Molecular Spectra and Molecular Structure of Heterocyclic Compounds.
Infrared and Near Ultraviolet Absorption Spectra of Pyridine N-Oxide Derivatives.

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The infrared and ultraviolet spectra of many pyridine N-oxide derivatives have been studied.

Ultraviolet spectra show a strong solvent effect in going from aprotic to hydroxylic solvents due to strong hydrogen bonding. Values of ΔH° for several systems $CH_3OH/XPyNO$ in tetrachloroethylene solution were evaluated by infrared techniques and a linear correlation ΔH° vs. $\Delta \nu OH$ has been found.

Features of the infrared and ultraviolet characteristic absorption bands were also investigated.

Introduction.

Infrared studies on pyridine N-oxides, especially concerning the location of the NO stretching vibration, have been reported in recent years (2-8). The dependence of the IR characteristics on the nature of substituents and solvents has been investigated (9-11).

The near ultraviolet absorption spectrum of pyridine N-oxide in the vapor phase has been studied by Ito and Hata (12) and by Ito and Mizushima (13), who reported a vibrational analysis on the discrete band system in the 330 mμ region.

Electronic spectra of substituted pyridine N-oxides in protic and aprotic solvents have been measured and their sensitivity to the solvents pointed out (14).

This paper, which follows previous research in this field (15-17), is concerned with the IR and the near UV absorption spectra of many pyridine N-oxides. The strong modifications which occur in both the vibrational and electronic spectra when recorded in hydroxylic solvents are mainly due to hydrogen bonding between the oxygen atom of the NO group and the hydroxylic group (18); consequently, the thermodynamic parameters associated with such interaction have been also evaluated.

Results and Discussion.

Infrared Spectra.
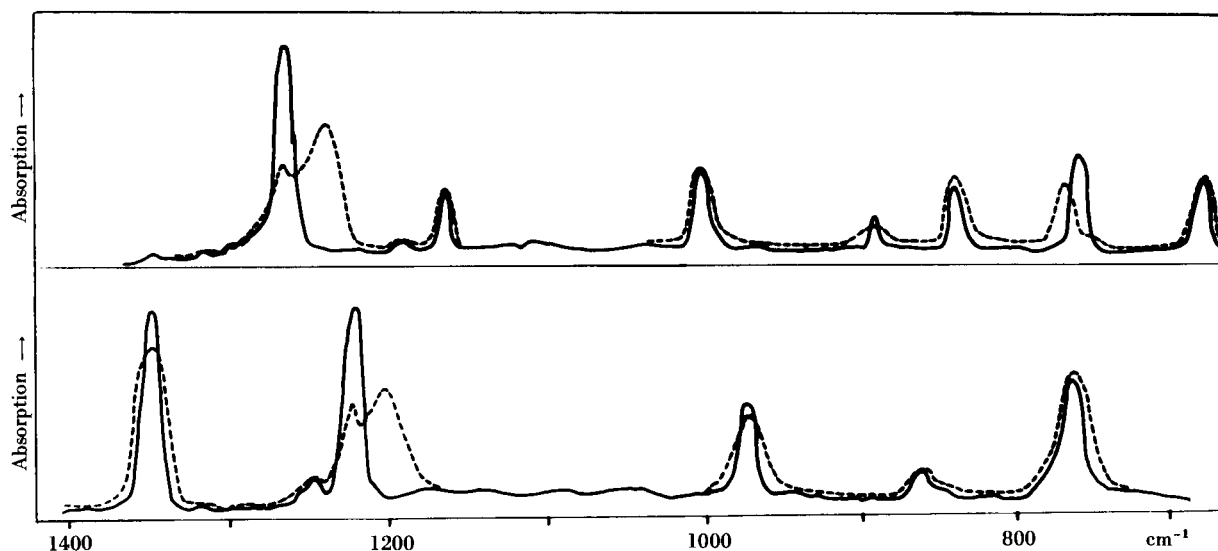
Investigations concerning the absorption bands of the

