

COMPLEXES OF CARBOXYLIC ACIDS WITH PYRIDINES AND PYRIDINE
N-OXIDES ¹

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Abstract - A brief survey is given of dielectric, spectroscopic, thermodynamic, colligative and conductivity properties of non-aqueous solutions of carboxylic acid complexes with pyridines and pyridine *N*-oxides. Selected problems of solid state are also reviewed. Solvent and isotopic effects, and the problem of localization of the H-bonded proton are stressed.

Introduction

To describe molecular interactions two different languages are used: one is used in experiment and the other in theory. In experimental studies molecular interactions are divided into specific (chemical) and nonspecific (physical).² Typical examples of specific interactions are hydrogen bonds (HB), charge-transfer (CT) interactions and strong dipole-dipole interactions. The nonspecific interactions consists of two main proofs: dispersion and electrostatic interactions. In quantum chemistry the interaction energy, ΔE , of the complex is decomposed into five additive components: electrostatic (E_{es}), polarization (E_{pol}), exchange repulsion (E_{ex}),

¹Dedicated to Professor A. R. Katritzky on his 65th birthday.

charge-transfer (E_{CT}), dispersion (E_{disp}), and correlation (E_{corr}); $\Delta E = E_{es} + E_{pot} + E_{ex} + E_{CT} + E_{disp} + E_{corr}$.³ Generally, any interaction between molecules or ions modifies all the internuclear distances in the partners. In most cases, however, these changes are very limited and remains below 1%. There are two types of interactions for which this rule no longer holds and where modifications brought about in some internuclear distances usually exceed 1%, in some cases being very important. These interactions are hydrogen bonds and electron donor-acceptor (E.D.A.) bonds (or CT complex).⁴

The purpose of this review is to show interactions in complexes of pyridines and their *N*-oxides with carboxylic acids, e.g. hydrogen bonds, proton transfer, aggregation (dipolar association), solvent and isotope effects. We will deal with the following H-bonds: $O-H \cdots N$, $O \cdots H-N^+$, $O-H \cdots O$, and $O \cdots H-O^+$, which can be used as models in biological systems.

H-Bonded Species in Solutions

Its studies is supported by studies of conductance, colligative properties, dielectric polarization, and several others experimental techniques^{5,6} in specifying several types of structure which may be in equilibrium with each other and with the monomeric acid (HA) and base (B) over different parts of the normal concentration range of solutions studies ($1 - 10^{-6}$ M). The simplest and the most clearly defined of these species are acid dimers $(HA)_2$ and polymers $(HA)_n$.^{7,8} Pyridine in water⁹ and pyridine *N*-oxide in benzene¹⁰ and low temperature matrix¹¹ form self-associates (multiple clusters), $(B)_n$. Well defined are also the 1:1 H-bonded complexes between acid and bases $(B \cdots HA)$, the 1:2 H-bonded complexes between base and acid dimer $(B \cdots HA \cdots HA)$, conjugated of the original acid-base pairs $(B^+H \cdots A^-)$, the 1:2 homocunjugated ion pair complex $(B^+H \cdots A^- \cdots HA)$ involving two molecules of acid and the 2:1 homoconjugated ion pair involving two molecules of base $(B^+H \cdots B)A^-$.^{7,8,12-23} The $B \cdot HA \cdot HA$ complexes have also been observed in solution containing stoichiometric amount of acid and base^{8,24} and they have also been obtained in crystal.^{25,26} When in the $B^+H \cdots A^- \cdots HA$ complex the first H-bond is weak and the second one is very strong its structure is

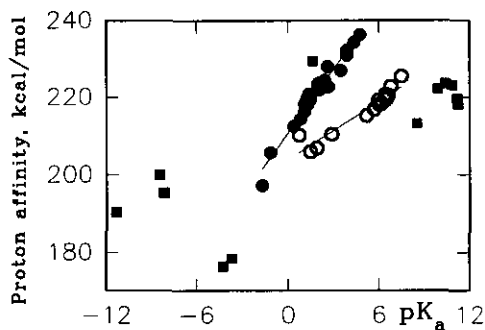
very similar to the acid salts of carboxylic acids, $(B^+H(A \cdot H \cdot A))$.²⁷

