Mischprobe mit dem authentischen Präparat des *dl*-Allomatrins zeigte keine Depression.

Zusammenfassung

Durch die katalytische Reduktion des 11-Cyanopyrido[2,3-*b*]chinolizon-(5) (XIII) wurde des 1,2,3,4,7,8,9,10-Octahydrid (XIV) erhalten. Ausgehend vom letzteren (XIV) wurde das *dl*-Allomatridin übergeführt.

(Eingegangen am 15. Juli, 1957)

UDC 547.82:544.621

83. **Hideyo Shindo**: Studies on the Infrared Spectra of Heterocyclic Compounds. IV.(1) Infrared Spectra of Monosubstituted Pyridine Derivatives.

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In the first paper(2) of the series, the infrared spectra of alkylpyridines were correlated with their structures in a closely similar way to that of substituted benzenes, and it was pointed out that the effect of electronegative ring-nitrogen appeared regularly in their spectra.

Systematic investigations on the infrared spectra of substituted pyridines have not been reported as yet and it has been desirable to establish a further correlation between structure and spectra when the compounds possess more varied substituents.(3)

The infrared spectra of amino-(4) and hydroxypyridines(5) have been studied and discussed in view of their tautomerisms. Costa, *et al.*(6) reported the infrared spectra of 4-nitro-, 4-chloro-, and 4-methoxypyridines, comparing them with those of their N-oxides, but no consideration was given on their ring vibrations.

In the present series of work, the infrared spectra of over ten kinds of α-, β-, and γ-substituted pyridines (38 compounds) were determined and correlated with the position and the nature of substituent, and furthermore, how the electronic effect of ring-nitrogen exerts an influence upon the absorption frequencies of ring substituent was examined and discussed, evaluating the ever-proposed σ-values for ring nitrogen.

Some of the spectra obtained are shown in Fig. 1 and discussions will be made below.

I. Ring C-H Out-of-plane Bending Vibrations

It was shown previously(2) that the correlation rules for ring CH out-of-plane bending vibrations of substituted benzenes also hold good for those of alkylpyridines by considering the number of adjacent free hydrogen atoms on the ring. All substituted pyridines examined exhibited characteristic strong absorptions in the region of 700 and 900 cm^{-1}, and, as shown in Fig. 2, they can almost be interpreted by the usual ranges quoted for corresponding substituted benzenes,(7) with the only exception of 3- and 4-ethoxycarbonyl

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* Nishi-Shinagawa, Shinagawa-ku, Tokyo (進藤英世).

1) Part III. H. Shindo: This Bulletin, **4**, 460(1956).

2) H. Shindo, N. Ikekawa: *Ibid.*, **4**, 192(1956).

3) cf. R.N. Jones, C. Sandorfy: "Technique of Organic Chemistry. IX. Chemical Applications of Spectroscopy," 537(1956).

4) C.L. Angyal, R.L. Werner: J. Chem. Soc., **1952**, 2911; J.D.S. Goulden: *Ibid.*, **1952**, 2939; L.C. Anderson, N.V. Seeger: J. Am. Chem. Soc., **71**, 340(1949).

5) J.A. Gibson, W. Kynaston, A.S. Lindsey: J. Chem. Soc., **1955**, 4340.

6) G. Costa, P. Blasina: Z. phys. Chem. (Frankfurt), **4**, 24(1955).

7) L.J. Bellamy: "The Infrared Spectra of Complex Molecules," Methuen & Co., London, 55(1954).