Figure 1. IR spectrum of pyridine N-oxide (above) and its d_5 derivative (below) in the range 1400-700 cm^{-1}: (—) 5.10^{-2} m/l of N-oxide in carbon disulfide (- - -) 5.10^{-2} m/l of N-oxide + 5.10^{-2} m/l of methanol in carbon disulfide.
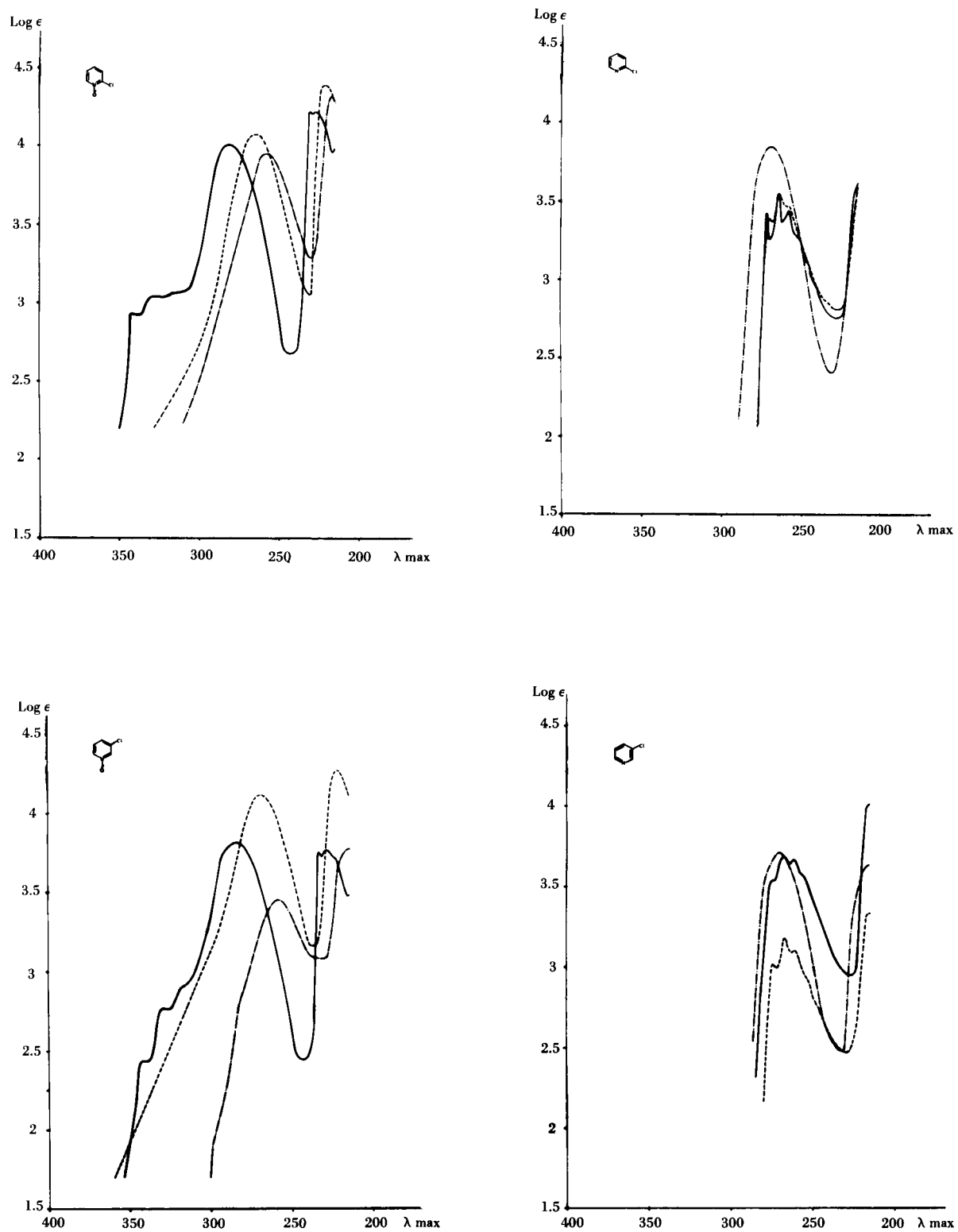
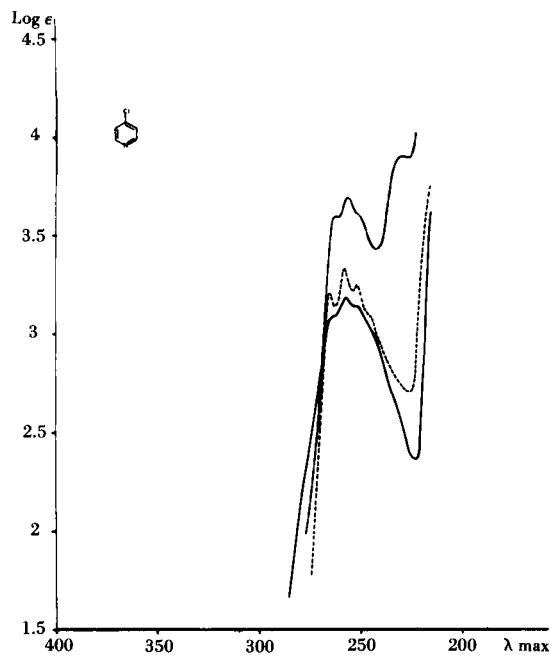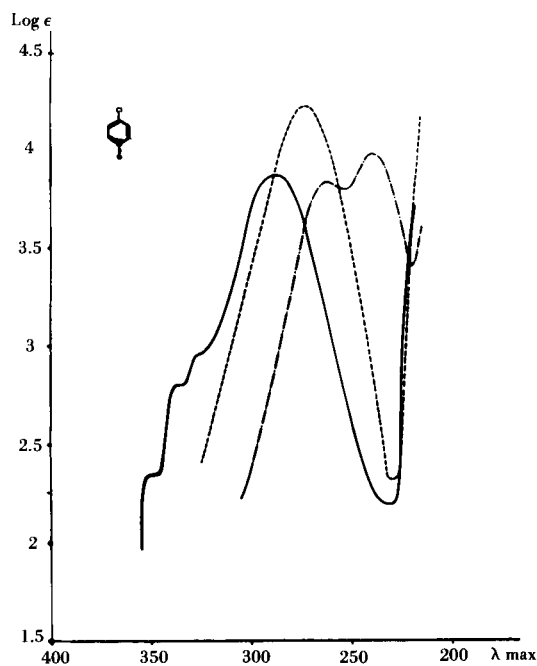Figure 2. UV spectra of chloro pyridine *N*-oxides and the corresponding basic pyridines: (——) cyclohexane; (. . . .) methanol; (-.-.-) 0.1 *N* hydrochloric acid.

