UDC 547.823 : 544.621

144. **Hideyo Shindo** : Studies on the Infrared Spectra of Heterocyclic Compounds. VII.[1] Hydrogen-Bond Effect on Pyridine 1-Oxide and its Derivatives.

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In previous papers, the strong absorption in the region of 1200 and 1300 cm^{-1} in the infrared spectra of pyridine 1-oxide and its derivatives was assigned to their characteristic N-O stretching frequencies,[2] and the correlation between their frequencies and the nature of ring substituents was pointed out and discussed.[3]

In the present study, infrared investigation was made on the hydrogen-bond effect in pyridine 1-oxide and its derivatives with some proton donors. The assignment for N-O stretching frequency could be further confirmed by observing the spectral change of the N-oxide compounds following hydrogen-bond formation with methanol in non-polar solvent, and the hydrogen bonding power of the variously substituted derivatives was estimated in terms of the magnitude of shift of the bonded OH stretching frequency, correlating it to the nature of ring substituent. Furthermore, the electronic effect of the N-oxide function under solvated state was examined and discussed.

I. Solvation Effect of Methanol and Water

The infrared spectrum of pyridine 1-oxide in carbon disulfide solution containing methanol in various ratios is shown in Fig. 1. The most remarkable change is observed for the strong band at 1265 cm^{-1}, which markedly diminishes in intensity with increasing concentration of methanol accompanying the appearance of a complementary new band in a lower frequency near 1250 cm^{-1}, and at the concentration of 0.6*M* methanol the strong band at 1244 cm^{-1} becomes predominant.

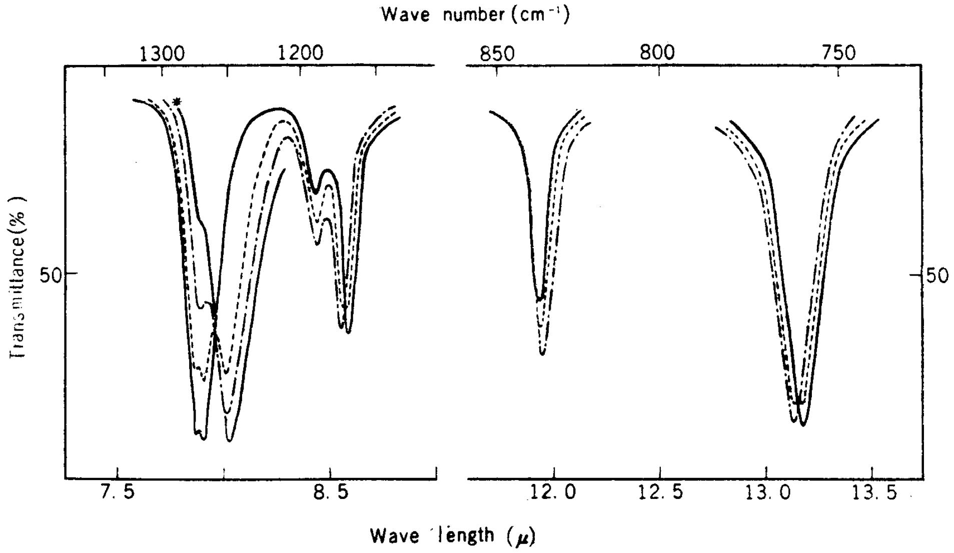


Fig. 1. Change in the Infrared Spectrum of Pyridine 1-Oxide on adding Methanol

——— 0.03*M* in CS_2 —·—·— +0.3*M* MeOH

········ +0.15*M* MeOH   *——— +0.6*M* MeOH

[*1] Nishi-shinagawa, Shinagawa-ku, Tokyo (進藤英世).

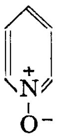
[1] Part VI. H. Shindo : This Bulletin, **7**, 407(1959).

[2] *Idem.* : *Ibid.*, **4**, 460(1956).

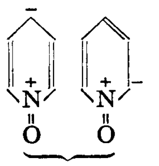
[3] *Idem.* : *Ibid.*, **6**, 117(1958).

Such a behavior is that expected only for N–O stretching absorption and it is considered that the hydrogen-bond formation between methanol and oxygen of the N-oxide group like (IV) prevents the contribution of mesomeric structure like (II) in the resonance system of pyridine 1-oxide (I–III), and the resultant decrease in the double-bond character of N–O bond causes a displacement of its stretching frequency to a lower frequency.

