U.D.C. 547.831.2 : 544.621

56. **Hideyo Shindo and Shinzo Tamura :** Studies on the Infrared Spectra of Heterocyclic Compounds. II.[1] Infrared Spectra of Methylquinolines. (1).

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In the preceding paper,[1] the infrared spectra of alkylpyridines were correlated with their structures, particularly with the position of the alkyl substituents, and discussions were made on the basis of the characteristic properties of pyridine ring and its similarity to the benzene ring. Spectral studies on substituted quinolines also have been little made and it would be interesting to discover how far the correlation rules in the case of benzenes and pyridines are applicable in fused ring systems such as that of quinolines, in which the substituent bonds are themselves considered to be a part of the ring system. In the present studies the infrared spectra of quinoline, isoquinoline, and seven monomethylquinolines were determined and were found to be correlated with their structures. These compounds gave highly characteristic bands in finger print region of the spectrum, and it seems that the data provided are useful in the analysis of tar bases. Di- and trimethylquinolines are now being studied.

The spectrum of isoquinoline has been reported by Freiser *et al.*[2] Hannan *et al.*[3] published the spectra of five quinolinethiols, and Bellamy discussed the spectra of quinoline, isoquinoline, and three dimethylquinolines in his publication.[4] However, no systematic investigation has been made and the data available are very limited.

The spectra obtained are shown in Fig. 1 and are discussed below.

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

Substituted quinolines, as well as other aromatic compounds, give rise to strong bands in the region of 700∼900 cm^{-1} due to the out-of-plane deformation vibrations of the hydrogen atoms remaining in the ring. In the case of fused ring compounds in which two or more benzene rings are condensed, it has been shown that the correlation rule for benzenes still appears to hold good if each ring is considered separately, but it has been also noticed that there are always greater displacement from one compound to another than in the case of usual substituted benzene, and the increase of the number of substituents makes this region often too complex for ready identification of the type of substitution. For example, Orr and Thompson[5] traced a strong band near 750 cm^{-1} corresponding to the *ortho*-disubstituted benzene in carcinogenic hydrocarbons which contain 1,2-disubstituted fused ring structure, but there are shift of over ±10 cm^{-1} in many cases. Colthup[6] indicated that a wider range of frequencies is to be expected in substituted naphthalenes, while Cannon and Sutherland[7] found that this method of interpretation fails in pyrene and in molecules with more compactly condensed ring system.

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[1] H. Shindo, N. Ikekawa : This Bulletin, **4**, 192(1956).

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Fig. 1. Infrared Absorption Spectra in the Range of 700~1650 cm^{-1} (1)

