$CHCl_3$. After drying over Na_2SO_4 and removal of the solvent, the residue was purified by passing through alumina column using ether and 90 mg. (67%) of (XII), m.p. 57~60°, was obtained. *Anal.* Calcd. for $C_8H_6N_2$: C, 73.84; H, 4.61; N, 21.53. Found: C, 73.50; H, 4.64; N, 21.20. U.V. λ_{max}^{MeOH} mμ (log ε): 261 (3.70), 301 (3.46), 313 (3.42).

Picrate: m.p. 205~206°. *Anal.* Calcd. for $C_8H_6N_2 \cdot C_6H_3O_7N_3$: C, 46.80; H, 2.51; N, 19.50. Found: C, 46.72; H, 2.60; N, 19.36.

Summary

The reaction of sodium salt of 3-carboxyquinaldine and formaldehyde gave 2-hydroxyethyl-3-quinolinecarboxylic acid lactone, which was led to the amide, and its oxidation gave 1-hydroxy-2,10-diazaanthracene. 2,10-Diazaanthracene was obtained from this 1-hydroxy compound. 1,7-Naphthyridine was synthesized from 4-chloro-1,7-naphthyridine via 4-hydrazino compound.

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77. Nobuo Ikekawa: Studies on Naphthyridines. IV.[1] Infrared Spectra of Naphthyridines.

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Many data on infrared spectra of polymethylnaphthalenes,[2~4] polychloronaphthalenes,[5] and methylquinolines[6] have been published, but those of naphthyridines have not been reported yet. In the present work, infrared spectra of six 1,6-naphthyridines, four 2,7-naphthyridines, and two 1,7-naphthyridines were determined and the bands of out-of-plane deformation vibration of hydrogen atoms on the naphthyridine ring were compared with those of naphthalenes. Position and intensity of the bands of these compounds are summarized in Fig. 1.

There is little difference between the influence of chlorine atom and of methyl group on the absorption of out-of-plane C-H deformation vibrations, as in the case of naphthalenes.[5] In the out-of-plane C-H deformation frequencies of alkylpyridines,[7] the nitrogen in the ring may be considered as a substituent and the band positions are correlated with the number of adjacent hydrogen atoms remaining in the ring. In substituted naphthalenes and quinolines, the bands due to adjacent free hydrogen atoms on each ring can generally be correlated respectively with the strong absorption between 900 and 700 cm^{-1}. It was found, however, that the spectra of some derivatives of fused ring system showed abnormal absorption depending on the position of free hydrogen atoms on the ring.

The spectra of 1,6-naphthyridine and its derivatives (I to VI) show strong bands in the range of 790~760 cm^{-1} corresponding to three adjacent hydrogen atoms on the A-ring. The compounds possessing two adjacent hydrogen atoms on the B-ring (I to III) exhibit the band near 835 cm^{-1} and the bands of isolated hydrogen on the B-ring of the

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1) Part III: This Bulletin, **6**, 401(1958).
2) American Petroleum Institute Research Project 44, Infrared Spectra (1956).
3) W.L. Mosby: J. Am. Chem. Soc., **74**, 2564(1952).
4) C.G. Cannon, G.B.B.M. Sutherland: Spectrochim. Acta, **4**, 373(1951).
5) L. Cencelj, D. Hadži: *Ibid.*, **7**, 274(1955).
6) H. Shindo, S. Tamura: This Bulletin, **4**, 292(1956).
7) H. Shindo, N, Ikekawa: *Ibid.*, **4**, 192(1956).

compounds (IV to VI) appear in the region of 880 and 860 cm^{-1}. The bands in 820~810 cm^{-1} region of the compounds (I to VI) may be considered to arise from in-plane deformation vibrations of 1,6-naphthyridine ring. 5-Methyl-1,6-naphthyridine (II) was obtained from the Skraup reaction of 4-amino-2-picoline 1-oxide.[8] The structure of this compound is proved by its spectrum showing a band at 834 cm^{-1} due to the two adjacent hydrogen atoms. The bands at 814, 804, and 825 cm^{-1} respectively in 4-chloro-1,7-naphthyridine (VII), 3-methyl-2,7-naphthyridine (VIII), and 1-chloro-3-methyl-2,7-naphthyridine (IX) are thought to arise from two adjacent hydrogen atoms on the ring. The bands near 880 cm^{-1} are due to isolated hydrogen.