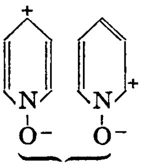
The hydrogen-bond effect in the ultraviolet spectra of N-oxide compounds has been extensively studied by Kubota[4] and it has been shown that their absorption maxima shifted markedly to a shorter wave-length following hydrogen-bond formation, which was also attributed to the decrease in the contribution of mesomeric structure (II).



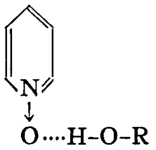
(I)



(II)



(III)



(IV)

The formation of hydrogen-bond was clearly indicated by the OH absorption of methanol. As will be discussed later, on dissolving pyridine 1-oxide in dilute carbon tetrachloride solution of methanol, a broad band due to hydrogen-bonded OH link appeared with its maximum at 3360 cm^{-1}. It is well known, in general, that a stretching frequency shifts to a lower frequency in a solvent with a larger dielectric constant, irrespective of the participation of hydrogen bond, but the behavior in this case differs from that involving hydrogen-bond formation. On adding acetone, which does not possess an active hydrogen but has a large dielectric constant, instead of methanol, the band at 1265 cm^{-1} showed only a minor shift to a lower frequency continuously with increasing concentration of acetone, and even in solution containing 10% of acetone the shift was only 5 cm^{-1}.

On the other hand, as can be seen from Fig. 1, no such distinct shift was observed in any other bands of pyridine 1-oxide. The bands at 1182, 1166, and 1014 cm^{-1} appeared at 1181, 1168, and 1014 cm^{-1}, respectively, in solution containing 0.6*M* methanol, allowing the assignment of ring CH in-plane bending and ring vibrations for the former two and the latter, respectively. The band at 759 cm^{-1} showed an appreciable shift to a higher frequency to 762 cm^{-1}, while that at 669 cm^{-1} did not show any shift, and these are attributable to ring CH out-of-plane bending vibrations, being in agreement with the result reported by Ōi[5] on mono-substituted benzenes. The band at 841 cm^{-1}, which was first assigned to N–O stretching mode[6] and has been recognized to be also a characteristic absorption for the N-oxide compounds,[3,7] was not so sensitive to hydrogen-bond formation, showing a shift of only 3 cm^{-1} to a lower frequency on adding 0.6*M* methanol, and this band is assumed to be due to some coupled vibration involving some contribution of the N–O mode. If this band were due to N–O bending mode, it should show a shift to a higher frequency by methanol, but this is not the case.

A similar phenomenon was also observed for most of substituted derivatives, but N–O stretching frequency in some of these compounds showed this change in a more complex manner, as illustrated in Fig. 2. In 4-methyl derivative, bonded N–O band first appearing near 1245 cm^{-1} again diminishes in intensity as the concentration of me-

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[4] a) H. Hirayama, T. Kubota : Ann. Repts. Shionogi Research Lab., **2**, 121(1952). b) T. Kubota: Yakugaku Zasshi, **74**, 831(1954). c) T. Kubota : *Ibid.*, **77**, 785(1957).

[5] N. Ōi : Yakugaku Zasshi, **77**, 501, 504(1957).

[6] M. Ito, N. Hata : Bull. Chem. Soc. Japan, **28**, 260(1955).

[7] A.R. Katritzky, *et al.* : J. Chem. Soc., **1958**, 2192, 2195.

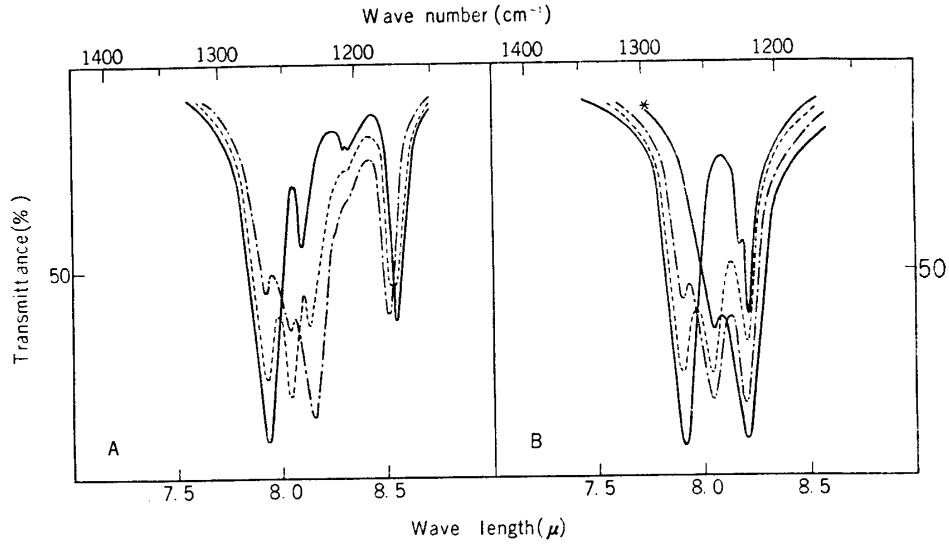

Fig. 2. Hydrogen-bond Effect on the N–O Stretching Frequency

A : 4-Methylpyridine 1-oxide B : 2-Methylpyridine 1-oxide

——— $0.03M$ in CS_2 –·–·– $+0.4M$ MeOH

········ $+0.2M$ MeOH *——— + ca. $3M$ MeOH (in CCl_4)