In polar solvents complexes form simple ions B^+H and A^- , and homoconjugated ions $(AHA)^-$ and $(BHB)^+$,²⁸ but in nonpolar solvents (e.g. hydrocarbons, benzene) they form aggregates or micelles.^{29,30} These aggregates catalysis some organic reactions.³¹ To explain the high observed conductivity (Λ) of concentrated solutions in solvent of low ϵ , triple ion hypothesis $(ABA)^+$ and $(BAB)^-$ was introduced.³² Triple ions are not confirmed by the other studies.³³⁻³⁵ In the literature the encounter complexes $(HA \cdot B)$ and the solvent separated ion pair $(A^- // HB^+)$ are also postulated.⁶ Finally, hydrates should be mentioned. All solvents contain trace of water and in low concentrated solutions (10^{-4} - 10^{-6} M) hydrates may be dominate species.^{36,37}

Strength of Acids and Bases

The ionization constants of acids and bases converted to pK_a values are a measure of relative tendencies to lose or gain protons in solution.^{38,39} In the gas phase a proton affinity [$PA = \Delta H_f(B) + \Delta H_f(H^+) - \Delta H_f(B^+H)$, where ΔH_f is a heat of formation of the species stated in parenthesis] are used.⁴⁰ Contribution of solvation differs these two scales; in the gas phase contribution of solvation energy is minimal and in solution maximal.

Figure 1. Plot of PA against pK_a (H_2O) for pyridines (\circ), pyridine *N*-oxides (\bullet), and others (\blacksquare) (data from ref. 41).



In study of H-bonded complexes their properties are often plotted against $\Delta pK_a = pK_a(B^+H) - pK_a(AH)$ or $\Delta PA = PA(A^-) - PA(B)$. No general relation exists between pK_a and PA. For some compounds, e.g. pyridines and their *N*-oxides, phenols and carboxylic acids linear relations are observed (Figure 1).⁴¹

Dielectric Studies

The subject of dielectric properties of H-bonded liquids and solutions has been reviewed in several papers^{42,43} and the increase of dielectric polarization in systems with H-bond is a well known phenomenon. The polarity of H-bonds, $\Delta\mu = \mu_{\text{AHB}} - \mu_{\text{AH}} - \mu_{\text{B}}$, defined as the excess dipole moment which is localized along the A-H bond was found to be based on experimental results, usually in the range 0.3-0.6 D, for weak H-bonds and increase to 8-12 D for $\text{A}^{\cdot\cdot\cdot}\text{HB}^+$.

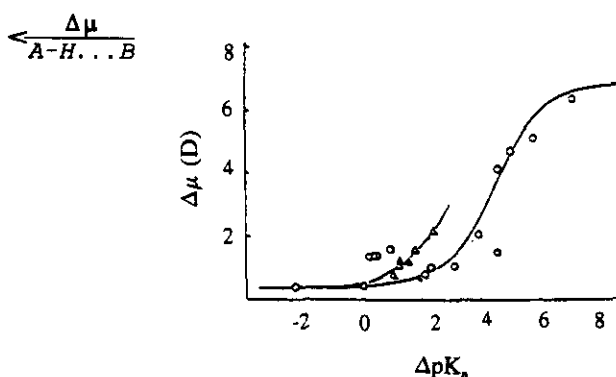


Figure 2. Polarity of hydrogen bonding ($\Delta\mu$) plotted against $\Delta\text{p}K_{\text{a}}$ for carboxylic acid-pyridine systems: (O) aliphatic, (Δ) aromatic acids (from ref. 16).

