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37. **Hideyo Shindo* and Nobuo Ikekawa****: Studies on the Infrared Spectra of Heterocyclic Compounds. I.[1] Infrared Spectra of Alkylpyridines.

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In the previous paper, Tsuda and Maruyama[2] reported the characteristic infrared bands of methylpyridines in fingerprint region for use in the analysis of tar bases. The purpose of the present paper is to establish the correlation between the absorption frequencies and the position of alkyl substituents. The infrared spectra of eight ethylpyridines and nineteen methylpyridines were determined under the same conditions, and the out-of-plane C–H deformation frequencies and pyridine ring skeletal vibrations could be correlated respectively with their structures.

I. Out-of-plane C-H Deformation Frequencies

Aromatic compounds show strong absorption bands in the region of 700 and 900 cm^{-1}, originating in the out-of-plane deformation vibration of the ring hydrogen. In the case of substituted benzenes, an extensive investigation has been made, and it has been shown that the principal factor determining their frequencies is the number of free hydrogen atoms in the ring which are adjacent to one another.[3] However, in the case of substituted pyridines only limited data are available. Cannon and Sutherland[4] suggested from the spectra of four methylpyridines that, by including the nitrogen as a substituent, their frequencies show a good agreement with the corresponding substituted benzenes. For example, pyridine can be compared with mono-subtituted benzenes.

From our investigation, it was concluded that the correlation rule for substituted benzenes holds good also for substituted pyridines. In Fig. 1, the absorption frequencies of methylpyridines are compared with the usual ranges for the corresponding substituted benzenes depending upon the number of adjacent free hydrogen atoms on the ring, and a good coincidence is shown between the two absorption ranges. An additional band at 709 cm^{-1} in 3,5-lutidine can be interpreted as the correspondence to symmetrical trisubstituted benzenes. 1,3,5-Trimnthylbenzene, for example, absorbs with strong intensity at 687 cm^{-1}.

However, it is also noted that, in spite of methyl homologs, the displacements within each range in Fig. 1 are considerably great, particularly in the case of compounds containing one or more isolated hydrogen atoms. Some of them show a considerable deviation from the normal range of substituted benzenes. It may be due to the fact that the positions on the pyridine ring have different effects on absorption frequencies depending upon the electronegativity of ring nitrogen. Taking this into consideration, it becomes clear that the displacement order shown in Fig. 1 has a distinct relationship with their structures. In general, additional isolated free hydrogen atom on the ring does not produce any absorption associated with its own C–H bond, but effects lowering of the frequency of the corresponding methyl substituted compounds. For example, 3,4- (Ⅶ) and 2,4-lutidine (Ⅷ) absorb at lower