thanol increases, accompanied with an enhancement of the second band appearing near $1230\,cm^{-1}$, and at a sufficiently high concentration, the strong band at $1227\,cm^{-1}$ becomes predominant. Such a behavior was observed for 3–methyl and 4–methoxy derivatives as well as 2– and 4–methyl derivatives, while simple behavior was observed for 4–nitro, 4–chloro, 4–ethyl, and 2,4–dimethyl derivatives as well as pyridine 1–oxide.

As a reason for such complex behavior, following two possibilities can be considered: i) The presence of two different states during the formation of hydrogen bond, wherein N–oxide and methanol molecules bind in 1:1 and 1:2 ratio, respectively, and ii) mechanical interaction between the vibrations. The first possibility, however, seems to be unlikely because of the following reasons: i) 2,4–Dimethyl derivative in which a larger basicity is expected for the N–O bond than those of 2– and 4–methyl derivatives did not show this phenomenon, and ii) the same phenomenon was observed for 2– and 4–methyl derivatives on adding isopropanol and *tert*–butanol, where such a duplicate bonding should be considerably inhibited from steric view–point, in particular, in 2–methyl derivative. On the other hand, all the spectra showing this phenomenon have a satellite band in a lower frequency side of the N–O band and the observed behavior can be reasonably explained as being due to vibrational interaction between these two frequencies. In 4–methyl derivative, Fermi resonance is assumed to occur between the medium band at $1236\,cm^{-1}$ and the bonded N–O band appearing near $1240\,cm^{-1}$, this interaction is considered to become more serious as the concentration of methanol increases because of the gradual displacement of the bonded N–O peak to a lower frequency owing to the increase in dielectric constant of the medium, and, at sufficiently high concentration, the contribution of N–O stretching mode can be replaced gradually by the lower frequency band, resulting in its enhancement. In 2–methyl derivative, similar interaction can be assumed to occur with the medium band at $1217\,cm^{-1}$, which corresponds to the band shown by most of the N–oxides in the range of 1150 and 1200 cm^{-1} and has a characteristic of showing slight shift to a higher frequency by methanol.

On the other hand, N–O stretching frequencies in acetyl and ethoxycarbonyl derivatives did not show any appreciable shift on addition of methanol, and in 3–methyl derivatives the magnitude of shift was considerably smaller than those observed in other methyl derivatives. All these compounds are those which showed[3] a considerable deviation in the linear relation between N–O frequency and σ–value of the substituent, and the above observations indicate that in these cases some vibration mode other than N–O stretching mode also considerably contributes to the observed N–O stretching absorptions. In carbon tetrachloride solution containing 10% methanol these compounds showed a shift of only 5~15 cm^{-1}, in contrast to the larger shift of 20~40 cm^{-1} in most of the N–oxides, as shown in Table I. 3,5–Dimethyl derivative, which shows its N–O frequency at abnormally high frequency of 1319 cm^{-1}, shows the band at 1170 cm^{-1} with the comparable strength, and as shown in Table I, both showed a shift to a lower frequency by the same magnitude by methanol and water, suggesting that in this case N–O stretching mode contributes to these two absorptions to approximately the same extent.

TABLE I. N–O Stretching Frequencies of Substituted Pyridine 1–Oxides in Solvated State