When, for a given family of H-bonded complexes (e.g. pyridines with carboxylic acid¹⁶ or phenols⁴² in a given solvents, $\Delta\mu$, is plotted against $\Delta\text{p}K_{\text{a}}$ in water a sigmoidal curve, as shown in Figure 2, are always obtained. This type of dependence is very similar to acid-base titration plot and it can be predicted based on the thermodynamic model of proton transfer of Huyskens and Zeegers-Huyskens.⁴⁴ If for the proton a double minimum potential is assumed and both states ($\text{A-H}\cdot\cdot\cdot\text{B}$) and ($\text{A}^{\cdot\cdot\cdot}\text{H-B}^+$) are treated as tautomeric forms of the bridge (eqn. 1), then the equilibrium constant of the proton transfer, K_{PT} , can be expressed by equations (2) or (3).



$$\log K_{\text{PT}} = \Delta\text{p}K_{\text{a}} + C \quad (2)$$

$$\log K_{\text{PT}} = \xi\Delta\text{p}K_{\text{a}} + C' \quad (3)$$

where $\Delta\text{p}K_{\text{a}} = \text{p}K_{\text{a}}(\text{B}^+\text{H}) - \text{p}K_{\text{a}}(\text{AH})$, and C is a constant which includes the energy of solvation processes.

To fit the experimental curve an empirical parameters $\xi < 1$ must be introduced (eqn. 3), which takes into account the fact that, in reality, both compounds ($A-H \cdots B$ and $A^- \cdots H-B^+$) are not independent from each other. Another explanation of ξ is based on the fact, that in a solution except $A-H \cdots B$ and $A^- \cdots H-B^+$, other species are present, and hence K_{PT} is apparent constant, K_{exp} . Thus ξ and C' described contributions of these additional species.

Infrared Spectroscopy

Ir spectra of complexes of pyridines and their *N*-oxides with carboxylic acids show the broad (continuous) absorption in the 3000-400 cm^{-1} region, typical for strong H-bonds (Figure 3). Intensity of the broad absorption and the shape of absorption in the carbonyl-carboxyl region are the main source of information on the H-bonds in these complexes.

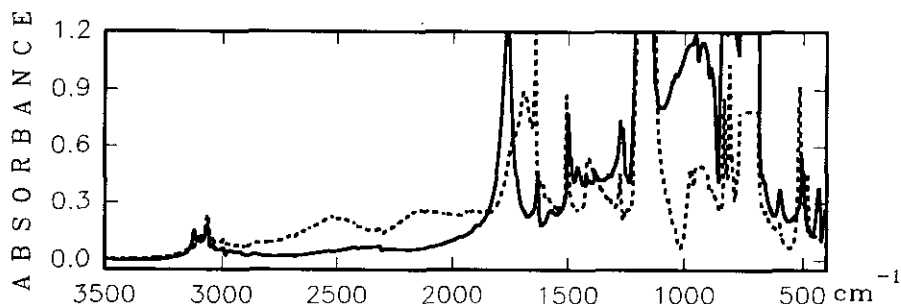
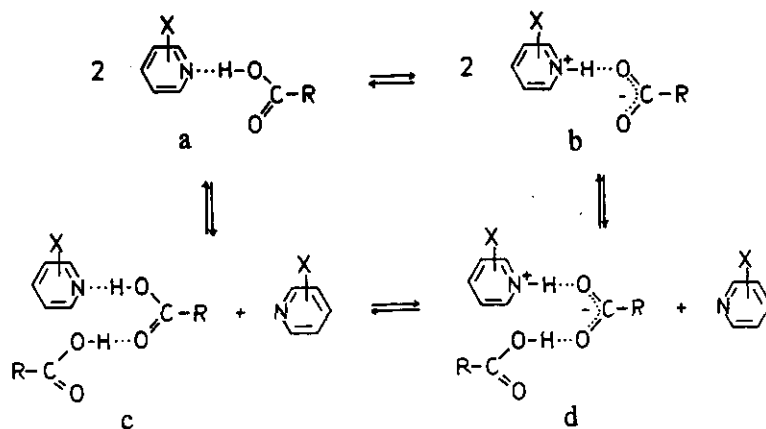


Figure 3. Infrared spectra of complexes of trifluoroacetic acid with 4-methylpyridine (.....) and 4-methylpyridine *N*-oxide (—) in CH_2Cl_2 .