NO stretching vibrations in aromatic N-oxides (mainly in pyridine N-oxides) have been done in some detail. It has been suggested that either a band at about 1260 cm⁻¹ or a band at about 840 cm⁻¹ is associated with such vibrational transitions (in the first case the band at 840 cm⁻¹ and in the second case the band at 1260 cm⁻¹ were assigned to vibrational modes involving the C-H groups in some way (2-8)).

Figure 1 shows the IR spectra of pyridine N-oxide and its d₅ derivative in the range 1450-650 cm⁻¹. Only the band at 1260 cm⁻¹ is present in both the spectra (19) while the remaining part of the spectra is strongly modified. Based on these results the band at 1260 cm⁻¹ is assigned to the NO stretching vibration.

The frequencies corresponding to the NO bands for the compounds investigated are collected in Table I. Although such bands are rather sensitive to the nature and ring position of the substituent, no satisfactory correlation between wave numbers and the Hammett's substituent constants (σ) could be found; for example, pyridine N-oxide absorbs at 1265 cm⁻¹ while its 3CH₃- $(\sigma = -0.07)$ and 4CH₃-$(\sigma = -0.17)$ derivatives absorb at 1288 cm⁻¹ and 1262 cm⁻¹, respectively.

In systems consisting of methanol and a pyridine N-oxide (in about equimolar amounts) dissolved in an inert solvent, where an equilibrium of the following type takes place,

$$CH_3OH + ONPyX \rightleftharpoons CH_3OH\ldots ONPyX \quad I$$

(Py = residue pyridine nucleus; X = substituent)
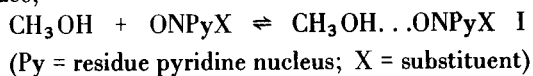
two additional bands at about 3350 cm⁻¹ and at about 1230 cm⁻¹ appear in the spectrum. These bands, which are in isosbestic equilibrium with the absorptions at 3645 cm⁻¹ $(\nu\ OH)$ free and at about 1260 cm⁻¹ $(\nu\ NO)$ free, respectively, are assigned to $(\nu\ OH)$ bonded and to $(\nu\ NO)$ bonded transitions.
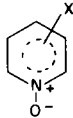
In Figure 1, where the spectra of h₅ and d₅ pyridine N-oxides in carbon disulfide and carbon disulfide plus methanol are superimposed, the isosbestic point for the bands at 1260 cm⁻¹ can be easily found.

Results of the systems investigated are collected in Table I; while the hydroxylic shifts $(\Delta\ \nu\ OH)$ can be reasonably correlated with the electron-attracting or electron-releasing power of the substituents, no consistent trend for the shifts of the NO band $(\Delta\ \nu\ NO)$ can be found. Therefore the hydroxylic shifts $(\Delta\ \nu\ OH)$ seem to be the only useful IR parameters in evaluating the substituent effects in such systems.

The fact that Hammett's law is not followed in a reasonable way is probably due to the existence of some degree of coupling between the NO stretching vibration and other vibrational modes having the same symmetry and which absorb in the same region. This explanation also accounts for the difference between NO vibration of pyridine N-oxide (1265 cm⁻¹) and d₅-pyridine N-oxide (1225 cm⁻¹): if no coupling were present, the NO stretching vibrational frequencies should be the same for both compounds.

TABLE I

Free and Bonded NO Stretching Frequencies of Substituted Pyridine N-Oxides;
Absorption of OH Bands Bonded with Substituted Pyridine N-Oxides in Tetrachloroethylene Solution.

	σ (a)	$(\nu \text{ NO})_f$ (b)	$(\nu \text{ NO})_b$ (b)	$\Delta \nu \text{ NO}$ (b)	$(\nu \text{ OH})_b$ (c)	$\Delta \nu \text{ OH}$ (c)
X = H	0.000	1265	1246	19	3368	277
2,3,4,5,6-D		1224	1200	13	3366	279
2-CH$_3$		1264	1250	14	3366	279
2-C$_2$H$_5$		1265	1240	25	3368	277
2-CH$_2$-C$_6$H$_5$		1261	1245	16	3360	285
2-Cl		1282	1279	8	3420	225
2-Br		1277	1268	9	3420	225
3-CH$_3$	-0.069	1288	1280	8	3366	279
3-Cl	0.373	1264	1257	7	3325	250
3-Br	0.391	1265	1255	10	3455	240
3-I	0.352	1262	1251	11	3400	245
4-CH$_3$	-0.170	1262	1246	16	3330	315
4-C$_2$H$_5$	-0.151	1278	1259	19	3336	307
4-CH$_2$-CH$_2$-CH$_3$		1258	1243	15	3340	305
4-CH(CH$_3$)$_2$	-0.151	1260	1245	15	3340	305
4-CH$_2$-C$_6$H$_5$		1263	1246	17	3346	299
4-Cl	0.227	1273	1253	20	3388	257
4-Br	0.232	1273	1252	21	3390	255
2-4-CH$_3$		1250	1234	16	3332	313
2-5-CH$_3$		1284	1275	9	3355	290
2-CH$_3$-5-C$_2$H$_5$		1279	1266	13	3355	290
2-6-CH$_3$		1259	1243	16	3374	271
2-4-CH$_3$	-0.239	1259	1255	4	3328	317
2-4-6-CH$_3$		1249	1235	14	3339	306

(a) Taken from G. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, 1962, p. 87. (b) Values in carbon disulfide solution. (c) Values in tetrachloroethylene solution, $(\nu \text{ OH})_f = 3645 \text{ cm}^{-1}$.