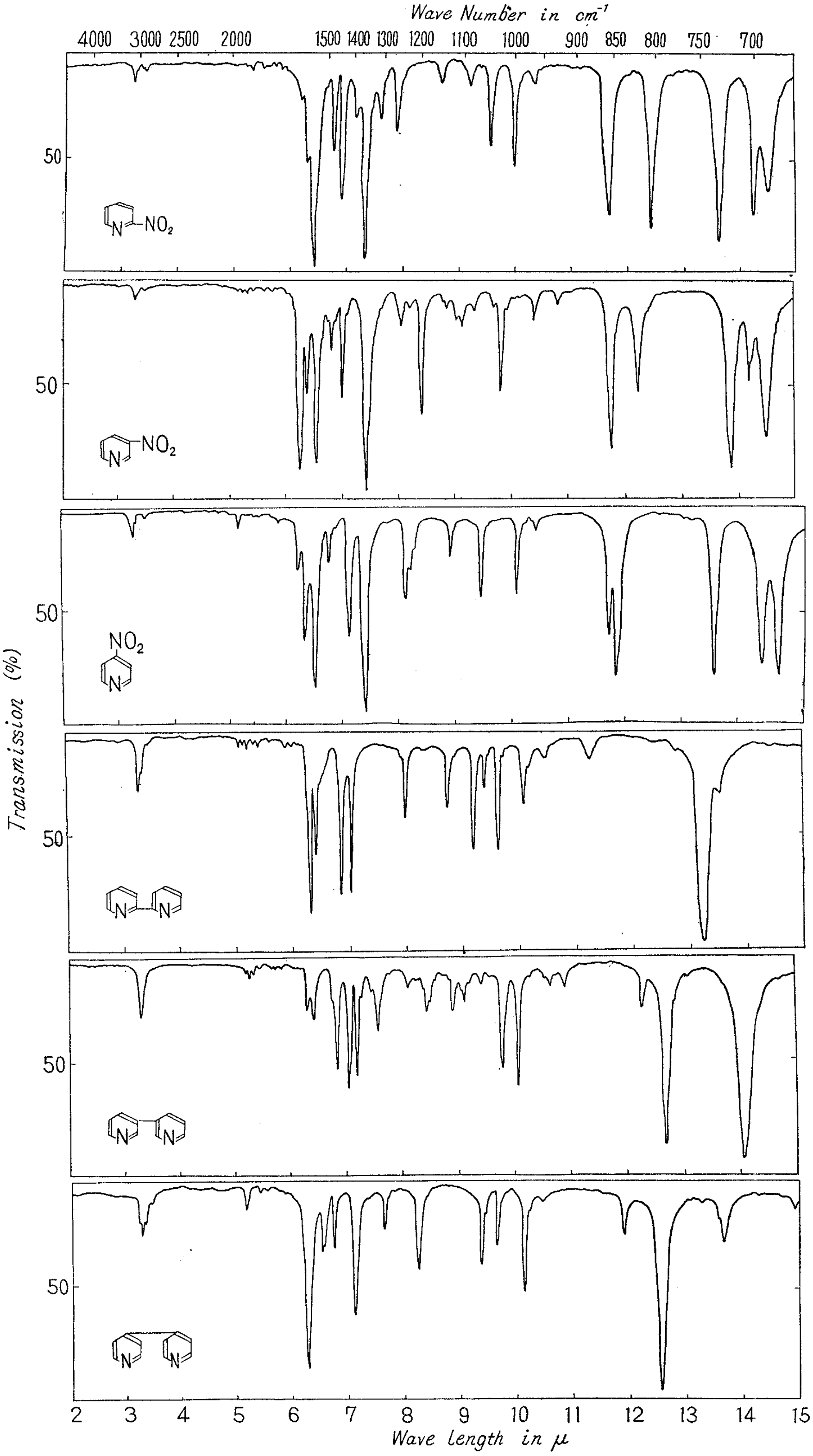

Fig. 1. Infrared Absorption Spectra of Some Substituted Pyridines (1)

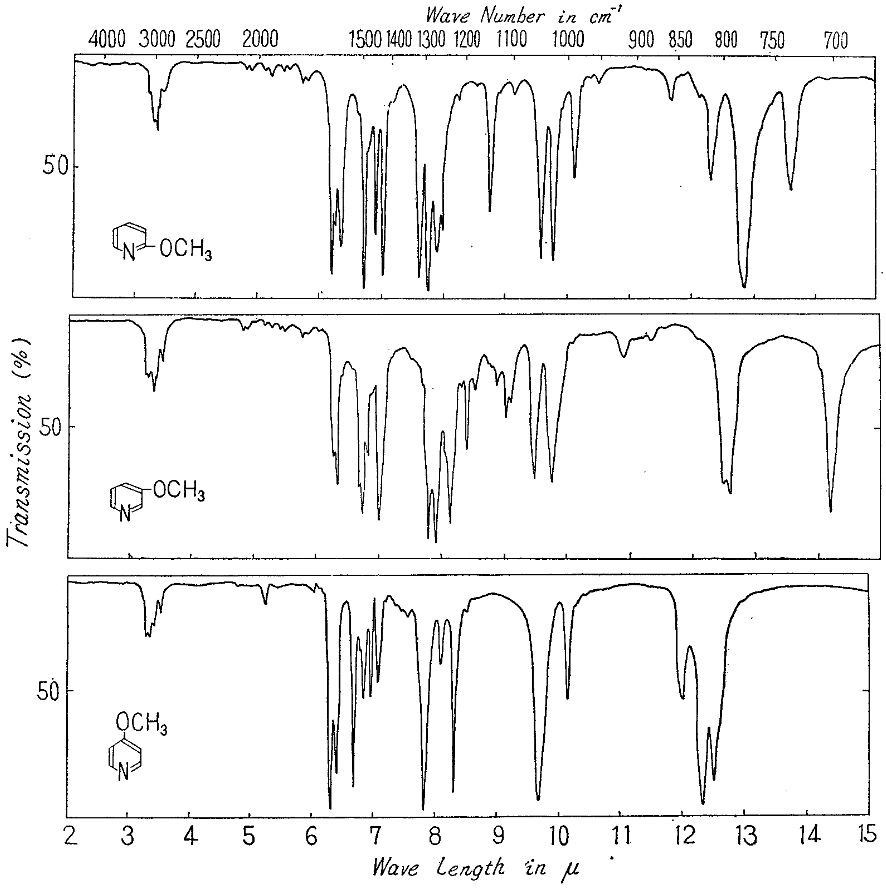

Fig. 1. Infrared Absorption Spectra of Some Substituted Pyridines (2)

derivatives which do not show any strong absorption in these expected regions. Generally, however, β-derivatives absorb at a slightly higher frequency region than *meta*-substituted benzenes and it becomes rather difficult to differentiate β- from γ-derivatives by only this absorption, but they always show an additional very strong absorption between 690 and 730 cm^{-1}, which is more characteristic for β-substitution type.

After all, it is more profitable to use the following as the usual ranges for substituted pyridines.

α-Substituted pyridines (four adjacent free hydrogens) : 740~780 cm^{-1} v. s
(Only nitro derivative absorbs at higher region than this)
β-Substituted pyridines (three adjacent free hydrogens) : 770~820 cm^{-1} m~s
and always 690~730 cm^{-1} v. s
γ-Substituted pyridines (two adjacent free hydrogens) : 790~850 cm^{-1} s

A smaller displacement within each range has a distinct relation with the nature of substituent. As shown in Fig. 2, it was generally found that the presence of a strongly electron-attracting substituent such as nitro or cyano group give rise to a considerably higher frequency shift of these vibrations towards the extreme edge of each expected range, but the appreciable higher frequency shifts were also observed for pyridines with a strongly electron-donating substituent such as amino or methoxyl group. Kross, *et al.*[8] indicated that the depletion of π-electron density in the ring due to the effect of substituents in substituted benzenes results in the displacement of CH out-of-plane bending vibrations to higher frequency, especially in the cases in which a large contribution of quinonoid structure is expected. In three pentamethylpyridines where

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[8] R. D. Kross, V. A. Fassel, M. Margoshes : J. Am. Chem. Soc., **78**, 1332(1956).

only one CH bond remains in the ring, the bending vibrations of α– and γ–CH bonds appeared at a considerably higher frequency than that of β–CH bond, and it was assumed[2)] to be due to the depletion of π–electron density at α– and γ–positions by the electronegative effect of ring nitrogen. The higher frequency shifts observed for pyridines with a strongly electron–attracting substituent can be explained also by the term of further depletion of π–electron density due to an additional electron–attraction by the substituent, in accord with the above assumption. The similar shifts observed for amino– and methoxy–pyridines cannot be explained so easily. In the case of α– and γ–derivatives, it may be explained by the large contribution of *ortho*– and *para*–quinonoid structures which was caused by conjugation between the ring nitrogen and a strongly electron–donating substituent also results in a depletion of π–electron density