Substituent	σ–Value	ν_{N-O} (cm^{-1}) in					
		CS_2 or CCl_4	10% MeOH[a)]	(MeOH)[b)]	$\Delta\nu$	H_2O[b)]	$\Delta\nu$
4–NO_2	0.778	1303	1269	(1269)	−34 (−34)	1248	−55
3–CN	0.678	1307	1289		−22		
			1267		−40	1258	−49
4–CN	0.628	1301				1242	−59
4–$COCH_3$	0.516	1256	1244		−12	1235	−21
4, 4–Bipyridil			1238	(1230)		1222	
4–Cl	0.227	1269	1236	(1230)	−33 (−39)	1219	−50
Nil	0.000	1264	1235	(1224)	−29 (−40)	1217	−47
3–CH_3	−0.069	1283	1268		−15	1263	−20
3,5–$(CH_3)_2$	−0.138	1319	1312		− 7	1308	−11
		1170	1163		− 7	1160	−10
4–C_2H_5	−0.151	1260	1223	(1218)	−37 (−42)	1214	−46
4–CH_3	−0.170	1260	1242 sh.		−18		
			1223	(1215)	−37 (−45)	1213	−47
4–OCH_3	−0.268	1240	1208	(1204)	−32 (−36)	1203	−37
4–$OCH_2C_6H_5$	−0.416	1238	1203	(1203)	−35 (−35)	1203	−35
4–NH_2	−0.660		1199	(1198)		1198	
2–CH_3		1260	1240		−20		
			1218		−45	1215	−48
2,4–$(CH_8)_2$		1248	1227	(1218)	−21 (−30)	1213	−35
2,6–$(CH_8)_2$		1255	1230		−25	1216	−39
2,4,6–$(CH_3)_3$		1247	1225	(1215)	−22 (−32)	1212	−35

a) approx. 1% solution; cell thickness, 0.2 mm.
b) AgCl windows; thickness, approx. 0.025 mm.

Among several bands observed in lower frequency region, ring CH out–of–plane bending frequency could be selected by the characteristic of showing an appreciable shift to a higher frequency on addition of methanol. For example, in 4–substituted derivatives the band near 820 cm^{-1} showed an appreciable shift to a higher frequency, while that near 760 cm^{-1} did not show any shift, indicating that the former is attributable to ring CH out–of–plane bending vibration. In the same way, the former could be selected for this mode from the two bands at 816 and 799 cm^{-1} in 2,4–dimethyl derivative. Thus, the assignment for this vibration for various types of substitution reported previously[2),3)] could be confirmed.[*2]

As expected from its larger dielectric constant, water showed a larger solvation effect on N–O stretching frequency than methanol, causing a shift of 40~50 cm^{-1}, as shown in Table I. It is of interest to note that the frequency difference between the value in methanol and that in water has a definite trend of decreasing with decreasing

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[*2] The bands at 695 (w), 758 (m), and 1099 (w) cm^{-1} in the spectrum of 2,4,6–collidine 1–oxide reported previously[2)] were found to be due to some impurities in the sample.

electron-attracting power of the substituent and no appreciable difference was observed in the componds with 4-alkoxy and 4-amino groups. The larger ionic character of the N-O bond in the compounds with a strongly electron-donating substituent such as 4-alkoxy and 4-amino groups is expected to make it easier for hydrogen-bond formation, and the above result seems to indicate that these cempounds are in almost perfectly solvated state in methanol solution as well as in water, where the electron migration from the N-O bond to the ring is almost impossible. These results are in good agreement with those obtained in ultraviolet spectra,[3a)] in which the absorption maximum of pyridine 1-oxide shifted to a shorter wave-length with increasing dielectric constant of the solvent, and in water solution the maximum almost coincided with that of pyridine, in which the contribution of mesomeric structure corresponding to the structure (II) is negligible.

II. Comparison of the Strength of Hydrogen Bond

In 0.01M carbon tetrachloride solution, methanol is almost completely in free state, showing only a sharp band due to free OH stretching vibration at 3645 cm^{-1}. On dissolving 0.02M pyridine 1-oxide in this solution, a new broad band attributable to hydrogen-bonded OH vibration appeared with its maximum at 3360 cm^{-1}, as shown in Fig. 3, providing a clear indication of the formation of a hydrogen bond between methanol and pyridine 1-oxide.

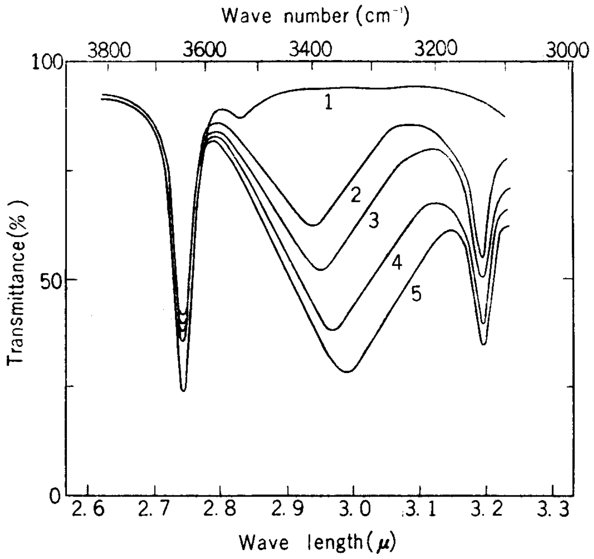

Fig. 3. Bonded OH-Absorption in the System (0.01M MeOH in CCl_4+0.02M substituted pyridine 1-oxide)

1 : Reference
2 : 3-Chloropyridine 1-oxide
3 : 4-Chloropyridine 1-oxide
4 : Pyridine 1-oxide
5 : 4-Methylpyridine 1-oxide
(LiF prism; cell thickness, 20.0 mm.)