The Carbonyl Region

The pioneering work of Barrow¹² attacked the nature of H-bonded ion-pair system in nonpolar media by ir spectroscopy. This method has been widely used in several laboratories.^{8,13,18,45-52} and various species were characterized. From integrated intensity of the $\nu C=O$ band the K_{PT} values⁴⁷ or the percentage proton transfer^{18,52} were estimated.

Scheme 1.



Derivative spectroscopy⁵³ is a useful technique for identifying overlapped peaks by accounting band profiles. Small shoulders on intense peaks can be readily identified in even-order derivative spectra. In the second derivative spectra in the carbonyl region of pyridine complexes with trifluoroacetic acid (Figure 4) the following species (a) $B \cdot HA$, (b) $B^+H \cdot A^-$, (c) $B \cdot HA \cdot HA$, and (d) $B^+H \cdot A^- \cdot HA$ are recognized (Scheme 1).⁸ All of the species are present in complexes of the medium strong pyridines ($X = H$ or D , 3-Me and 4-Me). Two species (a) and (c) are found for complexes of the weakest, when $X = 4-CN$ and 3-Br, and another two (b) and (d) for complexes of the strongest pyridines, where $X = R-NMe_2$ and 2,4,6-Me₃. Complete formation of the 1:1 complexes requires an excess of pyridines. Fermi resonance of overtones due to pyridines and the acid with continuous absorption is also observed.

In complexes of pyridine *N*-oxides with carboxylic acids the H-bonds are much different than these in pyridine complexes. A single carbonyl band in the second derivative spectra (Figure 4) of the equimolar mixtures of substituted pyridine *N*-oxides with trifluoroacetic acid implies that complexation is complete and hydrogen bonds are described by a strongly asymmetrical quasi-single minimum potential.^{23,49} The equimolar complexes interact with a second molecule of the acid and the second H-bond causes only a minor effect on the first H-bond and this effect is independent of proton-acceptor properties of *N*-oxides. The equimolar complexes interact also with a second molecule of *N*-oxide to form a homoconjugated complex $(BHB)^+A^-$ and this interaction is controlled by the pK_a of the *N*-oxide.

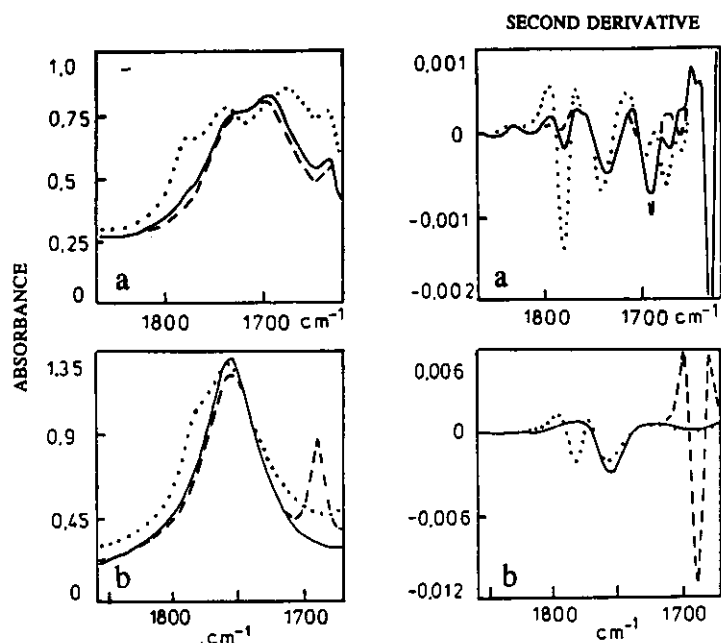


Figure 4. Absorbance and second derivative spectra of mixtures of trifluoroacetic acid with (a) 3-methylpyridine and (b) 4-ethoxypyridine *N*-oxide; base-acid ratio (—) 1:1, (---) 2:1, (· · · · ·) 3:4; from refs. 8, 23.