Ultraviolet Spectra.

The spectra of the pyridine N-oxides investigated were obtained (range 210-350 mμ) in cyclohexane (sometimes isooctane), methanol, and 0.1 N hydrochloric acid. The spectra of 2-, 3-, and 4-chloropyridine N-oxides are reported in Figure 2. For comparison the spectra of the corresponding pyridine derivatives are also shown.

In order to present more consistent data, a few spectra already reported in the literature have been included. This was done because it is known (15-17) that the UV bands of these compounds are very sensitive to the nature of the solvents, and because different solvents were employed by different investigators.

A schematic representation of the absorptions of such compounds is given in Figure 3; two regions of absorption at about 280 mμ and at about 330 mμ, due respectively to a π-π^* and to a n-π^* transition, are readily observed in almost all the compounds investigated.

Absorption at 280 mμ.

The strong band due to a π-π^* transition is perhaps the most striking feature of the aromatic N-oxides; usually aliphatic N-oxides do not exhibit any comparable absorption in this region. Furthermore, comparison of the spectra of pyridine N-oxides with those of the corresponding basic aromatic heterocyclic compounds (see Table II; see also Figure 3) shows a sharp difference in
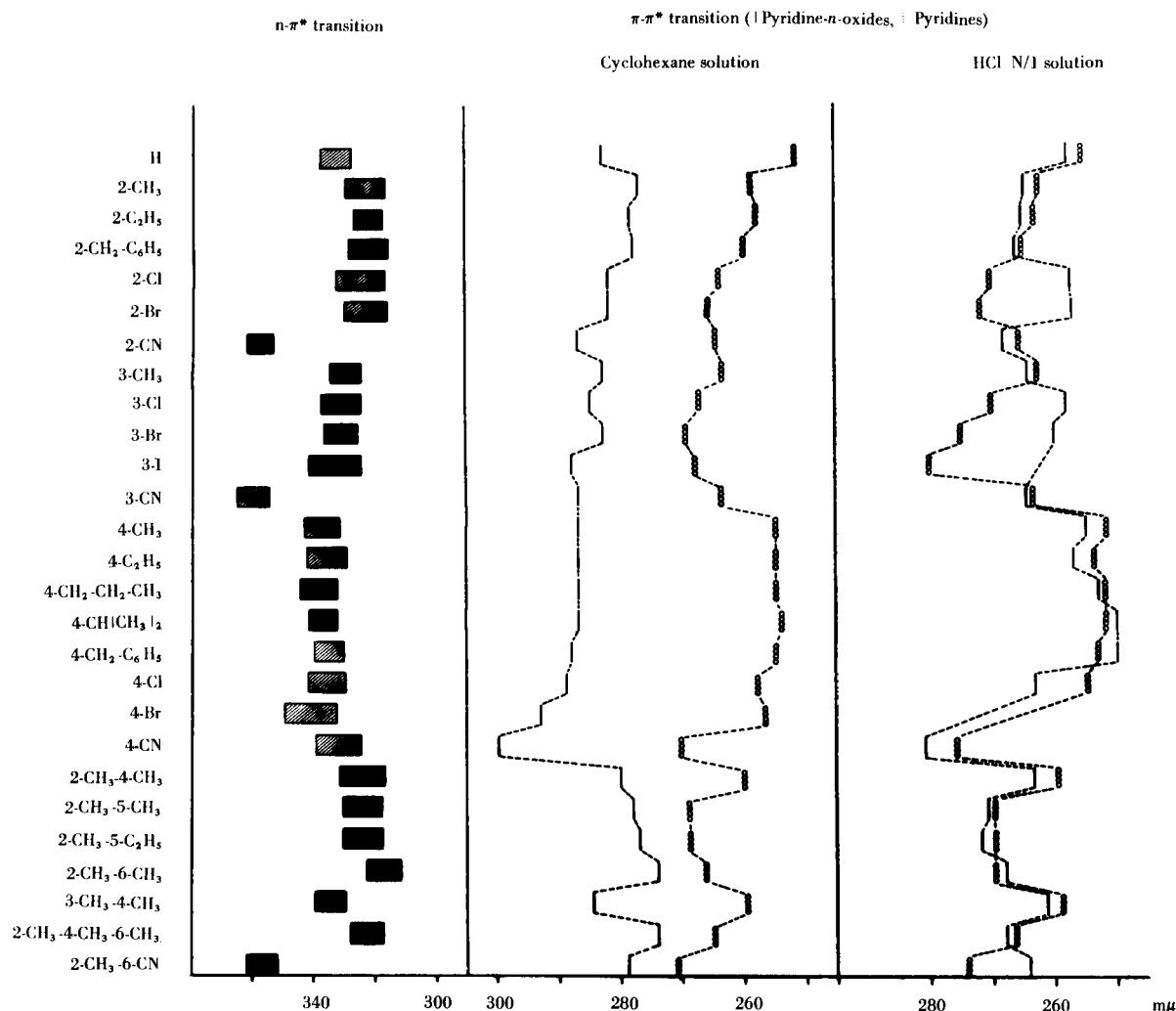
Figure 3. Sketch of the π-π* and n-π* transitions for the compounds investigated.