It is well established that the stronger the hydrogen bond, the larger is the magnitude of shift of the bonded OH absorption.[8)] In linear hydrogen bond in crystal, it has been shown that the frequency shift is a monotonic and nearly linear function of the OH···O distance, in which the smaller the distance, the larger is the $\Delta\nu$ value.[9)] Therefore, the hydrogen-bonding ability of N-oxide compounds should be estimated in terms of the magnitude of shift of the bonded OH frequency and the comparison for various substituted derivatives may be possible.

The bonded OH frequencies of methanol and phenol were determined for various substituted pyridine N-oxides and are shown in Table II. It was found that the magni-

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8) a) R.M. Badger : J. Chem. Phys., **5**, 839(1937), **8**, 288(1940). b) L.P. Kuhn : J. Am. Chem. Soc., **74**, 2492(1952).

9) G.C. Pimentel, C.H. Sederholm : J. Chem. Phys., **24**, 639(1956). K. Nakamoto, M. Margoshes, R.E. Rundle : J. Am. Chem. Soc., **77**, 6480(1955).

TABLE II. Bonded OH Frequencies of Methanol and Phenol in Hydrogen Bonding with Substituted Pyridine 1-Oxides

Substituent	σ-value	Bonded OH frequency (cm^{-1})$^{a)}$			
		MeOH (ε)	$\varDelta\nu$	PhOH	$\varDelta\nu$
Reference		3645		3620	
4-NO_2	0.778	$^{b)}$		3272	348
3-NO_2	0.710	$^{b)}$		3246	374
3-CH_3, 4-NO_2	0.709	3448$^{c)}$	197	3244	376
3-CN	0.678	$^{b)}$		3226	394
4-$COOC_2H_5$	0.522	3430	215	3190	430
4-$COCH_3$	0.516	3416	229	3194$^{d)}$	426
3-$COOC_2H_5$	0.398	3406	239	3172	448
3-Cl	0.373	3401 (0.11)	244	3179	441
3-$COCH_3$	0.306	$^{b)}$		3168	452
4-Br	0.232	3389	256		
4-Cl	0.227	3383 (0.16)	262	3159	461
None	0.000	3360 (0.26)	285		
3-CH_3	−0.069	3351	294		
3,5-$(CH_3)_2$	−0.138	3349	296		
4-C_2H_5	−0.151	3345	300		
4-CH_3	−0.170	3340 (0.34)	305		
4-OCH_3	−0.268	3320	325		
4-$OCH_2C_6H_5$	−0.416	3316	329		

a) 0.02*M* or saturated soln. in 0.01*M* MeOH or PhOH/CCl_4. Cell thickness, 20.0 mm.
b) Could not be determined because of low solubility of the sample.
c) The preciseness is uncertain because of weakness of the band.
d) Acetophenone showed a weaker bonded OH absorption at 3434 cm^{-1} due to the -C=O···H-O-Ph bond.

tude of shift from that of free OH absorption has a close connection with the electronic nature of the substituents, and an excellent linear relation was found by plotting these frequencies (or $\varDelta\nu$ values) of methanol against the σ-values[10] of the substituents, as shown in Fig. 4-A, this correlation line obeying the equation, $\nu=3360+118\sigma$ or $\varDelta\nu=285-118\sigma$. This indicates that the hydrogen-bonding ability of N-oxide compounds increases as the electron-donating power of the substituents increases, but decreases as their electron-attracting power increases. As the hydrogen-bonding ability should be determined by the relative electron density about oxygen atom, it is considered that, as the σ-value of the substituent decreases, the contribution of mesomeric structure (II) decreases and that of (III) increases, and the resultant increase in ionic character of the N-O bond causes a larger ability to accept a proton.

As discussed in a previous paper,[3] a linear relationship exists between the N-O stretching frequency and σ-value of the substituent, and accordingly a linear relation also exists between the N-O frequency and the $\varDelta\nu$ value for individual compound, in which the lower the N-O frequency, the larger is the $\varDelta\nu$ value. The fact that acetyl, ethoxycarbonyl, and 3-methyl derivatives which showed a considerable deviation in the relation of the N-O frequency[3] also gave a linear plot in their $\varDelta\nu$ values (Fig. 4-A) further confirms the view that the observed deviation originates not in the nature of the N-O bond but in some vibrational interaction.