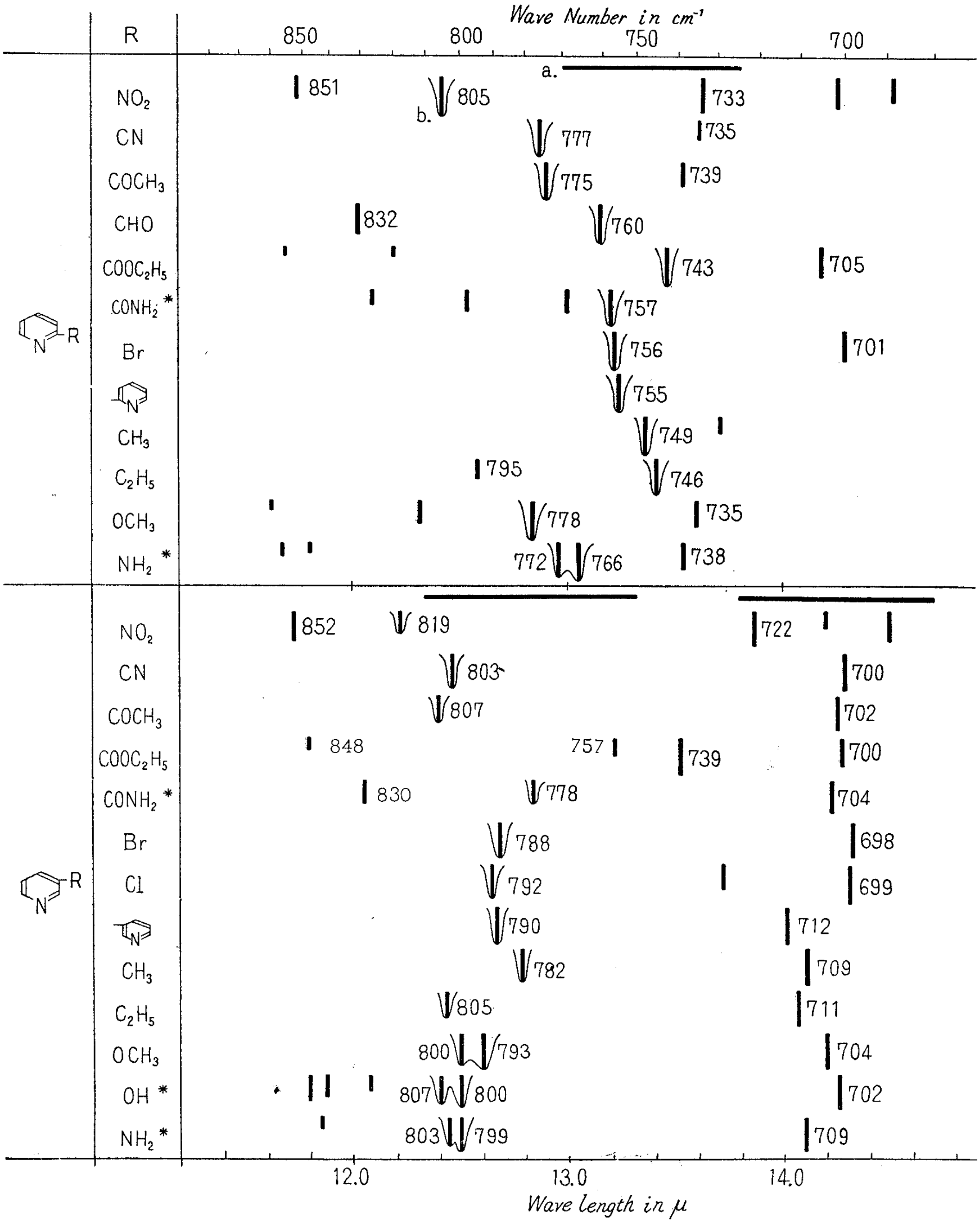

Fig. 2. Position and Intensity of Absorption Bands of Substituted Pyridines (700∼900 cm⁻¹ region) (1)

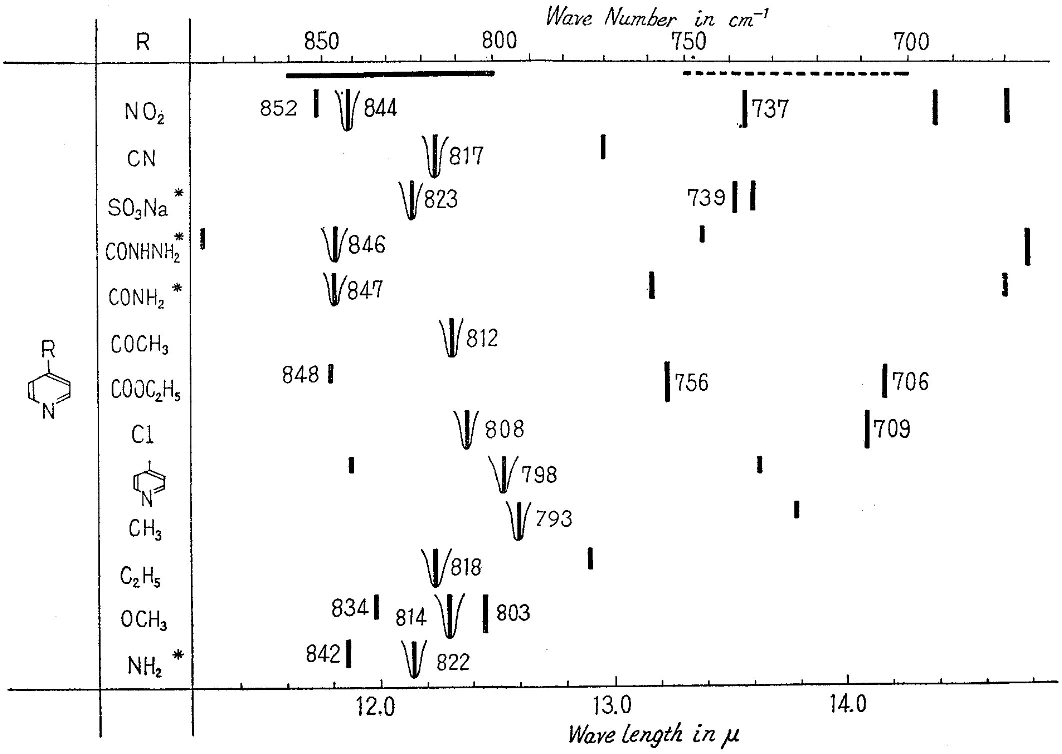

Fig. 2. Position and Intensity of Absorption Bands of Substituted Pyridines (700~900 cm⁻¹ region) (2)

