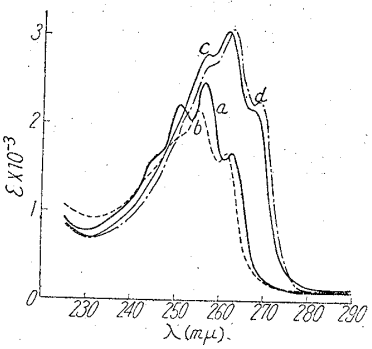
In the spectra of pyridines in 1*N* sulfuric acid containing 1% ethanol, their absorption maxima are in the same position as those in the 0.1*N* sulfuric acid solution and the increase of the intensity is not remarkable.

Solvent Effect The general tendency of a maximum peak to shift in different



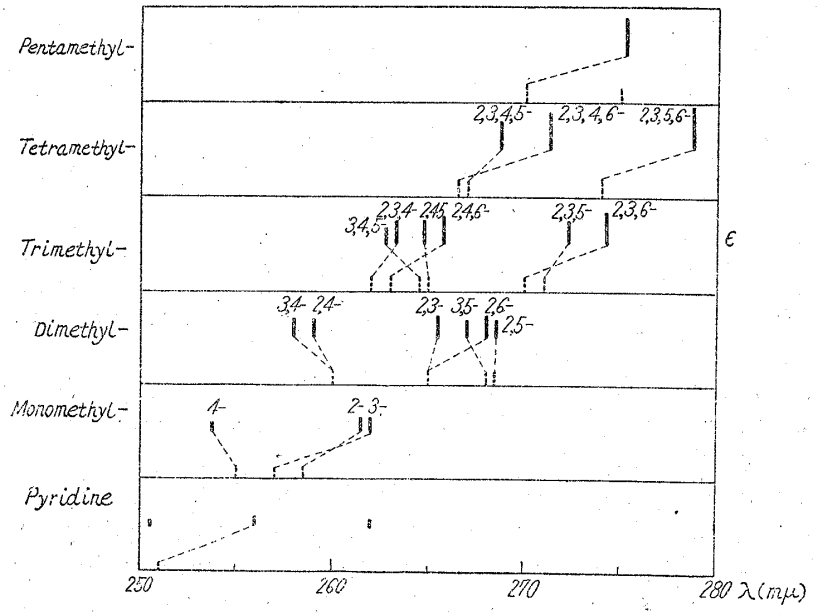
a Pyridine
b 4-Methylpyridine
c 2- 〃
d 3- 〃

Fig. 9. Ultraviolet Spectra of Pyridine and Picolines (in 0.2*N* H_2SO_4 solution containing 1% ethanol)



a Pyridine
b 4-Methylpyridine
c 2- 〃
d 3- 〃

Fig. 10. Ultraviolet Spectra of Pyridine and Picolines (in 0.1*N* NaOH solution containing 1% ethanol)



····· in cyclohexane —— in 10% ethanol

Fig. 11. Position and Intensity of Absorption Maximum of Methylpyridines

TABLE I. Ultraviolet Absorption Characteristics of Methylpyridines

Compound	10% EtOH			Cyclohexane		0.2 N H_2SO_4		0.1 N NaOH	
	λ_{max} (mμ)	ε_{max}	Calc. λ_{max}	λ_{max} (mμ)	ε_{max}	λ_{max} (mμ)	ε_{max}	λ_{max} (mμ)	ε_{max}
Pyridine	250.5 256 262	1,900 2,050 1,350	256	251	1,320	255 ~255.5	4,350	250.5 256 ~256.5 262	2,210 2,450 1,670
4-Methylpyridine	253.5 ~254	2,290	252.0	255	1,420	252	4,500	255 261	2,130 1,660
2- 〃	261.5	3,180	262.5	258.5	2,200	261.5 ~262	5,410	257 261.5	2,800 3,050
3- 〃	262	3,270	261	257	1,920	262	5,800	257.5 262.5 268.5	2,690 3,090 2,250
3,4-Dimethylpyridine	258	3,410	257.5	260	1,920	258	4,960	259	2,450
2,4- 〃	259	4,210	259	260	2,210	258.5	5,820	259 ~259.5	2,910
2,3- 〃	265.5	5,030	267.5	265	2,770	266.5 ~267	7,440	265	3,710
3,5- 〃	267	3,530	266	268	2,560	267.5 ~268	6,420	267	3,360
2,6- 〃	268	5,530	268.5	265	2,520	269 ~270	7,600	266 ~266.5	4,270
2,5- 〃	268.5	4,560	267.5	268.5	2,830	269	6,720	268	3,580
3,4,5-Trimethylpyridine	262.5 ~263	3,920	262.5	264.5	2,100	261.5 ~262	4,300	261.5 ~262	2,450
2,3,4- 〃	263 ~263.5	5,600	264	262	2,260	263.5	6,700	262 ~262.5	3,410
2,4,5- 〃	264.5 ~265	5,400	264	265	2,580	265	7,060	264	3,140
2,4,6- 〃	265.5 ~266	6,350	265.5	263	2,460	265.5 ~266	7,720	263.5 ~264	4,600
2,3,5- 〃	272 ~272.5	5.650	272.5	271	3,770	273 ~273.5	6,820	271	4,310
2,3,6- 〃	274 ~274.5	7,690	274	270	2,520	274.5 ~275	8,480	270.5	4,800
2,3,4,5-Tetramethylpyridine	268.5 ~269	6,660	269	267	2,920	269	6,660	267.5	3,570
2,3,4,6- 〃	271 ~271.5	8,400	270.5	266.5	3,210	271 ~271.5	8,220	268	4,180
2,3,5,6- 〃	278.5 ~279	9,620	279	274	3,730	279.5	10,060	274.5 ~275	5,700
Pentamethylpyridine	275 ~275.5	9,800	275.5	270 275	3,000 2,920	275.5	8,840	272	5,110