the two systems of absorptions. Both the strong hypso-chromic and hyperchromic effects which occur in the spectra of pyridine N-oxides suggest the existence of a strong interaction between the NO group and the π electrons of the ring.

Spectral data for the compounds investigated are collected in Table II; absorption maxima are given in mμ with the corresponding molar extinction coefficient, ϵ_m, in parentheses, in cyclohexane, methanol and 0.1 N hydrochloric acid; spectra for the related pyridines have also been recorded and their values are given in Table II for comparison. Since fine structure is only rarely shown by the compounds under investigation, the values in Table II refer mainly to location of absorption maxima.

Hydrogen Bonding Effects.

These π-π* transitions show a blue shift in going from cyclohexane to methanol solutions. Such hypsochromic effects which are the same as that observed for the bands associated with the n-π* transitions at 330 mμ (see below), occur consistently for all of the compounds examined, the average shift being 15 mμ (see Table II, columns 1 and 2). These facts can be explained on the basis of stabilization of the ground state by hydrogen bonding formation for which there is no corresponding significant modification at the excited level, since hydrogen bonding of any considerable strength is improbable in such a state. Because in the hydrogen bonding between pyridine N-oxides and methanol the oxygen atom of the NO group is in-

TABLE II

π-π* Bands of Pyridine N-Oxide and Pyridine Derivatives

| X	Pyridine N-Oxides			Pyridines		
	Cyclohexane mμ (log ε m)	Methanol mμ (log ε m)	Hydrochloric Acid 0.1 N mμ (log ε m)	Cyclohexane mμ (log ε m)	Methanol mμ (log ε m)	Hydrochloric Acid 0.1 N mμ (log ε m)
H	283 (4.11)	263 (4.15)	257 (3.57)	251 (3.30)	253 (3.62)	255 (3.74)
2-CH₃	277 (4.08)	259 (4.07)	264 (3.64)	259 (3.40)	262 (3.55)	262 (3.61)
2-C₂H₅	279 (4.36)	261 (4.04)	265 (3.67)	258 (3.42)	261 (3.56)	263 (3.85)
2-CH₂-C₆H₅	278 (4.05)	262 (4.20)	266 (3.73)	260 (3.55)	262 (3.63)	265 (3.88)
2-Cl	282 (4.01)	265 (4.06)	257 (3.25)	264 (3.54)	263 (3.55)	270 (3.85)
2-Br	282 (4.09)	266 (3.80)	257 (3.28)	266 (3.55)	265 (3.26)	272 (3.89)
2-CN	287 (3.96)	275 (3.99)	268 (3.97)	265 (3.69) (a)	265 (3.55)	266 (3.70)
3-CH₃	283 (4.4) (a)	264 (4.09)	264 (3.51)	264 (3.34) (a)	263 (3.42)	263 (3.71)
3-Cl	285 (3.82)	269 (4.11)	258 (3.45)	267 (3.68)	267 (3.16)	270 (3.70)
3-Br	283 (3.77)	270 (4.09)	260 (3.80)	269 (3.40)	262 (3.29)	275 (3.67)
3-I	287 (4.09)	269 (4.07)	(b)	268 (3.42)	273 (3.17)	280 (3.54)
3-CN	286 (4.33) (a)	273 (4.07)	264 (3.27)	264 (3.32) (a)	265 (3.39)	264 (3.67)
4-CH₃	286 (4.17)	264 (4.20)	255 (3.47)	255 (3.20)	255 (3.40)	252 (3.68)
4-C₂H₅	286 (4.18) (a)	265 (4.18)	257 (3.49)	255 (3.19) (a)	256 (3.31)	254 (3.67)
4-CH₂-CH₂-CH₃	286 (4.20)	265 (4.18)	253 (3.57)	255 (3.21)	255 (3.31)	252 (3.66)
4-CH(CH₃)₂	286 (4.11)	266 (4.12)	250 (3.43)	254 (3.23)	255 (3.31)	282 (3.66)
4-CH₂-C₆H₅	287 (4.24)	267 (4.18)	250 (3.71)	255 (3.26)	256 (3.39)	253 (3.76)
4-Cl	288 (3.87)	273 (4.22)	263 (3.83)	258 (3.17)	257 (3.33)	255 (3.69)
4-Br	293 (4.34)	275 (4.26)	(b)	257 (3.21)	259 (3.37)	(b)
4-CN	300 (4.03)	291 (4.29)	281 (4.25)	271 (3.44)	272 (3.46)	276 (3.72)
2-CH₃-4-CH₃	280 (4.4) (a)	261 (4.11)	263 (3.56)	260 (3.31)	260 (3.44)	260 (3.77)
2-CH₃-5-CH₃	278 (4.05) (a)	259 (4.04)	271 (3.67)	269 (3.47) (a)	269 (3.55)	270 (3.83)
2-CH₃-5-C₂H₅	277 (4.05) (a)	260 (4.04)	272 (3.66)	269 (3.47) (a)	269 (3.55)	270 (3.85)
2-CH₃-6-CH₃	274 (4.04)	258 (4.01)	268 (3.78)	267 (3.52)	267 (3.64)	270 (3.93)
3-CH₃-4-CH₃	284 (4.04) (a)	264 (4.16)	261 (3.49)	260 (3.29)	259 (3.39)	258 (3.69)
2-CH₃-4-CH₃-6-CH₃	274 (4.09)	259 (4.10)	268 (3.77)	265 (3.46)	264 (3.58)	267 (3.90)
2-CH₃-6-CN	279 (3.91) (a)	271 (3.91)	264 (3.92)	271 (3.64) (a)	271 (3.64)	274 (3.89)