The Broad Absorption

An infrared absorption band or bands can be characterized by a number of parameters of which an integrate intensity, A (eqn. 4) and a centre of gravity, ν' (eqn. 5) are of great importance.

$$A = 1/(c \cdot l) \int_{\text{band}} \log(I_0/I) d\nu \quad (4)$$

$$\nu' = \int \nu \log(I_0/I) d\nu / \int \log(I_0/I) d\nu \quad (5)$$

where I_0 is the intensity of radiation on the sample at wavenumber ν , I is the transmitted intensity, c is the sample concentration, and l is the path length.

In complexes of pyridines and their *N*-oxides with carboxylic acids the protic vibration overlap on the skeletal vibration caused the broad absorption. These two absorption can be separated graphically⁵⁴⁻⁵⁶ or nongraphically,⁵⁷ and characterized by A or ν' . In Figure 5 the centre of gravity, ν' and the difference

between the proton affinity, ΔPA , for complexes with pyridines and pyridine *N*-oxides, respectively, are displayed. The maximum shift of ν' is observed when ΔPA reached 109 and 102 kcal/mol, respectively, for complexes of pyridines and pyridine *N*-oxides.⁵⁸ These differences may suggest a difference in electrostatic interactions in the complexes, resulting from delocalizations in $RC_5H_4N^+H$ and $RC_5H_4N^+OH$ ions. The turning points correspond to 50% of the proton transfer from acid to bases and agree well with the data obtained from dipole moments.^{58,59}

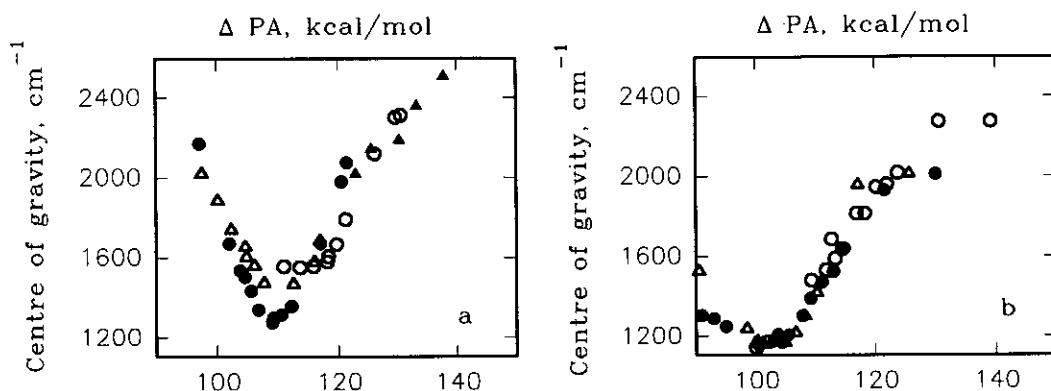


Figure 5. Plot of the centre of gravity (ν') of the broad absorption against the difference between proton affinities, ΔPA for complexes of acetic (\blacktriangle), monochloroacetic (\circ), dichloroacetic (\bullet), and trifluoroacetic (\triangle) acids with (a) pyridines and (b) pyridine *N*-oxides; data from ref. 57b,58.