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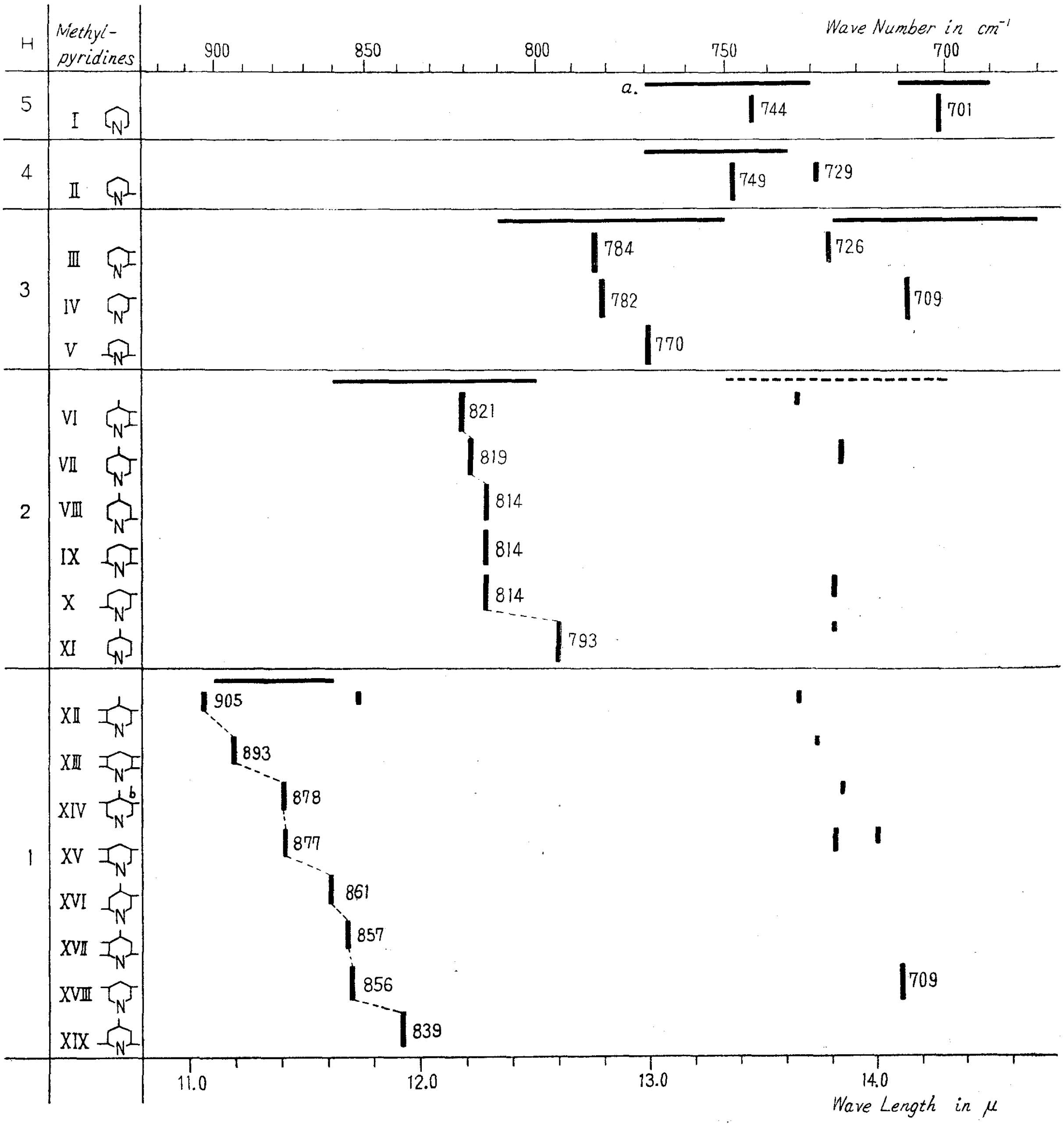
[2] K. Tsuda, M. Maruyama : This Bulletin, **1**, 146(1953).

[3] N. B. Colthup : J. Opt. Soc. Amer., **40**, 397(1950).

[4] C. G. Cannon, G. B. B. M. Sutherland : Spectrochim. Acta, **4**, 373(1951).

Fig. 1. Position and Intensity of the Absorption Bands of Methylpyridines (700~900 cm^{-1} range)



H : Number of the adjacent free hydrogen atoms on the ring.
a : These horizontal lines represent the overall ranges for substituted benzenes quoted by Bellamy.[7)]
b : 319 cm^{-1} band of 3,4,5-collidine (This Bulletin, **1**, 283(1953)) is assumed to be attributable to 3,4-lutidine.

frequencies than that of 2,3,4-collidine (VI) and do not show any absorption between 860 and 900 cm^{-1}, in which one expects an absorption associated with the isolated free hydrogen atom.

Free hydrogens isolated from one another on the ring also result in a single absorption which is displaced to a lower frequency as their number increases. In this case, difference of the effect depending upon their positions can be observed clearly. The compounds containing only one hydrogen atom on the ring absorb at lower frequencies in the following order : α-H (XII), 905 cm^{-1}; γ-H (XIII), 893 cm^{-1};

β-H (XVII), 857 cm^{-1}. In particular, β-hydrogen causes an absorption at a far lower frequency than the others. This is probably due to the strengthening of the C–H bond at β-position by the greater π-electron density than that at α- or γ-position.