(a) Isooctane solution. (b) Very broad maximum of absorption.

volved, as can be seen by the results obtained in the IR section (the ν NO absorption band is shifted toward lower wave numbers when the NO group is hydrogen bonded), it seems very likely that the oxygen atom in the excited state is significantly charged.

Protonation Effects.

The schematic representation in Figure 3 shows that in 0.1 N hydrochloric acid the absorptions of pyridine N-oxides and the corresponding parent pyridines are very nearly the same. Since, in such solutions both series of compounds exist only as conjugated acids (N-hydroxy-pyridinium (II) and pyridinium (III) ions, respectively), the results above strongly suggest that the electronics in II and III are very similar in both the ground and the excited states.
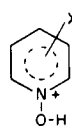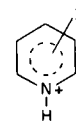
II   III

In fact no significant interactions can be expected in II under such conditions. The slight differences in the absorption values which still remain (see Table II, columns 3 and 6) do not appear consistent; they are probably due to a superimposition of several weak independent effects.

Substituent Effects.

The results collected in Table II clearly show that usually the absorptions of ring-substituted pyridine N-

oxides are very close to that of the unsubstituted parent molecule. 2-Substituted derivatives often exhibit a slight hypsochromic effect (while in the corresponding pyridines a bathochromic effect is always found); this is probably due to stabilization of the ground state by a direct interaction between substituent groups and the oxygen atom.

The contribution of the substituents to the position of the absorptions of polysubstituted derivatives can be considered only roughly additive (20).

TABLE III

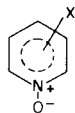K Values for the Equilibria (I) at Various Temperatures

X =	$K_{30°}$	$K_{40°}$	$K_{50°}$	$K_{60°}$
2-Cl	7.6	6.1	4.8	3.8
3-Cl	7.9	6.1	4.9	3.9
H	9.2	6.9	5.3	4.1
3-CH$_3$	18.3	14.5	10.7	8.2
2-CH$_2$-C$_6$H$_5$	10.5	8.2	6.2	4.5
3-5-CH$_3$	23.0	16.9	12.7	9.6
2-4-CH$_3$	25.4	18.6	13.4	9.9
4-CH$_3$	45.9	32.7	23.4	16.9
4-C$_2$H$_5$	22.5	16.2	11.6	8.2
4-CH(CH$_3$)$_2$	23.6	17.5	11.8	8.6

TABLE IV

Thermodynamic Parameters for the Systems Investigated

Pyridine N-Oxide Derivatives	$-\Delta H°$ Kcal/mole	$-\Delta G°_{298°K}$ Kcal/mole	$-\Delta S°$ e.u.
2-Cl	4.6	1.29	11.3
3-Cl	4.9	1.32	12.0
H	5.4	1.40	13.4
3-CH$_3$	5.5	1.79	12.3
2-CH$_2$C$_6$H$_5$	5.7	1.50	13.9
3-5-CH$_3$	5.7	1.84	13.0
2-4-CH$_3$	6.3	2.02	14.4
4-CH$_3$	6.6	2.38	14.1
4-C$_2$H$_5$	6.7	1.96	16.0
4-CH(CH$_3$)$_2$	6.8	2.00	16.3

Absorption at 330 mμ.

The band which appears at about 330 mμ in almost all of the compounds examined in hydrocarbon solvents, is attributed to a n-π^* transition where one of the p electrons is excited from the non-bonding orbital of the oxygen
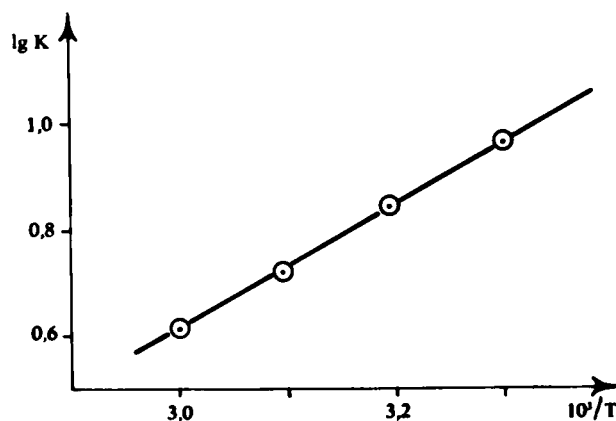

Figure 4. Correlation of logK vs. 1/T.

atom to an anti-bonding π^* orbital (13). The vibrational fine structure in cyclohexane as well as the strong blue shift in hydroxylic solvents (13-17) easily supports such an assignment.