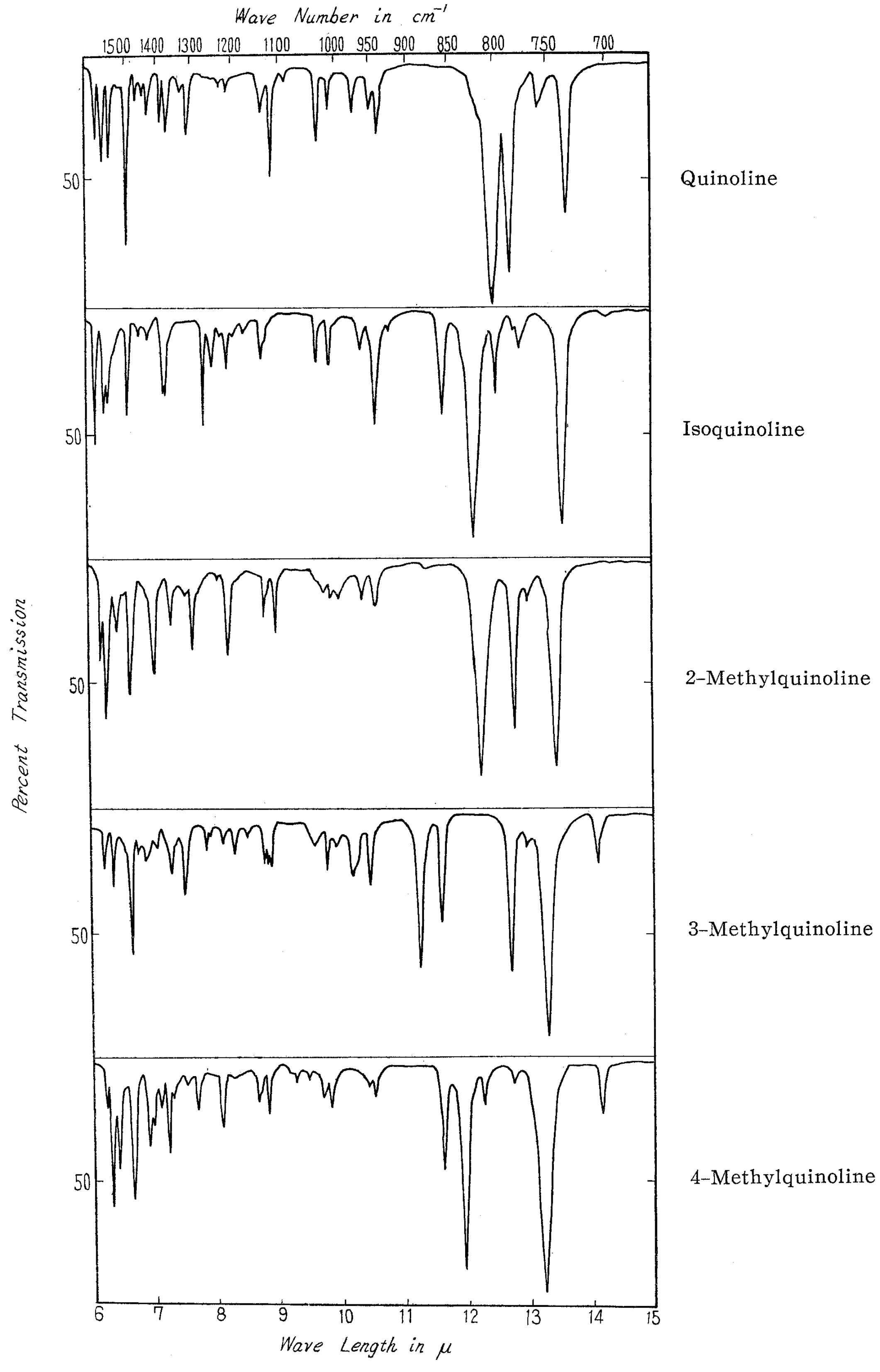