Furthermore, γ-C–H bond absorbs at appreciably lower frequency than α-C–H bond, and this may be considered to indicate that the electron-donating effect of four methyl substituents toward the γ-position is greater than that toward the α-position.

The particular lowering effect of the β-hydrogen is the most significant through this series. Thus, 2,4,6-collidine (XIX, two C–H bonds at β and β') is displaced to 839 cm^{-1}, which is lower than that of 3,5-lutidine (XVIII, three C–H bonds at α, α', and γ). Moreover, 2,4,5-collidine (XVI, two C–H conds at α and β) absorbs at a considerably lower frequency than 2,3,5-collidine (XV, two C–H bonds at α and γ). The displacement of this absorption in 2,4-lutidine (VIII) to a lower frequency is greater than that of 3,4-lutidine (VII) when compared to 2,3,4-collidine (VI). All these are explained by the term of a greater lowering effect of β-C–H bond due to its position effect.

On the other hand, 3,4,5-collidine (XIV, two C–H bonds at α and α') and 2,3,5-collidine (XV, two C–H bonds at α and γ) absorb at about the same frequency, indicating that the interaction between α- and γ-positions is small.

Furthermore, 2,4,5-collidine (XVI, two C–H bonds at α and β) absorbs at approximately the average frequency (861 cm^{-1}) of 3,4,5-collidine (XIV, two C–H bonds at α and α') (878 cm^{-1}) and 2,4,6-collidine (XIX, two C–H bonds at β and β') (839 cm^{-1}), and increase of free hydrogen atom at α in 2,3,5,6-tetramethylpyridine (XIII, C–H bond at γ) give rise to a displacement to lower frequency by 16 cm^{-1} (XV) and 21 cm^{-1}

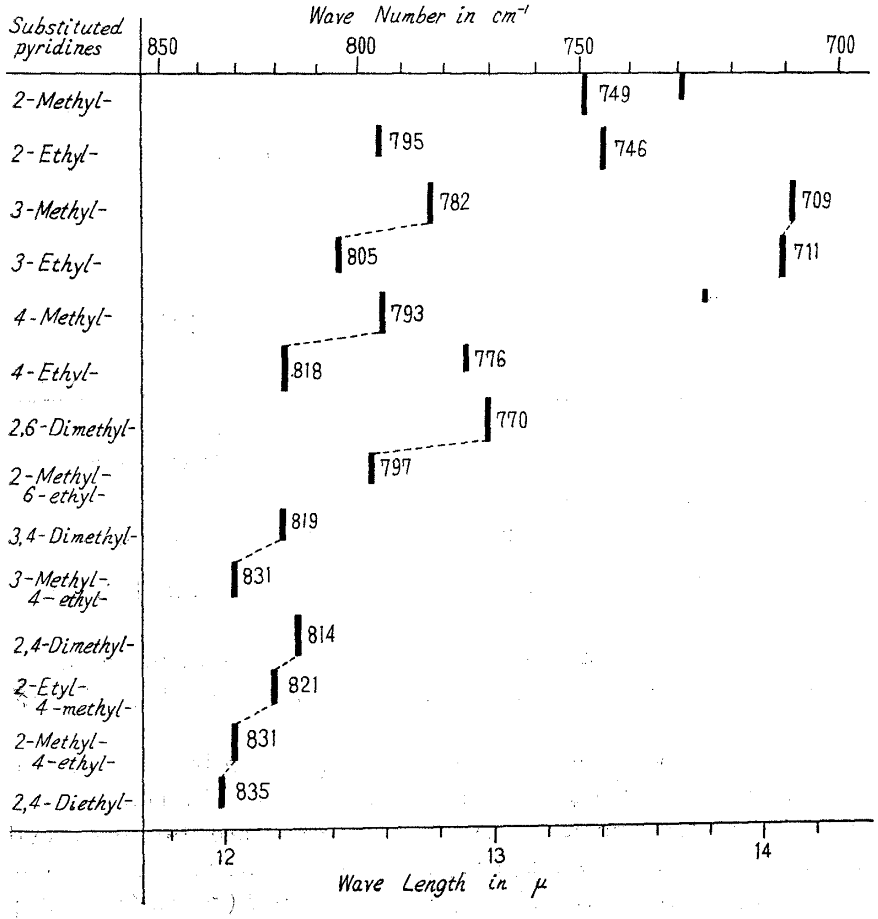


Fig. 2.