A sketch showing the position of this band in the compounds examined is given at the left-hand-side of Figure 3 and refers to cyclohexane. Since this band is almost always partially overlapped by the strong π-π^* absorptions at 280 mμ, the results reported in Figure 2 have to be considered as only approximate. However, in most cases there appears to be a dependence of the absorption maxima upon substituents consistent with that exhibited by the bands at 280 mμ. The parallel trend of these two bands in going from cyclohexane to methanol can be ascribed in both cases to a stabilization of the ground state by hydrogen bond formation.

Proton-Acceptor Properties.

The effects due to the nature and position of ring substituents on the basicity of the oxygen atom in pyridine N-oxide derivatives has also been investigated. Thermodynamic parameters associated with equilibria (1) have been evaluated by using IR techniques (21,22). Tetrachloroethylene, which is known to be one of the most convenient inert solvents for use in IR (23-25) was selected.

The enthalpy of association was determined from a plot of log K vs. 1/T (the actual equation is lnK = - Δ H°/RT+C) fitted to the best straight line by the method of least squares. The equilibrium constants, K, obtained at four different temperatures, are given in Table III; no evidence for a change in Δ H° values with the temperature was found for any system. Plot of log K vs. 1/T for the system, methanol + pyridine N-oxide in tetrachloroethylene is shown, as an example, in Figure 3. $K_{298°K}$ values were obtained by extrapolation from the previous equations

(independent measurements made at $298°K$ gave very satisfactory agreement). $\Delta G°_{298°K}$ and $\Delta S°$ values have been evaluated by the usual relations, $\Delta G° = -RT\ln K$ and $\Delta G° = \Delta H° - T \Delta S°$, respectively. From a statistical treatment of the data, the reproducibility of the thermodynamic values (see also reference 26) is believed to be better than ± 0.3 Kcal/mole for $\Delta H°$ values, ± 0.2 Kcal/mole for $\Delta G°$ values and ± 0.5 e.u. for $\Delta S°$ values.

Thermodynamic data for equilibria (I) are summarized in Table IV. As can be seen, both the nature and the position of ring substituents affect the proton acceptor capability of the oxygen atom in these compounds; with electron-releasing groups (for instance, 4-alkyl groups) the electron density of the oxygen atom is increased (a limit structure like V is favored) and hence the measure of energy of hydrogen bonding is higher. However, with electron-attracting substituents like the chlorine atom where a limit structure like VI is expected to be more significant, the strength of the hydrogen bonding should be weaker and, in fact, a lower measure of the hydrogen bond energy was obtained.

IV   V   VI
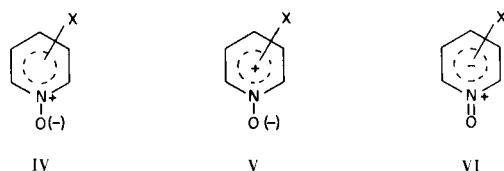
A plot of $\Delta H°$ vs. $\Delta \nu$ OH yields a straight line with a positive slope (see Figure 5). The existence of a linear correlation between a thermodynamic parameter like $\Delta H°$ (which is a measure of all the processes involved in the formation of the new bonding) and a spectroscopic property like $\Delta \nu$ OH (which depends on the weakening of the OH linkage alone), can be justified considering that both solvent (tetrachloroethylene) and proton-donor (methanol) are always the same and there are no major modifications of the structure of the proton-acceptor molecules (XPyNO); therefore, the different strengths of the hydrogen bonding in the systems examined only arise from the electron-withdrawing or electron-releasing power of the substituents.

Of course the results shown in Figure 5 also suggest the possibility of using such correlation for predicting reasonable values for the hydrogen bonding energy in systems such as 1 and hence, in evaluating the basicity of the oxygen atom in pyridine N-oxides by the easily measured $\Delta \nu$ OH values.

Conclusions.

From the results of the present investigation, the following conclusions can be drawn.

(1) The NO stretching vibration, located at 1260 cm^{-1} indicates some degree of coupling with other vibrational

modes; therefore, these values cannot be used for structural purposes.

(ii) The absorptions due to π-π^* and n-π^* transitions in the near ultraviolet region are strongly blue-shifted in hydroxylic solvents mainly by hydrogen bonding formation.

(iii) The strength of the hydrogen bonding between methanol and pyridine N-oxides as measured by $\Delta H°$ values is between 4.6 and 6.8 Kcal/mole (tetrachloroethylene) depending on the nature and position of ring substituents (the range of the energies can be, of course, enlarged if more powerful electron-donor or electron-attractor substituents are involved).