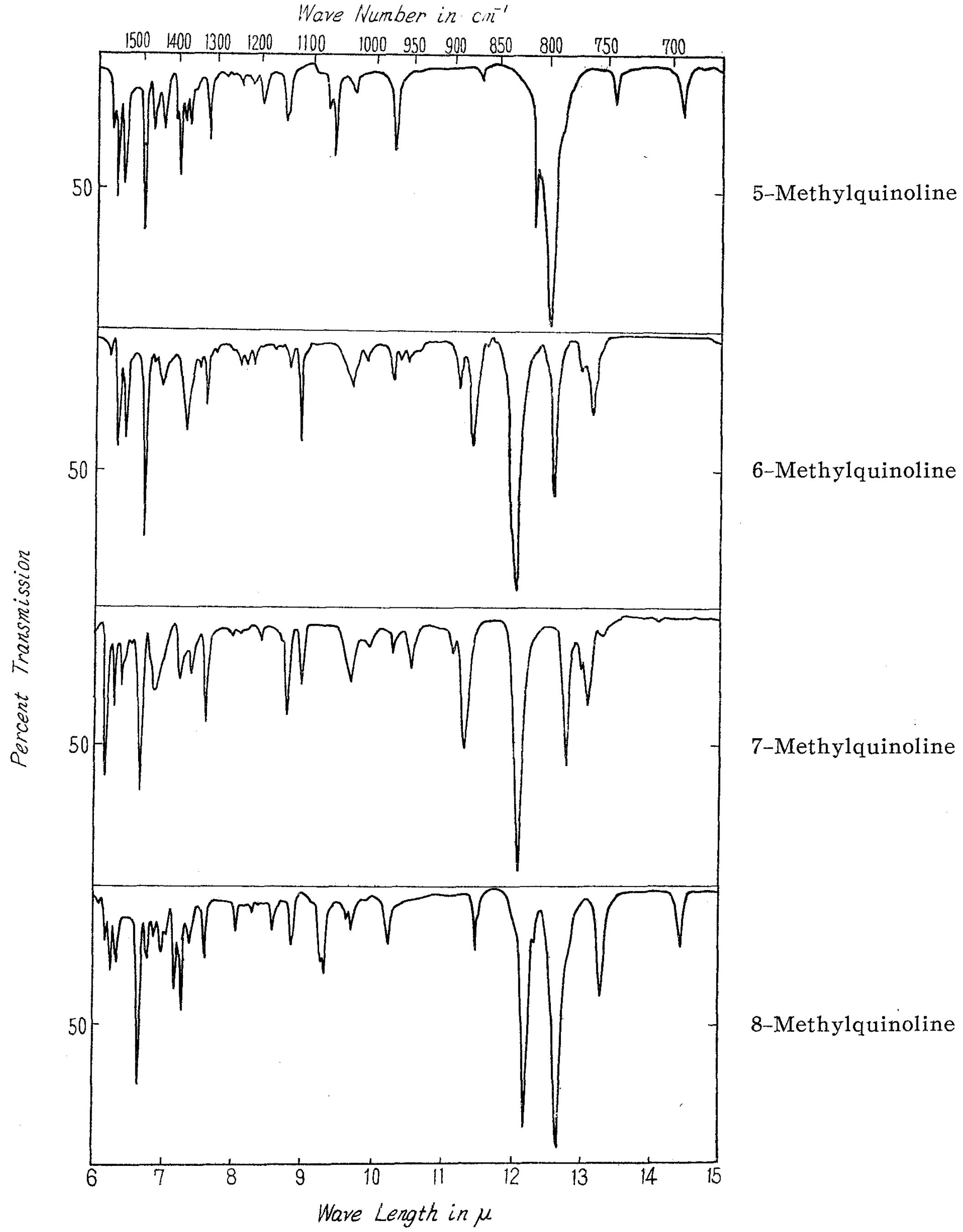