As can be seen from Fig. 3 a large increase was observed also in their intensities as the $\varDelta\nu$ value increases. Since the intensity of the bonded OH absorption under constant conditions is considered to be an approximate measure of the equilibrium constant

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

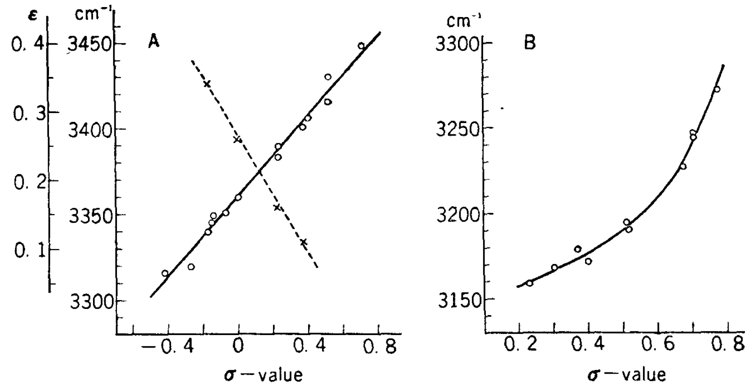

Fig. 4. Relation between Hydrogen-bonding Ability of Substituted Pyridine 1-Oxide and the σ-Value of the Substituent

A : Bonded OH frequency (-○-) and intensities (--×--) of methanol.
B : Bonded OH frequency of phenol.

in the formation of a hydrogen bond, this result indicates that the stronger the hydrogen bond, the larger is the equilibrium constant, and the observed intensity (ε) seems to be also a linear function of the σ-value of the substituent (Fig. 4-A).

Diethyl ether and acetone shows the $\Delta\nu$ values of 151 and 100 cm^{-1}, respectively, following hydrogen-bond formation with methanol.[8b] The larger $\Delta\nu$ value of 200~300 cm^{-1} observed in the N-oxide compounds indicates that these are considerably stronger proton acceptors than ether and ketonic oxygens, this being considered to be due to the large electronegativity of the oxygen in the charge distribution as N^+-O^-.

The hydrogen-bonding ability of some methylpyridines and aliphatic amines has been studied by Tamres, *et al.*,[11] showing that the bonded OD frequency of methanol-*d* had a linear relation against the pKa value of the bases. Jaffe[12] correlated the pKa values of the substituted pyridine 1-oxides with the σ-values of the substituents and, more recently, showed[13] that the linear relation between them could be improved in the fit by the use of σ^+- and σ^--values for electron-withdrawing and -releasing substituents, respectively. In the present study, however, the $\Delta\nu$ value showed a better linear relation against the usual σ-values rather than the modified values, although the reason for this disagreement is difficult to understand at present.

It is expected that 2-methyl group has a similar effect to that of 4-methyl group, giving rise to a considerable increase in $\Delta\nu$ value. As shown in Table III, however, the introduction of 2-methyl group showed no appreciable increase but even an appreciable

Table III. Bonded OH Frequencies of Methanol and *tert*-Butanol in Hydrogen Bonding with Substituted 2-Methylpyridine 1-Oxides

Substituent	Bonded OH frequency (cm^{-1})[a]					
	MeOH	$\Delta\nu$	$\Delta(\Delta\nu)$	*tert.*-BuOH	$\Delta\nu$	$\Delta(\Delta\nu)$
Reference	3645	ref.		3620	ref.	
None	3360	285	ref.	3365	255	ref.
2-CH_3	3358	287	+ 2	3360	260	+ 5
4-CH_3	3340	305	+20	3335	285	+30
2,4-$(CH_3)_2$	3335	310	+25	3335	285	+30
2,6-$(CH_3)_2$	3363	282	− 3	3369	251	− 4
2,4,6-$(CH_3)_3$	3346	299	+14	3336	281	+26

a) 0.02*M* soln. in 0.01*M* MeOH or *tert.*-BuOH/CCl_4. Cell thickness, 20.0 mm.