Out-of-plane deformation vibrations of 2,7-naphthyridine and1 -chloro-2,7-naphthyri-

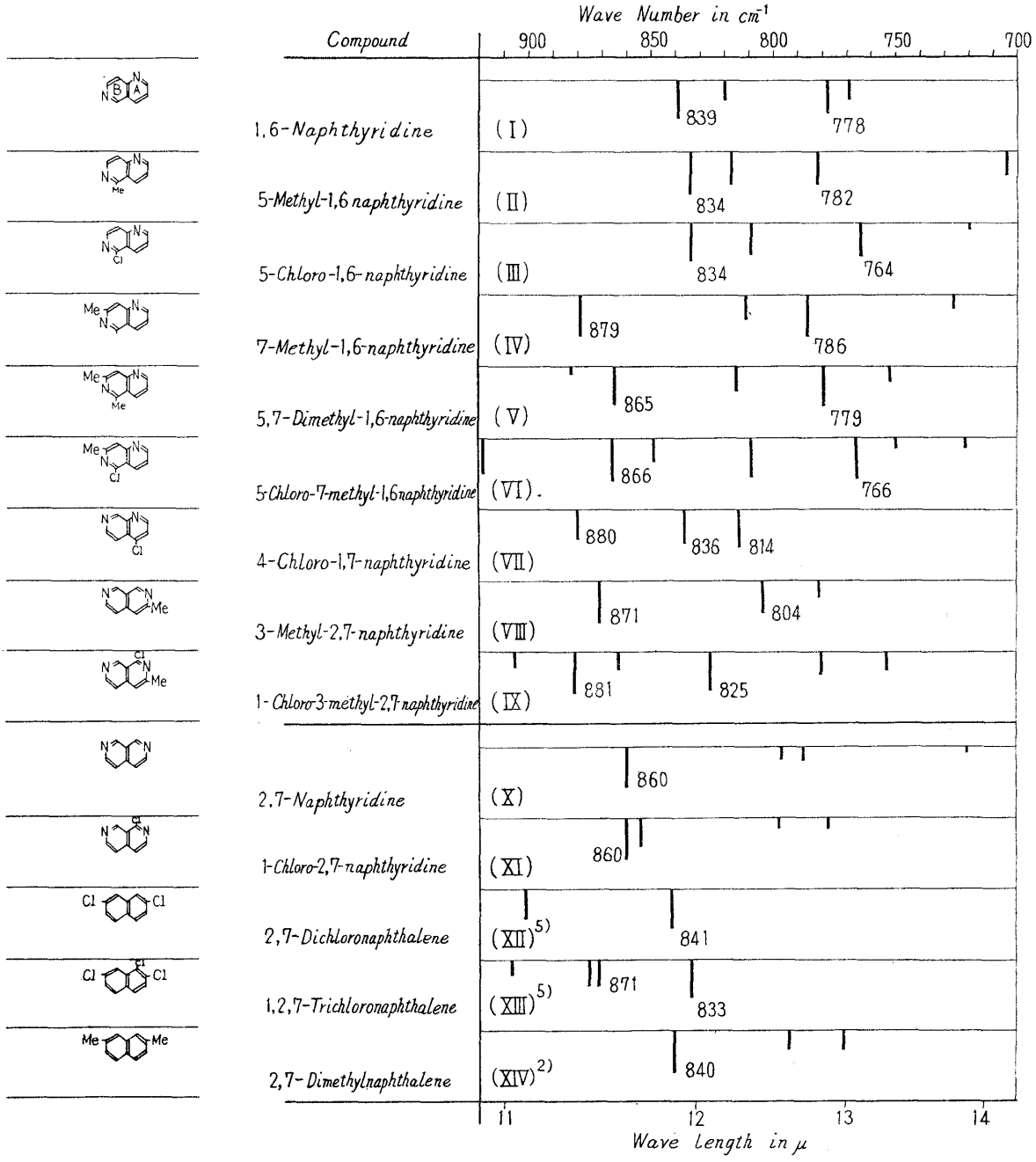


Fig. Ia. Position and Intensity of Absorption Bands

8) T. Kato, F. Hamaguchi, T. Oiwa : This Bulletin, **4**, 178(1956).