* : Nujol mull; others in CS_2 solution.

a : These horizontal lines represent the overall ranges for the corresponding substituted benzenes.

b : These are absorptions assigned to ring CH out-of-plane bending frequencies.

in the ring, but this does not give any explanation for the shifts similarly observed for β-derivatives, because the β-substituent cannot conjugate with the ring nitrogen and *meta*-methoxy group in aromatic ring exerts a slightly electron-attracting effect to the ring.

Of course, that the ring π-electron density is not the only principal factor determining the exact frequencies is shown, for example, by the fact that a large higher-frequency shift ordinarily observed with ethylbenzenes⁽⁹⁾ and ethylpyridines⁽²⁾ compared to their corresponding methyl derivatives cannot be explained on this basis. Recently, Godar, *et al.*⁽¹⁰⁾ pointed out that 6,7,8,9-tetrahydro-5-cyclohepta[*b*]pyridine showed this absorption at a much higher frequency than could be expected for this type and explained it by the assumption that it is due to the steric inhibition of the vibration of 4-hydrogen on the pyridine by one of the methylene groups of the cycloheptane ring. This steric factor may be another factor determining the frequency and may give an explanation for the higher frequeny shifts in ethyl derivatives described above.

It is notable that three bipyridyls do not show any appreciable shift to a higher frequency. From the studies on their ultraviolet spectra,⁽¹¹⁾ it has been shown that these compounds have a large contribution of quinonoid structures, involving a double bond between both rings, in their excited states. The fact that these bipyridyls show their ring CH-bending vibrations at approximately the mean frequencies between halogen and methyl derivatives, as shown in Fig. 2, seems to indicate that the state of

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9) D. A. McCaulay, A. P. Lien, P. J. Launer : J. Am. Chem. Soc., **76**, 2354(1954).
10) E. Godar, R. P. Mariella : *Ibid.*, **79**, 1402(1957).
11) P. Krumholz : *Ibid.*, **73**, 3487(1951).

the ring CH bonds in these compounds is in just the same conditions as that of pyridine itself, suggesting that there is no appreciable contribution of ionic quinonoid structures in the ground state of these compounds.

II. Characteristic Absorptions between 990 and 1220 cm^{-1}

Bellamy[12)] suggested that a series of weak absorptions in this region shown by substituted benzenes were very characteristic in their frequencies for the type of substitutions. Recently, Randle, *et al.*[13)] found that the absorption near 1020 cm^{-1} in mono–

Table I. Characteristic Absorptions in 990∼1220 cm^{-1} Region

I. 2-Substituted Pyridines

Substituent group	Near 1140 cm^{-1}	Near 1040 cm^{-1}	Near 990 cm^{-1}
NO_2	1147[a] w	1042 m	994 m
CN	1151 w	1045 m	992 m
$COCH_3$	1144 w	1043 m	994 m
CHO	1147 w	1042 w	995 m
$COOC_2H_5$	*b*)	1045 m	995 m
$CONH_2$[e]	1145 w	1045 w	998 m
Br	1144 w	1042 m	986 m
sym. dipyridyl	1145 w	1041 m	993 w
CH_3	1147 m	1049 m	998 w
C_2H_5	1147 m	1050 m	995 m
OCH_3	1140 s	1044 s	998 m
NH_2[e]	1142 s	1040 w	988[a] m

II. 3-Substituted Pyridines

Substituent group	Near 1190 cm^{-1}	Near 1120 cm^{-1}[c]	Near 1020 cm^{-1}
NO_2	1190 m	*d*)	1019 m
CN	1185 m	1121 w	1025 s
$COCH_3$	1193 w	1117 w	1021 m
$COOC_2H_5$	1192 w	*b*)	1026 s
$CONH_2$[e]	1202 s	1125 m	1030 s
Br	1188[a] v.w	1114 w	1007 s
Cl	1186 w	1114 w	1015 s
sym. dipyridyl	1190[a] w	1126 w	1026 m, 998 m
CH_3	1190 w	1122 w	1029 m
C_2H_5	1186 w	1125 w	1025 m
OCH_3	1190 m	1127 w	1022 m
OH[e]	1182 m	1125 w	1022 m
NH_2[e]	1195 w	1130[a] w	1016 m

III. 4-Substituted Pyridines

Substituent group	Near 1210 cm^{-1}	Near 1060 cm^{-1}	Near 990 cm^{-1}
NO_2	1232 m	1057 m	991 m
CN	1208 m	1067 w	990 m
$COCH_3$	1221 w	1065 m	992 w
$COOC_2H_5$	1212 w	1066 m	992 w
$CONHNH_2$[e]	1222 m	1064 w	996 s
$CONH_2$[e]	1225 m	1064 m	1003 m
Cl	1208, 1217 m	1063 m	993[a] v.w, 980 w
sym. dipyridyl	1212 m	1067 w	989 m
CH_3	1220 m	1070 v.w	994 m
C_2H_5	1219 m	*d*)	995 m
OCH_3	1211 s	*d*)	990 m
NH_2[e]	1220 s	1053 v.w	992 s

s : strong m : medium w : weak v.w : very weak

a) Rather broad band, others are very sharp bands. *b*) Overlapped ?

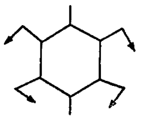
c) Generally not so distinct. *d*) Not distinct band.

e) Nujol mull; others in CS_2 solution.

[12)] L. J. Bellamy : *loc. cit.*, p. 69.