Fig. 1. Infrared Absorption Spectra in the Range of 700~1650 cm^{-1} (2)



Also in the case of substituted quinolines, it is expected that the same interpretation as described above is possible, although the more complex interaction may exist according to the ring nitrogen. Thus, by separating the quinolines into the componental carbocyclic and heterocyclic rings, the adjacent free hydrogen atoms on each ring could be correlated respectively with the strong band in this region of the spectrum. As will be seen from Fig. 2, however, some additionl bands which cannot be interpreted appear in many cases, which may cause an ambiguity in some cases.

In all compounds in which the carbocyclic ring is unsubstituted (I~V), a strong band appears between 730 and 760 cm^{-1} corresponding to the *ortho*-disubstituted benzenes, while the compounds in which the carbocyclic ring is substituted (VI~IX) do not absorb in this region to any appreciable extent, and these two types of substitution can be

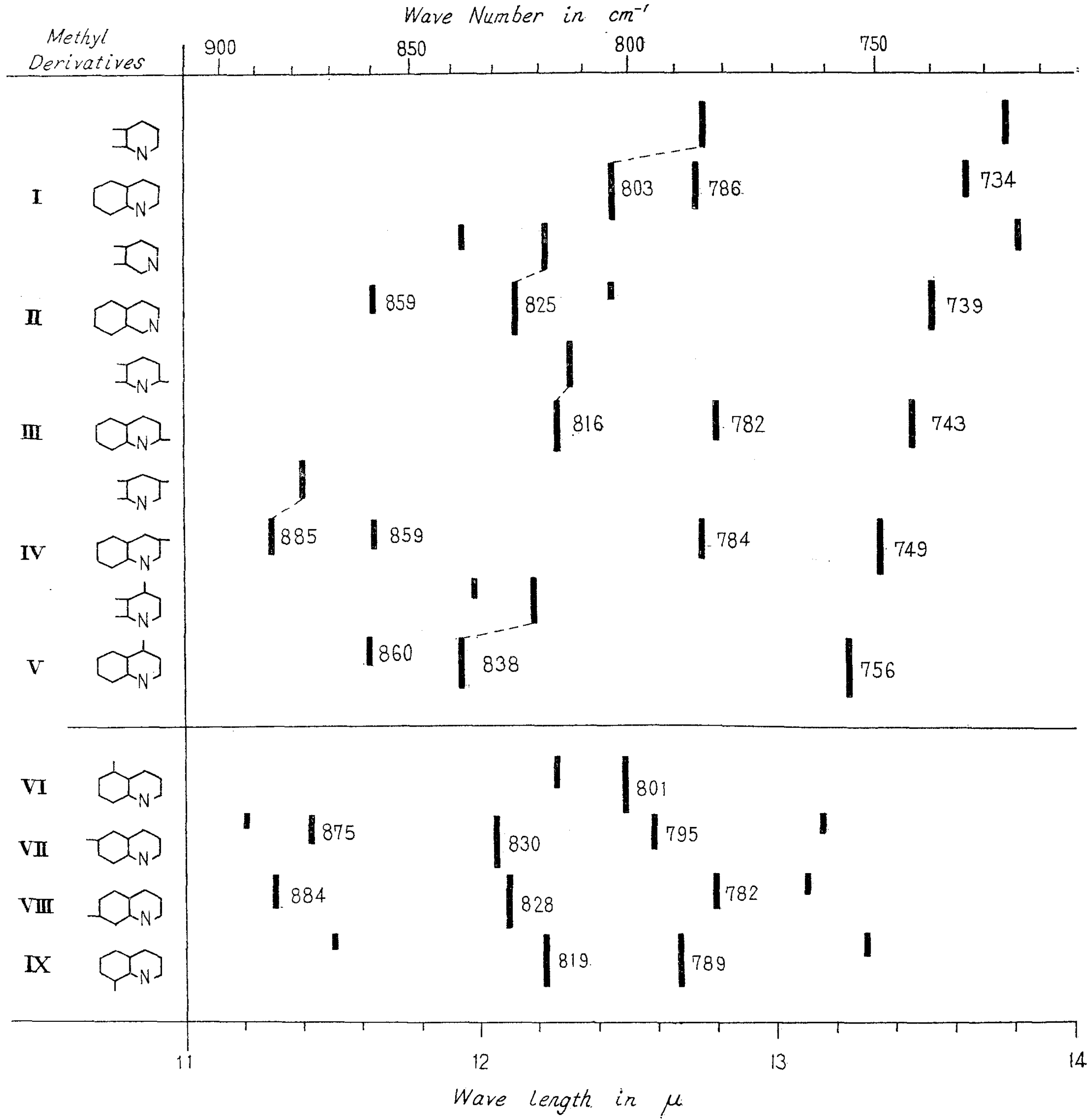


Fig. 2. Position and Intensity of Absorption Bands in Monomethylquinolines (700～900 cm^{-1} range)

differentiated in this way. The displacement of this band, however, is greater than usual, there being, for example, a shift of over 20 cm^{-1} on passing from quinoline to 4-methylquinoline. While it is possible to trace the band derived from the free hydrogen vibration of the heterocyclic ring, and when they are compared with the appropriate type of methyl-substituted pyridines, it is found that a strong band can be identified as this absorption always at a slightly higher frequency than that of comparable methylpyridine. For example, 3-methylquinoline can be compared with 2,3,5-collidine, and a strong band at 885 cm^{-1} of the former can be identified as the absorption derived from two isolated free hydrogen atoms on the heterocyclic ring, which is 7 cm^{-1} higher than that of the latter. A band near 780cm^{-1} of 2- and 3-methylquinolines cannot be interpreted, but usually the strongest band in this region can be reasonably identified as this absorption.

In compounds in which carbocyclic ring is subsituted (Ⅵ～Ⅸ), the bands due to the two rings are closed or overlapped. As indicated above, these compounds do not show a strong band in 730～760 cm^{-1} region. 5-Methyl- and 8-methylquinolines contain three adjacent free hydrogen atoms in both rings and their vibrations result in an extremely strong band near 790 cm^{-1}, with an additional weaker band near 820 cm^{-1} which cannot be interpreted. Both 6-methyl- and 7-methylquinoline strongly absorb near 830 cm^{-1}, corresponding to two adjacent free hydrogen atoms in the carbocyclic ring. In addition, both show a weak band near 880 cm^{-1} which might be associated with the vibration of the remaining isolated hydrogen atom in the same ring. The bands derived from unsubstituted heterocyclic ring, in most cases, also appear at higher frequencies than that of 2,3-lutidine, and it may be concluded that the out-of-plane C-H deformation frequency of pyridine ring is displaced to a higher frequency by condensation with benzene ring than that of the corresponding methyl-substituted pyridines.

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

In aromatic fused-ring compounds, as a bond fixation exists and the lengths of all bonds are not equal, their C=C stretching frequencies are more variable than in simple substituted benzene. Colthup[6] indicated a shift toward higher frequency of the 1600 cm^{-1} band and a broadening of the range of its subsidiary band in α- and β-substituted naphthalenes. It is inferred from the case of alkylpyridines[1] that there are more complicate interactions between the two rings in quinolines and isoquinolines.