Ault *et al.*⁶⁰ introduced the concept of a vibrational correlation diagram to compare the relative frequency shift $\Delta\nu/\nu_0$ [ν_0 is the stretching frequency of monomeric acid and $\Delta\nu = (\nu_{AHB} - \nu_0)$] of the hydrogen halide in a low temperature matrix with $\Delta = [PA(B) - PA(A^-)]/[PA(B) + PA(A^-)]$. Barnes⁶¹ extended this correlation to 195 compounds. Figure 6 shows correlation diagrams for complexes of pyridine and pyridine *N*-oxides with acetic acids in dichloromethane, which are broadly similar to those found by Ault⁶⁰ and Barnes.⁶¹ Thus the centre of gravity of the broad absorption in solution changes with proton affinity in much the same way as a relatively narrow frequency band in a low-temperature matrix. Complexes of pyridine and pyridine *N*-oxides differ in both position and shape of the turning point.

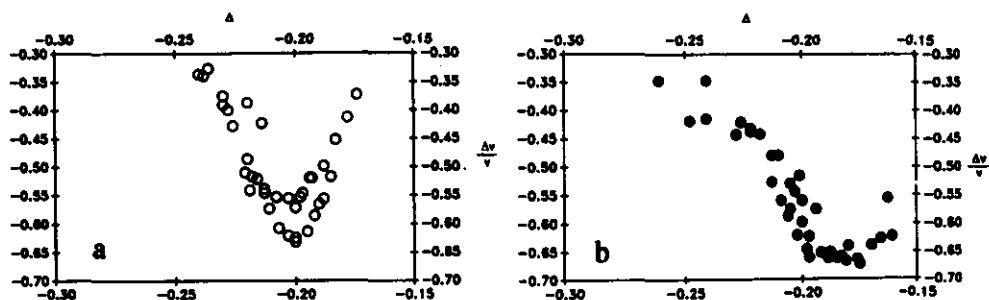


Figure 6. A plot of $\Delta\nu/\nu_0$ vs Δ for complexes of (a) pyridines and (b) pyridine *N*-oxides with acetic acids; from ref. 58.

^1H Nmr Spectra

Formation of H-bonds and protonation caused a downfield shift (up to 1 ppm) of CH protons in pyridine and pyridine *N*-oxide.⁶² The H-bonded protons in complexes have a chemical shift in downfield region of 13-20 ppm. The chemical shifts (δ_{H}) due to hydrogen bonding proton are generally concentration dependent.

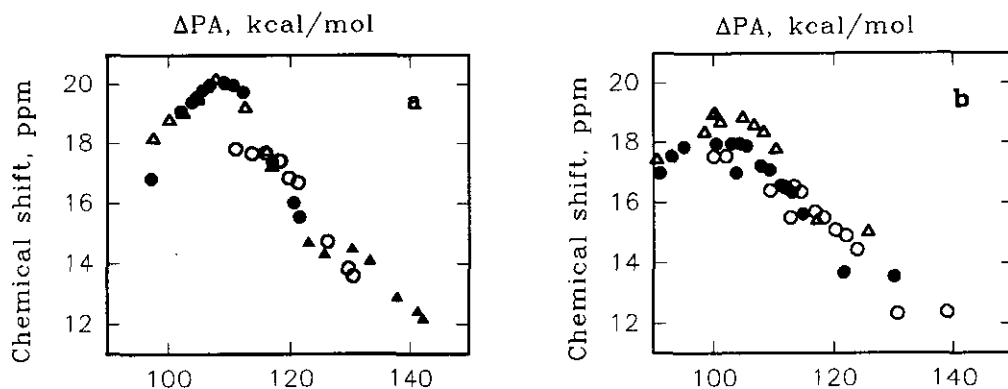
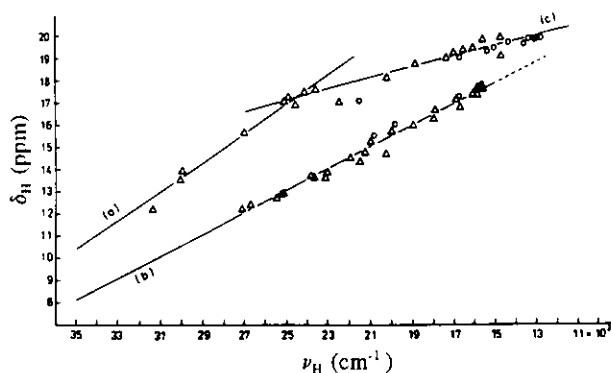