[13)] R. R. Randle, D. H. Whiffen : Trans. Faraday Soc., **52**, 9(1956).

and *para*-substituted benzenes is independent of the nature of substituent, but is related to their mass, assigning them to CH in-plane bending mode as (I). In the case of mono-substituted pyridines, it was found that they always show a series of weak absorptions in this region, the position of which is almost constant regardless of the nature of substituent and is very characteristic for the type of substitution. Observed frequencies are listed in Table I.


(I)

These absorptions are relatively weak in intensity, but are characterized by their sharpness, which makes them easy to identify. For example, these can be distinguished on this basis from the neighboring methyl rocking vibrations,[14] which appear at 1042, 1041, and 1039 cm^{-1} for α-, β-, and γ-picolines, respectively. β-Substituted pyridines are definitely characterized by a single sharp band between 1007 and 1030 cm^{-1}, whose intensity is relatively strong. 3,3′-Bipyridyl is an only exception showing an additional band near 990 cm^{-1}, but all other compounds of this type did not show any absorption near 990 cm^{-1}. Both α- and γ-derivatives show a sharp band between 990 and 1005 cm^{-1}, but they can be differentiated from each other by the presence of another band in the range of 1040$\sim$1050 cm^{-1} and 1050$\sim$1070 cm^{-1} for α- and γ-derivatives, respectively, and furthermore by the presence of a sharp band in the range of 1210$\sim$1230 cm^{-1} only for γ-derivatives. These absorptions may be attributed to ring CH in-plane bending mode involving a considerable ring vibration, from their independence upon the nature of the substituent.

It has been pointed out by Young, *et al.*[15] that the weak absorptions in the region of 1650$\sim$2000 cm^{-1} shown by substituted benzene are very characteristic for the type of substitution in their patterns. Recently, Whiffen[18] explained them as summation tones of their CH out-of-plane bending fundamentals. Corresponding absorptions are also expected in substituted pyridines, but in usual conditions of measurement, the absorptions in this region are so weak and complex as to be of no practical use, except for γ-derivatives which show a weak but distinct absorption at 1920$\sim$1950 cm^{-1} and, as exemplified in Fig. 1, they can be easily differentiated from other two types of substitution.

III. Ring Double-Bond Stretching Vibrations

Substituted pyridines examined usually showed two bands between 1560 and 1630 cm^{-1} and one band near 1500 cm^{-1}, similar to substituted benzenes, due to their ring double-bond stretching vibrations, but their exact frequencies and intensities are more variable. It was previously shown[2] that the relative intensity of two bands between 1560 and 1620 cm^{-1} in methylpyridines has a regular correlation with the position of methyl groups, and γ-methyl derivatives showed normal absorption patterns* where a band on a higher frequency side is more strong, while β-derivatives showed abnormal patterns where the relative intensities are perfectly reversed.

From Fig. 3, it can be found that the relative intensity of these two bands corresponds very regularly to change in the nature of the substituent, and that any electron-donating substituent on the ring (lower part of each column in Fig. 3) has an analogous effect to that of methyl group, but a strongly electron-attracting substituent (upper part of each column in Fig. 3) has a perfectly reverse effect. This behavior is most pronounced in nitro derivatives, the absorpition pattern of 4-nitropyridine being completely the same as that of 3-alkyl- or 3-methoxypyridines, while that of 3-nitropyridine is

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* Most of substituted benzenes show such absorption patterns and it has been shown that only in a few cases the relative intensities are reversed (L. J. Bellamy : *loc. cit.*, p. 61), but any systematic study about this point has not been made.

14) R.R. Randle, D.H. Whiffen : J. Chem. Soc., **1955**, 3497.

15) C.W. Young, R.B. Du Vall, N. Wright : Anal. Chem., **23**, 709(1951).

16) D.H. Whiffen : Spectrochim. Acta, **7**, 253(1955).

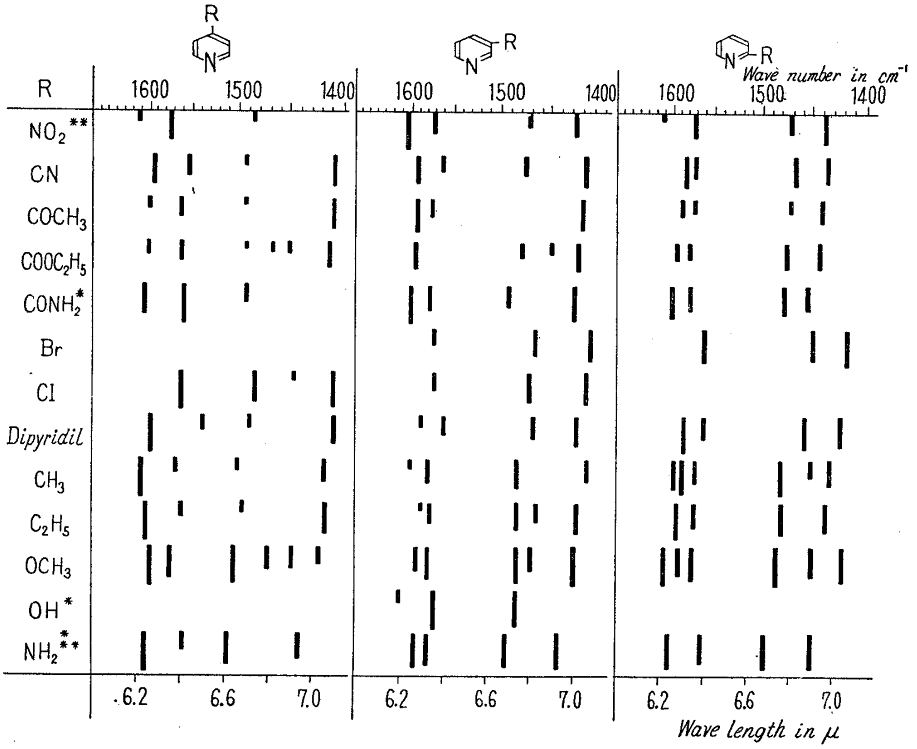

Fig. 3. Position and Intensity of Absorption Bands of Substituted Pyridines (ring double-bond stretching region)

* : Nujol mull; others in CCl_4 or $CHCl_3$ solution.