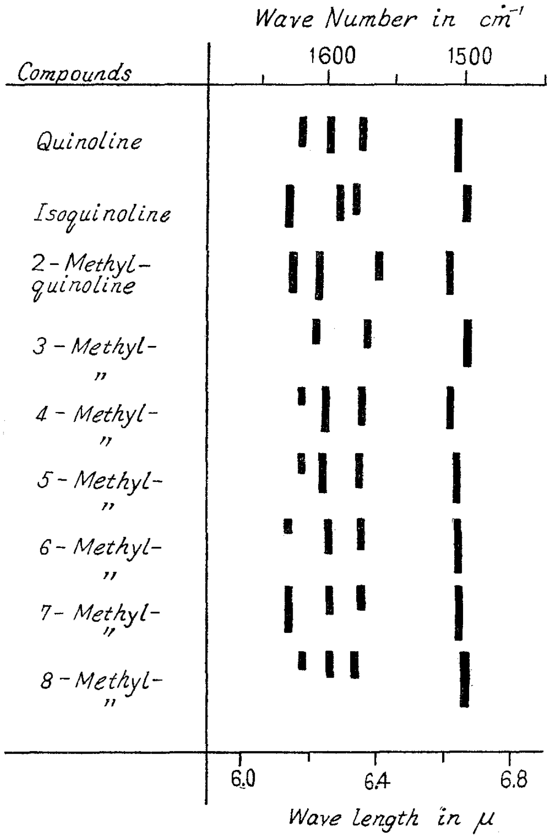
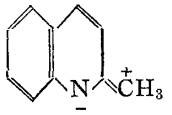
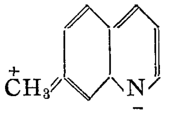


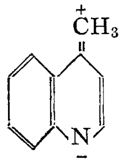
Fig. 3. Position and Intensity of Absorption Bands in Monomethylquinolines. (1450～1650 cm^{-1} range)

As shown in Fig. 3, isoquinoline and most quinolines examined showed complex absorption patterns of four bands in this region, and one additional band appears to be superimposed as compared with two or three bands of the usual benzenes or pyridines. A band near 1500 cm^{-1} in benzenes, which appears at a considerably lower frequency in alkylpyridines,[1] is displaced to a rather slightly higher frequency than 1500 cm^{-1}, and is always strong. The highest frequency band appeared near 1630 cm^{-1} which is higher than in the usual substituted benzene or pyridine. The intensity of this band is particularly variable and seems to have a correlation to the structure.

2-Methyl- and 7-methylquinolines which show this band strongly are expected to have the contribution of ionic structures in which the methyl group conjugates with the ring nitrogen as (III′) and (VIII′), respectively, to their resonance hybrid, while 3-methyl- and 6-methylquinolines, for which such structures cannot be written, do not show this band to any appreciable extent. However, 4-methylquinoline shows this band very weakly in spite of the possibility of such structure as (V′). Therefore, this might be one of the many factors involved. The exact correlations will be established in subsequent papers, with the study of larger number of spectra.


(III′)


(VIII′)


(V′)

The authors express their gratitude to Prof. K. Tsuda of the University of Tokyo for his helpful guidance throughout this work.

Experimental

Samples—Quinoline, and 6-methyl- and 8-methylquinolines were prepared by the Skraup reactions of aniline, *p*-toluidine, and *o*-toluidine, respectively. The Skraup reaction of *m*-toluidine produces a mixture of 5-methyl- and 7-methylquinolines, so that 5-methylquinoline was prepared by the catalytic reduction with Pd-C of 8-chloro-5-methylquinoline, which was obtained by the Skraup reaction of 6-chloro-*m*-toluidine. 7-Methylquinoline was prepared in the same way from 2-chloro-*m*-toluidine. 2-Methylquinoline (quinaldine) was prepared from aniline by the Döbner-Miller condensation. 3-Methylquinoline and 4-methylquinoline (lepidine) were obtained by the condensations of aniline respectively with methacrylaldehyde diacetate and methyl vinyl ketone. Isoquinoline was obtained from isoquinoline fraction of coal-tar base.

All samples were purified by vacuum distillation which followed recrystallisations of their sulfate from ethanol and liberation by alkali.

Method—The spectra were taken with a Perkin-Elmer Model 21 recording spectrometer with a rock salt prism. Samples were determined in 5.0% solution with the cell of 0.1 mm. thickness. CS$_2$ and CCl$_4$ were used as a solvent respectively for 1450$\sim$650 cm^{-1} and 1700$\sim$1450 cm^{-1} ranges.

Summary

The infrared spectra of quinoline, isoquinoline, and seven monomethylquinolines were determined. These compounds gave highly characteristic bands in the finger print region of the spectrum, which seem to be useful in the analysis of tar bases. The out-of-plane C-H deformation frequencies could be correlated with their structure in the same way as substituted benzenes or pyridines by separating the quinolines into the componental carbocyclic and heterocyclic rings. The absorption derived from free hydrogens on heterocyclic ring always appeared at a slightly higher frequency than that of comparable methylpyridines. C=C and C=N stretching frequencies showed more complex patterns and the highest band appeared in most cases near 1630 cm^{-1}, whose intensity is particularly variable and appears to have a correlation to the structures.

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