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11) M. Tamres, S. Searles, E. M. Leighly, D. W. Mohrman : J. Am. Chem. Soc., **76**, 3983(1954).
12) H. H. Jaffe, G. O. Doak : *Ibid.*, **77**, 4441(1958).
13) H. H. Jaffe : J. Org. Chem., **23**, 1790(1958).

decrease, indicating its rather weakening effect on hydrogen-bond ability. For example, 2,6-dimethyl and 2,4,6-trimethyl derivatives showed the decrease in $\Delta\nu$ value by 3 and 6 cm^{-1}, respectively, as compared to those of pyridine and 4-methylpyridine 1-oxides, respectively. These results are in agreement with that obtained in ultraviolet spectra[4c)] in which the equilibrium constant for the hydrogen-bond formation decreased largely in 2,6-dimethyl derivative.

The electronic effect of 2-methyl group on the N-O bond is considered to be essentially the same as that of 4-methyl group, thus a 2-methyl group shows the same effect on the N-O stretching frequency as that of a 4-methyl group, both causing the same magnitude of shift to a lower frequency.[3)] Therefore, the reason for the observed anomaly can be attributed mainly to the steric effect of 2-methyl groups in the formation of hydrogen bond. To test this effect, the same experiment was undertaken with *tert*-butanol and the result is shown in Table III. Contrary to expectations, however, any further decrease in hydrogen-bonding ability of 2-methyl derivatives was not observed on passing from methanol to *tert*-butanol, but this can be interpreted as indicating the steric effect of 2-methyl groups to be so large that the hydrogen bond is no longer affected by the bulkiness of alcohol residue. The presence of intramolecular hydrogen bonding between oxygen and 2-methyl group has been proposed by Ikekawa, *et al.*,[14)] and a weak intramolecular electrostatic interaction between them may be one of the factors concerned, but should not be very important, because of the reason mentioned above.

Phenol gave a much larger $\Delta\nu$ value than that of methanol, and the bonded OH frequency with pyridine 1-oxide showed a $\Delta\nu$ value of about 500~600 cm^{-1}, with its maximum overlapping with ring CH absorptions in the region of 3120 and 3050 cm^{-1}. This fact indicates that phenol is a considerably stronger proton donor than methanol. Absorption maxima were able to be determined for the compounds with an electron-withdrawing substituent, as shown in Table II. These frequencies showed an increase with increasing σ-value of the substituent, but there seems to exist a non-linear relation between them, as drawn in Fig. 4-B. The meaning of this relation is difficult to understand, but there remains a large question about the preciseness of the band maxima, in particular for the part of smaller σ-values, because of the close proximity of the maxima to that of CH absorptions and hence the possibility of occurrence of band interaction.

III. Electronic Effect of the N-Oxide Function under Solvated State

In an earlier work,[3)] electronic effect of the N-oxide function upon the ring was examined in terms of the frequency shift in a characteristic vibration of the ring substituent in non-polar solvent, deriving the σ-values of 0.25 and 1.18, respectively, for 4- and 3-position of pyridine 1-oxide. The marked disagreement of these values, in particular in that for 4-position, to the values of 1.35 and 1.48, respectively, obtained by Jaffe[15)] from the pKa values of the carboxyl derivatives in water and alcohol was assumed to be attributable to the difference in the conditions under which these values were derived. To gain more information on this point, the carbonyl stretching frequencies of 4- and 3-substituted pyridines and their N-oxides were carefully determined in methanol and water solutions. The results obtained are shown in Table IV.

In acetonitrile, which has a large dielectric constant but does not possess an active hydrogen, the carbonyl frequencies in acetyl derivatives showed a constant magnitude of shift to a lower frequency as compared to those in carbon disulfide. In methanol,

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14) N. Ikekawa, Y. Sato: This Bulletin, **2**, 400(1954).

15) H. H. Jaffe: J. Am. Chem. Soc., **76**, 3527(1954).

Table IV. Carbonyl Stretching Frequencies under Solvated State

Compounds	C=O (cm^{-1}) in						
	CS$_2$	CH$_3$CN[a)]	$\Delta\nu$	CH$_3$OH[b)]	$\Delta\nu$	D$_2$O[b)]*	$\Delta\nu$
4-Acetylpyridine 1-oxide	1693	1691	− 2	1696	+ 3	1691	− 2
3-Acetylpyridine 1-oxide	1706	1704	− 2	1705	− 1	1698	− 8
4-Acetylpyridine	1703	1700	− 3	1701	− 2	1693	−10
3-Acetylpyridine	1697	1694	− 3	1693	− 4	1684	−13
p-Nitroacetophenone	1701	1699	− 2	1697	− 4	c)	
Ethyl isonicotinate 1-oxide	1727	1724	− 3	1730	+ 3	1719	− 8
Ethyl nicotinate 1-oxide	1737	1734	− 3	1739	+ 2	1727	−10
Ethyl isonicotinate	1734	1731	− 3	1736	+ 2	1719	−15
Ethyl nicotinate	1730	1727	− 3	1731	+ 1	1712	−18
Ethyl *p*-nitrobenzoate	1732	1729	− 3	1731	− 1	c)	

a) 1.5∼2.0% solution; cell thickness, 0.1 mm.

b) conc. solution; AgCl windows; thickness, approx. 0.025 mm.

c) Insoluble.