** : NO_2 asym. stretching and NH_2-deformation frequencies were omitted from this figure.

completely the same as that of 4-alkyl- or 4-methoxypyridines. α-Derivatives showed an almost parallel behavior with that of γ-derivatives. Although there are some exceptions in which these effects are not so clearly observed(e.g. amino and cyano derivatives), these observations seem to indicate that the relative intensity of two bands has a direct relation to the type of π-electron distribution on the ring, and it is concluded that a structure such as increased polarization of the ring induced by ring nitrogen (namely, by electron-donation at 4-position or electron-attraction at 3-position) tends to show a normal absorption pattern, whereas a structure with decreased polarization (namely, by electron-attraction at 4-position or electron-donation at 3-position) tends to show an abnormal pattern.

The fact(2) that nitrotoluenes show parallel behavior with that of the corresponding picolines seems to suggest that the foregoing consideration in pyridines can be extended to other substituted aromatic rings.

IV. Effect of Ring Nitrogen on the Absorption Frequency of a Substituent

It is expected that any mass-insensitive vibration in aromatic compounds will be subject to both inductive and mesomeric effects, and the frequency shifts following changes in the substituents should be a quantitative measure of this resultant effect.(17) In fact, the presence of a linear relationship between the absorption frequency and Hammett's σ-value(18) of a substituent has been illustrated in many kinds of benzene derivatives, and Flett(19) pointed out that since the σ-factor provides a measure of

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17) Recently, Bellamy fully discussed on this point. cf. L.J. Bellamy : J. Chem. Soc., **1955**, 2818, 4221; L.J. Bellamy, Williams : *Ibid.*, **1956**, 2753.

18) a) L.P. Hammett : "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, Chap. VII (1940). b) H.H. Jaffe : Chem. Revs., **53**, 191(1953).

19) M. St. Flett : Trans. Faraday Soc., **44**, 767(1948).

electronic shifts occuring in aromatic ring, infrared frequency shifts can be used as a means of detecting electronic shifts in molecules, in suitable cases.

The foregoing consideration should also hold well for heteroaromatic ring, taking the heteroatom as a substituent in a benzene ring. In the case of substituted pyridines, it is expected that a direct consequence of the electronic effect of ring nitrogen toward each position of the ring should be reflected in an absorption frequendy shift of any substituent on the ring. On the other hand, Jaffe[20] proposed experimental σ-values of 0.93, 0.62, and 0.8 (or 0.4) for 4-, 3-, and 2-position, respectively, for ring nitrogen of pyridine from the rate of esterification of pyridine-carboxylic acids.

Thus, the frequency shifts of some substituted pyridines were carefully compared with those of substituted benzene derivatives, and the electronic effect of ring nitrogen was found to appear regularly on the absorption frequencies, evaluating the σ-values for ring nitrogen derived by Jaffe.

The results are shown in Table II and each group of compounds will be discussed below. Generally speaking, pyridine derivatives always showed an absorption at a considerably higher frequency than corresponding benzene derivatives, and, furthermore, γ-derivatives always showed the absorption at an appreciably higher frequency than β-derivatives, confirming the strongly electronegative effect of the ring nitrogen.

TABLE II. Absorption Frequencies of Ring Substituent

A. Acetylpyridines

Compound	C=O Stretching frequency (cm^{-1} in CS_2)[a]
4-Acetylpyridine	1703
3-Acetylpyridine	1697
2-Acetylpyridine	1704
p-Nitroacetophenone[d]	1701
Acetophenone	1692
p-Hydroxyacetophenone	1685
2-Pyridylaldehyde	1716
Benzaldehyde	1708

B. Ethoxycarbonylpyridines

Compound	C=O Stretching frequency (cm^{-1} in CS_2)[a]
Ethyl isonicotinate	1734
Ethyl nicotinate	1730
Ethyl picolinate	1722, 1750
Ethyl pyrazinate	1730, 1759
3,5-Diethoxycarbonylpyridine	1733
Ethyl *p*-nitrobenzoate[d]	1732
Ethyl benzoate	1724

C. Nitropyridines

Compound	NO_2 Stretching frequency (cm^{-1} in $CHCl_3$)[b]	
	Asymmetric	Symmetric
4-Nitropyridine	1539	1355
3-Nitropyridine	1533	1355
2-Nitropyridine	1548	1355
p-Nitrotoluene[d]	1517	1347

D. Pyridylnitriles

Compound	C≡N Stretching frequency (cm^{-1} in CCl_4)[c]
4-Pyridylnitrile	2245
3-Pyridylnitrile	2242
2-Pyridylnitrile	2245
Benzonitrile[d]	2237

E. Pyridine-carboxylic acids and amides

Compound	C=O Stretching frequency(cm^{-1} in Nujol mull)
Isonicotinic acid	1709
Nicotinic acid	1710
Picolinic acid	1727
Benzoic acid[d]	1691
p-Nitrobenzoic acid	1694
Isonicotinic amide	1683
Nicotinic amide	1681
Picolinic amide	1664

a) approx. 0.3% solution, cell thickness : 1.0 mm.
b) approx. 3% solution, cell thickness : 0.1 mm.
c) approx. 0.5% solution, cell thickness : 1.0 mm.
d) These benzene derivatives were measured at the same time for comparison.

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20) H. H. Jaffe : J. Chem. Phys., 20, 1554(1952).