Position of the Absorption Bands of Ethylpyridines (700~850 cm^{-1} range)

(XVIII) progressively. These indicate apparently that the effect of each position appears additively on actual frequencies.

Recently, Bellamy⁵⁾ has shown in several substituted benzenes that the out-of-plane C-H deformation frequencies in the aromatic ring have a linear relationship with Hammett's substituent constants. It is, therefore, reasonable to expect a similar relationship in substituted pyridines, although it may be more complex.

No data have been reported about ethylpyridines. As shown in Fig. 2, ethyl substitution always displaces the absorption of the corresponding methyl homologs to a higher frequency. This is in accord with the result of McCauly *et al.*⁶⁾ The 835 cm^{-1} band of 1,3,5-trimethylbenzene shows an ordinary displacement of about 10 cm^{-1} to a higher frequency in every ethyl substitution. In the case of pyridines the amount of the shift is more variable and it may be also due to the differences of the effect depending upon their positions.

However, these effects also appear additively as shown in 2,4-disubstituted compounds, 2-ethyl-4-methylpyridine and 2-methyl-4-ethylpyridine causing a shift by 6 cm^{-1} and 17 cm^{-1}, respectively, to higher frequencies from that of 2,4-lutidine, while 2,4-diethylpyridine shows 20 cm^{-1} shift, which is approximately equal to the sum of each shift of the two methylethylpyridines.

II. C=C and C=N Stretching Vibration Frequencies.

An aromatic ring shows a characteristic pair of absorptions between 1450 and 1600 cm^{-1} as a result of the resonance splitting of ring double-bond vibrations. Interactions between the C=C and C=N vibrations in the pyridine ring appear to cause absorptions in a very similar way to the benzene ring.

The absorptions of methylpyridines are shown in Fig. 3. There occur, in general, two bands between 1560 and 1620 cm^{-1}, and one between 1450 and 1500 cm^{-1}, which are very variable in their exact frequencies and intensities.

The latter band, which usually occurs in the benzene ring near 1500 cm^{-1}, ⁷⁾ appears to be displaced to a lower frequency region, so that in most cases it overlaps the methyl deformation. No consistent correlations could be found between these frequencies and their structures, but the relative intensity of the two bands between 1560 and 1620 cm^{-1} appears to be determined by the relative positions of the methyl substituents to nitrogen.

In pyridine itself, the lower frequency absorption, which is very weak or absent in the usual substituted benzenes, is more intense than the higher one, which is considered as the main absorption for substituted benzenes.⁷⁾ The effect of methyl substitution in pyridine on the intensity of these two bands is shownin Fig. 3, and the comparison of the first six compounds makes it clear that the 4-methyl substitution has a significant effect in increasing the intensity of the higher absorption band much more than the lower one, while 3-methyl substitution has no effect, and 2-methyl substitution has a slight effect in enhancing the higher band. Thus, 4-picoline absorbs in close similarity with the usual substituted benzenes.

These effects can be observed through all methylpyridines, and that of 4-methyl substituent appears particularly to be so predominant that all the compounds containing γ-methyl substituent show a stronger absorption at higher frequencies.

Nitrobenzenes and nitrotoluenes, which can be considered as analogous to pyridines and picolines in their electronic structure, show almost the same behavior.