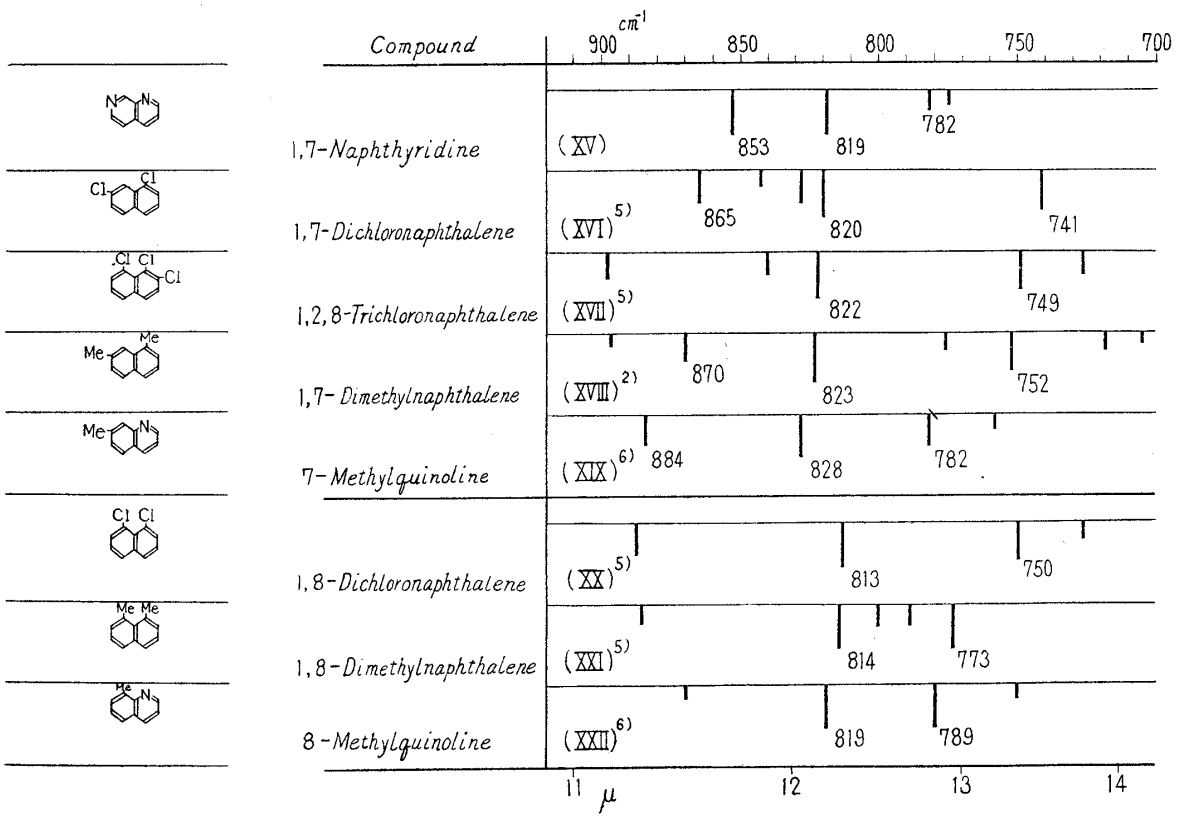
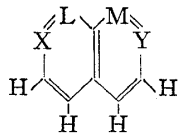


Fig. Ib. Position and Intensity of Absorption Bands

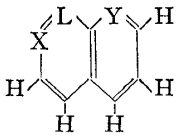
dine show abnormal absorption and these compounds have no band in the region of 840~800 cm^{-1} corresponding to two adjacent hydrogens on the ring, exhibiting only a strong band near 860 cm^{-1}. Naphthalene derivatives possessing free hydrogen in the same positions as in 2,7-naphthyridine show the band near 840 cm^{-1}. Compounds (XII) and (XIV) do not absorb in the region corresponding to isolated hydrogen. It has been found that if two adjacent hydrogen atoms in the two rings are adjoined, abnormal absorption will occur.

When three adjacent hydrogens and two adjacent hydrogens in two rings are adjoined, their absorptions appear in somewhat abnormal position, too, as shown in compounds (XV) to (XVIII). The band in the region of 800~750 cm^{-1} corresponding to three adjacent hydrogen atoms of 1,7-naphthyridine (XV) is very weak and that of compounds (XVI), (XVII), and (XVIII) shifts to a lower frequency, but the bands of 7-methylquinoline (XIX) appear in normal position. The bands at 750, 773, and 789 cm^{-1} in compounds (XX), (XXI), and (XXII), respectively, might be considered to arise from three adjacent hydrogen atoms. The strong bands near 815 cm^{-1} in these compounds cannot be interpreted but may originate from out-of-plane deformation vibrations.

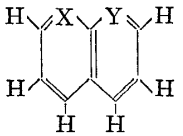
The abnormal absorptions in a fused ring system could be considered to depend on the symmetry of the molecule, but has not been pointed out in any past literature. The compounds showing abnormal absorptions are classified into three groups, namely (A) (X~XIV), (B) (XV~XVIII), and (C) (XX~XXII).



(A)

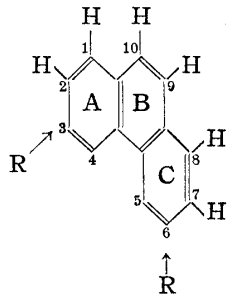


(B)



(C)

X, Y = C-R, N
L, M = C-H, C-R, N



In alkylphenanthrenes, the bands of out-of-plane deformation vibrations of two adjacent hydrogen atoms on the ring shift to a higher frequency when the ring is substituted with alkyl group at 3- or 6-position, as reported by Ochiai, *et al.*,[9] and by Dannenberg, *et al.*[10] This abnormality could be ascribed to the arrangement of free hydrogen atoms belonging to the first group.

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Experimental

Materials—The same samples of naphthyridines reported previously[1,11,12] were used.

Method—The spectra were determined with a Perkin-Elmer Model 21 recording spectrometer with a rock salt prism. All samples were determined in Nujol phase.

Summary

Infrared spectra of twelve kinds of naphthyridines were determined and compared with those of naphthalenes. It was found that in some kinds of compound, out-of-plane deformation vibrations of hydrogen atoms on the ring showed abnormal absorption.

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9) E. Ochiai, T. Okamoto, S. Sakai, M. Natsume : This Bulletin, **5**, 113(1957).
10) H. Dannenberg, U. Schiedt, W. Steidle : Z. Naturforschg., **8b**, 269(1953).
11) N. Ikekawa : This Bulletin, **6**, 263(1958).
12) N. Ikekawa : *Ibid.*, **6**, 269(1958).