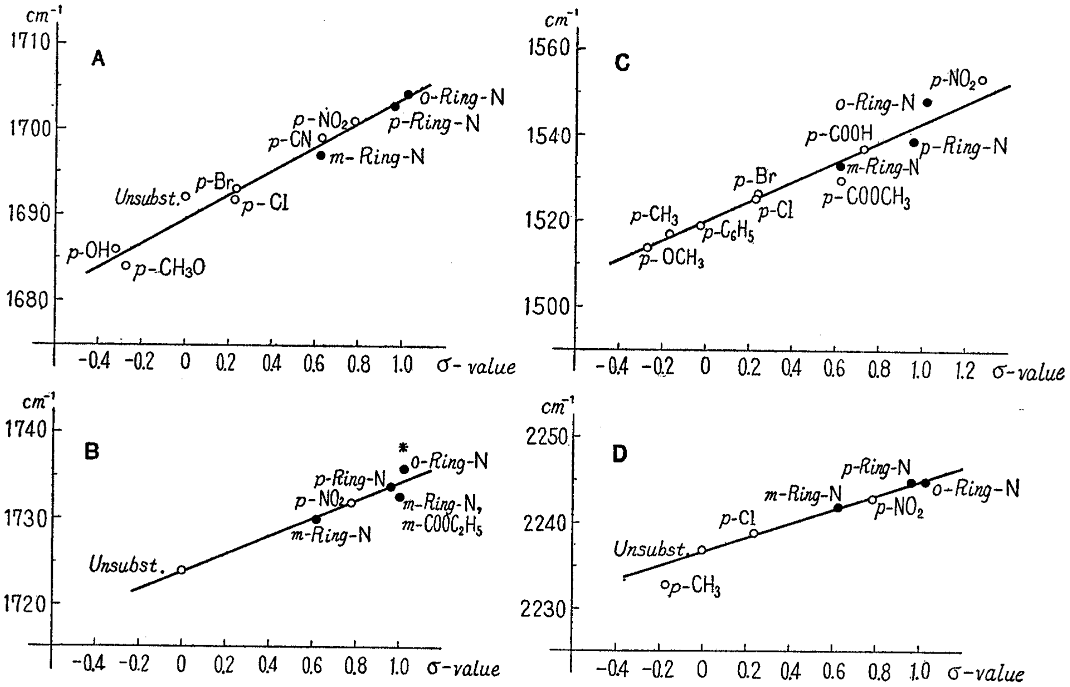

Fig. 4. Infrared Frequency vs. Hammett's Substituent Constant for :
A) acetyl derivatives, B) ethoxycarbonyl derivatives,
C) nitro derivatives, and D) cyano derivatives.
○ : substituted benzene derivatives
• : pyridine derivatives (* mean frequency of double bands)

I) Acetylpyridines—It has been shown by Fuson, *et al.*[21] that there is a linear relationship between the carbonyl frequencies of substituted acetophenones and the σ-values of the substituents. In Fig. 4-A, the carbonyl frequencies of 4- and 3-acetylpyridines in dilute carbon disulfide solution are plotted against the values of 0.96 and 0.62, respectively, and it was found that these two points lie fairly close to the same straight line as that of substituted acetophenones, confirming the validity of these σ-values for ring nitrogen. 2-Acetylpyridine absorbed at the highest frequency among the three, and a marked deviation will be caused if it is plotted against the value of either 0.8 or 0.4, which was derived from two different reactions by Jaffe,[20] and to form a linear plot the value of about 1.02 must be given as the σ-value for the 2-position of ring nitrogen. Although Jaffe[20] stated that Hammett's equation may not be applicable to reaction at side chain vicinal to an aza-nitrogen, the value of 1.02 is useful, at least in infrared frequency considerations, as was also verified later.

II) Ethoxycarbonylpyridines—As shown in Fig. 4-B, the carbonyl frequencies of 4- and 3-ethoxycarbonylpyridines also confirmed the validity of the σ-values for ring nitrogen by Jaffe.

2-Ethoxycarbonylpyridine showed in dilute carbon disulfide solution two bands in the C=O frequency region, weaker but sharp absorption at 1750 cm^{-1}, and a strong absorption at 1722 cm^{-1}, which is lower than that of ethyl benzoate (1724 cm^{-1}). Repeated purifications of the sample gave the same result and the cause of the double bands is not clearly understood. It was noticed, however, that the mean value of these two frequencies gives an approximate linear plot when it is plotted against the value of 1.02, as shown in Fig. 4-B.

Monoethoxycarbonylpyrazine also showed two absorptions in this region, a strong absorption at 1730 cm^{-1}, and a weaker one at 1759 cm^{-1}, both of which are much higher

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[21] N. Fuson, M.L. Josien, E.M. Shelton : J. Am. Chem. Soc., **76**, 2526(1954).

than those of 2-ethoxycarbonylpyridine, showing an additional electronegative effect of the *meta* ring-nitrogen. The presence of two rotational isomers,[22] in which the extent of dipolar interaction between C=O group and the ring nitrogen differs in the two with a consequential separation of C=O frequency, is one possible cause. However the fact that the relative intensity of the two bands did not change to any appreciable extent following the change of concentration in non-polar solvent* did not support this view. Fermi degeneracy is another possible cause and the nature of these two frequencies described above seems to support this view. This situation is similar to that of benzoyl chlorides,[19,23] which also show double bands in C=O frequency region. 2-Pyridylaldehyde showed a single absorption at 1716 cm^{-1}, which is considerably higher than that of benzaldehyde (1708 cm^{-1}). Therefore, the appearance of double bands may be a characteristic phenomenon of the ester carbonyl vicinal to an aza-nitrogen.

3,5-Diethoxycarbonylpyridine showed a single absorption at 1733 cm^{-1} which is appreciably higher than that of 3-ethoxycarbonylpyridine (1730 cm^{-1}) and gave an approximately linear plot when it was plotted against the sum of σ-values of *meta*-$COOC_2H_5$ group and of ring-N for 3-position, as shown in Fig. 4-B, suggesting that the effect of ring nitrogen appears on the frequency additively to that of other substituent.

III) Nitropyridines — It has been pointed out by Kross, *et al.*[24] that the asymmetric nitro stretching frequency of substituted nitrobenzenes has a linear relationship with the σ-value of the substituent, and, as shown in Fig. 4-C, it was found that the frequencies of nitropyridines also form a reasonably linear plots with the same σ-values that were used in carbonyl frequencies. Kross, *et al.*[24] used σ^*-values[18b] instead of σ-values for *p*-nitro and *p*-carboxyl groups in forming this relation, but for *para* ring-nitrogen it seems to be unnecessary to give the larger σ-value. It was shown[24] that the nitro symmetric stretching frequencies is in part influenced by the C-N stretching motion and compounds with an electron-attracting substituent show it at a nearly constant frequency. In accord with this, three nitropyridines showed this absorption at a constant frequency of 1355 cm^{-1}.