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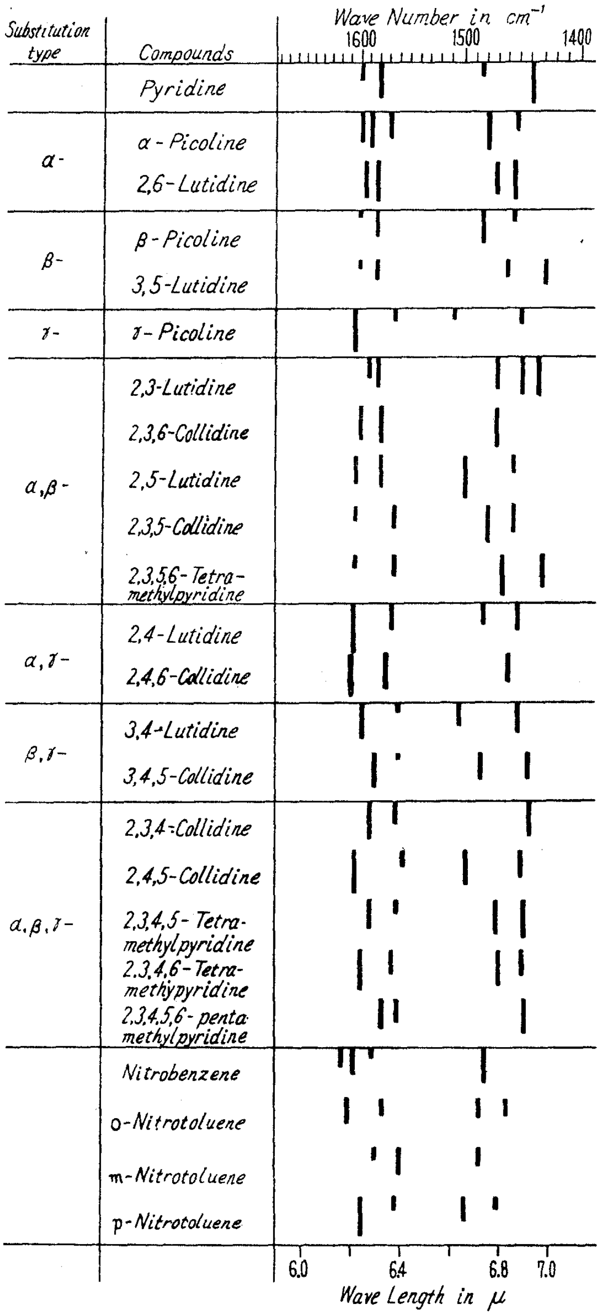

Fig. 3.

Position and Intensity of the Absorption Bands of Methylpyridines ($1400\sim1700\ cm^{-1}$ range)

Also, in this case, *p*-nitrotoluene shows the most normal absorption, while *m*-nitrotoluene exhibits very abnormal absorption, as shown in Fig. 3.

From the electronic viewpoint, it is expected that 4-methyl substituent may further increase the electronic asymmetry of the pyridine ring, and on the other hand, 3-methyl substituent may make it more symmetrical.

Therefore, it is concluded that the behavior of the spectra in this region cannot be explained by the term of electronic asymmetry, because, from this theoretical viewpoint, 3-methyl substitution should be the closest to the cases of usual benzene substitutions.

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Experimental

Materials—Samples of methylpyridines used were the same as those reported previously.[2] 2-Methyl-3-ethylpyridine was prepared by the method of Wibaut.[8] The other ethylpyridines were the same samples as those in the previous paper.[1]

Method—The spectra were obtained with a Perkin-Elmer Model 21 recording spectrometer with a rock salt prism. Samples were determined in 5.0~6.0% solution depending upon the increase of the number of alkyl groups, with the cell of 0.1 mm. thickness. CS_2 and CCl_4 were used as solvents, respectively, for 1450~650 cm^{-1} and for 1700~1450 cm^{-1} ranges.

Summary

The infrared spectra of eight ethylpyridines and nineteen methylpyridines were determined. The absorption spectra obtained are correlated with their structures and are discussed on the characteristic properties of the pyridine ring and its similarity to the benzene ring.

The conclusion are as follows : (i) Out-of-plane C–H deformation frequencies in alkylpyridines are determined principally by the number of adjacent free hydrogen atoms round the ring in a similar way to substituted benzenes, (ii) furthermore, their exact frequencies have a distinct correlation with the arrangement of hydrogen atoms round the ring, (iii) ethylpyridines always absorb at higher frequencies than those of the corresponding methyl homologs, and (iv) pyridine ring vibrations between 1450 and 1650 cm^{-1} are also regularly correlated to the structures.

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