manner in different solvents has been described above. It is interesting to note the relation between the shift of the main peak of methylpyridine (the effect of methyl group on the shift) and various solvents. The relation between the absorption maxima in polar and nonpolar solvents is shown in Fig. 11. As can be seen from that figure, the absorption maximum of methylpyridines possessing the methyl group in 2- or 6-position shifts markedly to a longer wave length region in a polar solution than in a nonpolar solution, but that of γ-picoline, and 3,4- and 2,4-dimethylpyridines shifts to a shorter wave length region. It will be seen from these results that the methyl group exhibits a hypsochromic effect in the γ-position and a bathochromic effect in the α-position. The methyl group in the β-position exhibits a hypsochromic effect on dimethylpyridine, but if methyl groups increase in number, its effect is diminished by the effect of the α-methyl group. When the absorption maximum in an acid solution is compared with that in an alkaline solution, the methyl groups attached to α-, β-, and γ-positions exhibit the same effect.

The bathochromic effect of a methyl group in a benzene ring has been shown by the series of benzene, toluene, and dimethylbenzene. Baker and Baly[3] reported that a methyl group introduced into the pyridine nucleus exhibited both a bathochromic and a hyperchromic effect, but it may be seen from the present experimental results that their conclusion needs partial correction. The ultraviolet absorption spectra of quinoline and 2-, 4-, 6-, and 7-methylquinolines are reported in the literature[6]. In comparing these spectra in the 310~320 mμ region, the methyl group in 2-, 6-, or 7-position of quinoline ring, as might be expected, tends to shift the quinoline absorption to longer wave lengths, but there is no such shift when the methyl group is introduced into the 4-position. In the case of nitrotoluenes, the shift to a longer wave length is in the order of *para*>*meta*>*ortho*. Hence, it may be suggested that the hypsochromic effect of the methyl group at the *para*-position to nitrogen atom is specific in the pyridine ring. Miller[9] has investigated the effect of the fluorine introduced into pyridine and quinoline ring on the absorption spectra and stated that the effect of fluorine is bathochromic in some positions and hypsochromic in others. The effect of the methyl group in pyridine ring on absorption spectrum may not be explicable from the resonance theory alone.

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Experimental

Material—The same samples as used in the previous report were freshly distilled before use.

Method—The ultraviolet absorption spectra were determined by the Backman Model DU spectrophotometer with the quartz cells of 10-mm. optical depth. Density measurements were never made at intervals of more than 2 mμ, while in the neighborhood of the maxima, the interval was decreased to 0.5 mμ. Water used for the solvent was distilled twice, and cyclohexane and ethanol were carefully purified by the usual procedures. The concentration of the solutions varied from 2×10^{-4} *mM* to 0.5×10^{-4} *mM*. The temperature was at 15±2°.

Summary

The ultraviolet absorption spectra of pyridine and nineteen kinds of methylpyridine isomers were measured in 10% ethanol, cyclohexane, acid, and alkaline solutions, and the results were compared. Generally speaking, the methyl group in the pyridine ring exhibited the bathochromic and hyperchromic effect, but the methyl groups in the γ-position showed a characteristic effect as compared with that in the α- or β-position.

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