IV) Pyridylnitriles[25] — C≡N stretching frequencies of three pyridylnitriles in dilute carbon tetrachloride solution also gave linear plots with σ-values, as shown with the data of substituted benzonitriles[19] in Fig. 4-D, further confirming the σ-values for ring nitrogen.

The carbonyl frequencies of pyridine-carboxylic acids[20] and their amides in solid state (Table II) did not show any reasonable shifts. For example, that of 2-acid amide group is at the lowest of the three in contrast with the results of other carbonyl frequencies in solution state, suggesting the importance of working in dilute non-polar solution when comparison of intramolecular effect is being sought.

From foregoing observations, it was concluded that any correlation rule established in substituted benzene derivatives between the absorption frequencies and σ-values of the substituents can be extended to pyridine derivatives by using the σ-values of 0.93, 0.62, and 1.02 respectively for 4-, 3-, and 2-position of pyridine. These correlations permit the frequency of pyridine derivatives to be predicted from data of benzene

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[22] cf. for example, J.L.H. Allan, G.D. Meakins, M.C. Whiting: J. Chem. Soc., **1955**, 1874; L.J. Bellamy, L.C. Thomas, P.L. Williams: *Ibid.*, **1956**, 3704.

[23] R.S. Rasmussen, R.R. Brattain: J. Am. Chem. Soc., **71**, 1073(1949).

[24] R.D. Kross, V.A. Fassel: *Ibid.*, **78**, 4225(1956).

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[26] Costa, *et al.* also found that CO frequency of these compounds lies in the range of 1695~1720 cm^{-1}, with the *ortho* derivatives showing the highest value. cf. G. Costa, E. Pauluzzi, Univ. studi. Trieste, Fac. Sci. Ist. chim., No. 12, 15(1956) (C.A., **49**, 4823(1957)).

* Only $CHCl_3$ solution gave a single absorption at 1723 cm^{-1}.

derivatives as well as from those of pyridines with other types of substitution. Furthermore, it is expected that this method of prediction of the frequeucy can be applied to other heteroaromatic compounds of nitrogen, such as pyrazine or pyrimidine derivatives, although in the fused ring system, such as quinoline, ring nitrogen may require different σ-values.

A strongly electronegative effect of ring nitrogen prevents the appearance of aromatic conjugation effect upon absorption frequencies, in many cases, to such an extent that there occurs a displacement of the frequency to the usual region of unconjugated compounds. For example, ethyl isonicotinate exhibits its carbonyl frequency at 1734 cm^{-1}, which is rather in the region of unconjugated esters of 1750~1735 cm^{-1} than in that of aryl esters, 1730~1717 cm^{-1}. Therefore, a care must be taken of this fact in the interpretation of the spectra of heteroaromatic compounds with nitrogen.

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Experimental

Materials—4-Nitro- (m.p. 50°), 4-chloro- (picrate, m.p. 144°), and 4-methoxypyridines (b.p_{30} 92~94°) were prepared by deoxygenation(27) of the corresponding N-oxides. 3- and 2-Nitropyridines (m.p. 55° and 71°) were prepared by oxidation(28) of the corresponding aminopyridines with perhydrol. The pyridylnitriles were prepared by dehydration(29) of the corresponding acid amides with P_2O_5. 2- and 3-Acetylpyridines (b.p. 190° and 220°) were prepared by ester condensation(30) of the corresponding ethyl carboxylate. 3-Chloro- and 3-bromopyridines (b.p. 148~149° and 172~173°) were prepared by Gattermann reaction(31) of 3-aminopyridine. 2-Pyridylaldehyde was prepared by the action of Ac_2O on α-picoline N-oxide.(32) 2-Bromopyridine(33) was prepared from 2-aminopyridine, 3-hydroxy-(34) and 3-methoxypyridines(35) from 3-aminopyridine, and 2-methoxypyridine by direct methylation of 2-pyridone.(36) Three dipyridyls were supplied by Prof. J. Haginiwa of the University of Chiba, 4-acetylpyridine was kindly supplied by Dr. N. Sugimoto of Osaka Laboratory of Gohei Tanabe & Co., ethoxycarbonylpyridines, acid amides, and aminopyridines were supplied by Mr. H. Mishima of this Laboratory, 4-sodium sulfonate was supplied by Mr. S. Sakai of the University of Tokyo, and 3,5-diethoxycarbonylpyridine was supplied by Mr. N. Ikekawa of the University of Tokyo. Isonicotinic acid hydrazide used is the commercial product of this company.

Method—Infrared spectra were measured with a Perkin-Elmer Model 21 double-beam spectrophotometer provided with a NaCl prism. Measurement of solution spectra was made as a 5~6% solution in CS_2 with the cell of 0.1 mm. thickness, and the region of 1400~1700 cm^{-1} as the same concentration in CCl_4.

2-Nitropyridine and 4,4′-dipyridyl are not so soluble and they were measured as 0.5~0.6% solution in CS_2, and the regions of 1400~1700 cm^{-1} and 850~900 cm^{-1} as 5~6% solution in $CHCl_3$.

For comparison of small frequency shifts, the measurements were made under the same conditions and the same time for each group of compounds, and the mean value of three measurements was adopted for every compound. Chart scale of 20 cm./μ was applied, scanning very slowly. Detailed conditions of measurements for each case are described under Table II.

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Summary

The infrared spectra of over ten kinds of α-, β-, and γ-substituted pyridines (38 compounds) were determined. The displacement of ring CH out-of-plane bending frequencies following the change in nature of the substituent as well as in its position was discussed. A series of weak absorptions in the region of 990 and 1220 cm^{-1} was found to be very characteristic for the type of substitution. The relative intensity of the two bands between 1550 and 1620 cm^{-1}, which originate in ring double-bond stretching vibrations, was found to be directly related to the type of π-electron distribution on the ring. The electronic effect of ring nitrogen toward each position of the ring was found to appear regularly as a frequency shift in the absorption of ring substituent. The linear correlations between the frequencies and σ-values of the substituents in substituted benzene derivatives could be extended to the substituted pyridines, by using the σ-values of 0.93, 0.62, and 1.02 respectively for 4-, 3-, and 2-position of the pyridine.

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