(iv) The existence of a linear correlation between $\Delta \nu$ OH and $\Delta H°$ values allows the prediction of the enthalpy of association by the measured $\Delta \nu$ OH shifts.
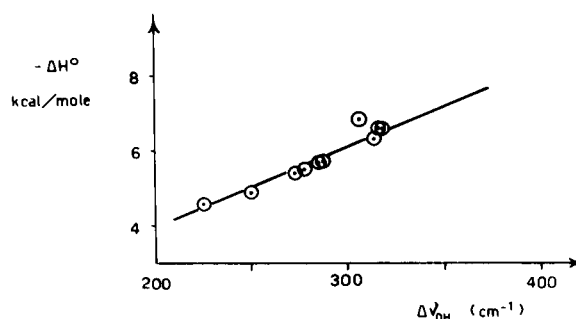
Figure 5. Correlation of ΔH vs. $\Delta \nu$ OH.

EXPERIMENTAL

Spectra.

The ultraviolet spectra were measured in cyclohexane (isooctane), methanol and 0.1 N hydrochloric acid and were recorded on a Cary 14 spectrophotometer using cells of 10 and 50 mm. thickness. The region between 210 and 350 mμ was the one usually investigated.

For the infrared spectra a Beckmann IR 4 double beam spectrophotometer equipped with lithium fluoride and sodium chloride prisms was employed. Sodium chloride cells of 1.0 and 0.1 mm. thickness were used. The results are believed to be accurate within ± 2 cm^{-1} for the (ν OH)$_f$ band, ±5 cm^{-1} for the (ν OH)$_b$ bands, and ± 1 cm^{-1} for the ν NO bands. Water vapor lines were used for calibrating the region at 3 μ; the correctness of the wave number of the remaining part of the spectrum was checked by employing a polystyrene film.

Thermodynamic Parameters.

Thermodynamic parameters were evaluated by employing the IR technique. The equilibrium constants were evaluated at four different temperatures (30°, 40°, 50°, 60° ± 1°) by following the free hydroxylic stretching frequency of methanol at 3645 cm^{-1}. Details of this method have already been published by one of us (20,21). In the range employed (5.10^{-3}—4.10^{-2} mole/liter) the

TABLE V

Pyridine N-Oxides	B.P. °C/mmHg	M.P. °C	Peroxyacid (a)	Crystallization Solvent
py-H$_5$, py-d$_5$	97-98/0.5	66	PA	(b)
2-CH$_3$	123-124/15		PA	
2-C$_2$H$_5$	133-134/12		PA	
2-CH$_2$-C$_6$H$_5$		99-100	PA	ethyl acetate
2-Cl		69	PA	ethyl acetate
2-Br		48-49	PA	ligroin
2-CN		119-120	PA	benzene
3-CH$_3$	84-86/1.5		PA	
3-Cl		60-61	PB	ligroin
3-Br		41-42	PB	ligroin
3-I		130-131	PB	benzene
3-CN		175-176	PA	ethanol
4-CH$_3$		183-184	PA	benzene
4-C$_2$H$_5$		114-115	PA	ethyl acetate
4-CH$_2$-CH$_2$-CH$_3$	124-125/1		PA	
4-CH (CH$_3$)$_2$	136/1.8		PA	
4-CH$_2$-C$_6$H$_5$		175	PA	(b)
4-Cl		168-169	PB	acetone
4-Br		144-145	PB	benzene
4-CN		223-224	PA	benzene
2-4-CH$_3$	112-113/1.5		PA	
2-5-CH$_3$	105-107/4		PA	
2-6-CH$_3$	128-129/14		PA	
3-4-CH$_3$		132-133	PA	benzene
3-5-CH$_3$	124/1.5		PA	
2-CH$_3$-5-C$_2$H$_5$	151/15		PA	
2-4-6-CH$_3$	83-84/0.5		PA	
2-CH$_3$-6-CN		127-128	PA	ethyl

(a) PA = peracetic acid; PB = perbenzoic acid. (b) Directly and repeatedly sublimed under high vacuum.

absorbance of the free hydroxylic stretching frequency was found to be a linear function of the concentration (since the Beer's law was strictly obeyed, no self-association of methanol was found (see also Reference (26)). An independent plot (absorbance/concentration) was drawn at each temperature. For the pyridine N-oxides a range of concentration from 2.10^{-2} to 8.10^{-2} mole/liter was generally chosen: the upper limit was imposed by the solubility of these compounds. Although no modifications of the equilibrium constants was ever found by changing the relative amounts of methanol and pyridine N-oxides, an excess of the latter was usually preferred (27). In order to prevent the possibility of absorption of moisture by the samples employed, all the solutions were handled in a dry box.

Solvents.

Tetrachloroethylene (reagent grade) was purified by distillation from anhydrous potassium carbonate immediately before use. Methanol, cyclohexane and isooctane (spectral grade) were purified by the usual methods (28).

Chemicals.

All of the pyridines were commercially available and were distilled over barium oxide until they were spectroscopically pure.

The pyridine N-oxides were prepared by peracid oxidation (29) of the corresponding pyridine derivatives. Their physical properties are reported in Table V. All the melting points and boiling points are uncorrected.

All the liquid compounds were repeatedly distilled while the solids were crystallized and sublimed under high vacuum immediately before use in order to remove any traces of moisture in the samples. All handling of compounds was carried out in a dry box.

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