* D$_2$O was used to avoid obscuring of 6-μ region by water absorption.

however, 4-derivative of the N-oxide showed an abnormal behavior showing an appreciable shift to a higher frequency than that in carbon disulfide, and this behavior is also apparent in heavy water, and 4-derivative of the N-oxide showed a shift of only 2 cm^{-1} in contrast to the larger shift of about 10 cm^{-1} in the other compounds. On the assumption that the solvation effect on the carbonyl oxygen is approximately constant throughout this group of compounds, the above observations are considered to indicate that the electron-releasing ability of the N-oxide function towards 4-position of the ring is considerably decreased following hydrogen-bond formation, causing an appreciable higher-frequency shift of the carbonyl frequency opposing the solvent effect on carbonyl oxygen. In ethoxycarbonyl derivatives this behavior is not so clear, probably because of the more complexity of the solvent effect on -COOR group, but in heavy water 4-derivative of the N-oxide showed the least magnitude of shift, its maximum coinciding with that of 4-derivative of pyridine.

Thus, in non-polar solvent and in polar solvent, provided that active hydrogen is not involved, the frequencies are in the increasing order of 4-pyridyl 1-oxide, 3-pyridyl, 4-pyridyl, and 3-pyridyl 1-oxide, while in polar solvent with active hydrogen this order is reversed in the first two, the frequencies increasing in the order of 3-pyridyl, 4-pyridyl 1-oxide∼4-pyridyl, and 3-pyridyl 1-oxide. This fact indicates that the σ-value of the N-oxide group towards 4-position of the ring considerably increases in polar solvent involving hydrogen-bond formation, this being considered to be due to the decrease in the contribution of mesomeric structure (II) following hydrogen-bond formation. Since in pyridine ring the contribution of mesomeric structure corresponding to the structure (II) is negligible, the σ-value of pyridine ring can be assumed to be unchanged by solvation. Then, although the precise value cannot be determined, from the comparison of these frequencies in heavy water it can be anticipated that the N-oxide function has a σ-value close to 0.93, that for 4-position of pyridine,[16)] towards 4-position of the ring under solvated state.

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16) H. Shindo: This Bulletin, **5**, 472(1957).

Experimental

Material—All samples used are the same as those used in the previous works.[2,3,16] Methyl derivatives were purified by low-pressure distillation prior to each measurement and much care was taken to avoid inclusion of water during the experiment, in particular, for the measurement of bonded OH frequency. Deuterium oxide used was of 99.5% purity, product of Stuart Oxygen Co. All solvents and other reagents used were purified by usual methods.

Method—Infrared spectra were measured with a Perkin-Elmer Model 21 double-beam spectrophotometer provided with NaCl and LiF prisms, for the regions below and above 2000 cm^{-1}, respectively. Detailed conditions of the measurements are described in Tables I～IV. The absorption of MeOH, when it was added, was extinguished by compensation of the same solvent, but hardly affected the region of 1100～1300 cm^{-1}. The measurements in water and methanol solutions were made as capillary film of the concentrated solution between two AgCl plates, and the thickness was approximately 0.025 mm. For comparing small frequency shifts as described in Section II and III, measurements were made under the same conditions and at the same time for each group of compounds, and the mean value of the three measurements was adopted. Chart scale of 20 cm./μ was applied, scanning very slowly.

Summary

Infrared investigations were made on the hydrogen-bond effect of pyridine 1-oxide and its derivatives with some proton donors.

The assignment for N-O stretching frequency (strong absorption in the region of 1190 and 1320 cm^{-1}) was further confirmed by observing the spectral change of N-oxide compounds following hydrogen-bond formation with methanol in non-polar solvent. The hydrogen-bonding ability of various derivatives was estimated in terms of the magnitude of shift in bonded OH frequency of methanol and an excellent linear relation was found by plotting these frequencies against the σ-values of the substituents. Anomalous behavior in 2-methyl derivatives was also pointed out and discussed. From a comparison of the frequency shift of the carbonyl stretching absorption in methanol and water, it was found that the electron-releasing ability of the N-oxide function towards 4-position of the ring is largely decreased in polar solvent with active hydrogen.

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