Figure 7. Plot of the chemical shift of hydrogen-bonded protons (δ_{H}) against the difference between proton affinities, ΔPA , for complexes of acetic (\blacktriangle), monochloroacetic (\circ), dichloroacetic (\bullet), and trifluoroacetic (\blacktriangle) acids with (a) pyridines and (b) pyridine *N*-oxides; data from ref. 58.

Nevertheless, the chemical shifts have usually been determined at only one concentration. Discrepancies between δ reported in the literature are often not due to experimental error but are resulted from different concentrations employed by different investigators. It has been proposed that spectroscopic parameters can be determined by extrapolation to infinite dilution to obtain "a concentration independent measurement". This procedure cannot be applied to ^1H nmr spectra, since the chemical shift of H-bonded protons is very sensitive to trace of water.³⁷

Figure 7 shows correlations of δ_{H} with ΔPA , for complexes of pyridines and pyridine *N*-oxides, respectively. In Figure 7b the points are more scattered than those in Figure 7a; this is caused by a trace of water, since some *N*-oxides are more hygroscopic than pyridines.

Figure 8. Plot of the chemical shift of hydrogen-bonded protons (δ_{H}) against the centre of gravity, (ν'), for complexes of pyridines with acids; from ref. 21.



In Figure 8 δ_{H} values for pyridine complexes are plotted versus ν' and the data can be resolved into a series of straight lines, each correlating δ_{H} with ν' for $\text{A-H} \cdots \text{B}$, $\text{A} \cdots \text{HB}^+$, and their mixtures.²¹ When molecular complexes and H-bonded ion pairs are considered, the contribution of inductive, mesomeric, steric, and ring current effects to the total shielding can be treated in the first approximation as constant for both species, then the separate lines derived for molecular complexes (eqn. 6) and ion-pairs (eqn. 7) are due to magnetic fields associated with charge density and by the difference in the magnetic anisotropy of the nitrogen atoms in pyridine and protonated pyridine, and the oxygen atoms (or halogens) in acids (Figure 8). From equations (6) and (7) the chemical shifts of "free" protonated pyridine and monomeric acid were estimated, respectively.

$$\delta_{\text{N}} +_{\text{H}} (\pm 0.24) = 33.174 - 6.501 * 10^{-3} \nu', \quad r=0.994, \quad n=9 \quad (6)$$

$$\delta_{\text{OH}} (\pm 0.26) = 25.350 - 4.927 * 10^{-3} \nu', r=0.990, n=29 \quad (7)$$

In complexes of pyridine *N*-oxide trifluoroacetates the proton is between the oxygen atoms and is separated from the positive charge of the ring by an oxygen atom, and single line is derived ($\delta_{\text{H}} (\pm 0.12) = 24.298 - 4.722 * 10^{-3} \nu', r=0.997, n=24$).⁵⁸

Carbon-13 Nmr Spectroscopy

Empirical models based on the additivity of fixed increments have proved, in the past, to be very powerful in the elucidation of ¹³C spectra in organic structural analysis.⁶³ More recent studies⁶⁴⁻⁶⁹ suggest that strict additivity does not always apply, e.g. in disubstituted benzenes and substituted pyridine *N*-oxides.

Pyridine *N*-oxides show a large shielding effect (~10 ppm) at C-2, C-4, and C-6 relative to that observed in corresponding pyridines.⁷⁰ Changes in the chemical shifts of pyridines and pyridine *N*-oxides caused by H-bonds or protonation are much smaller than those induced by a substituent.⁶⁸⁻⁷² These two effects, the H-bonds and substituents are non additive. Detection of H-bonds can be made significantly more difficult by medium polarity effects and by protonation. In Table 1 the H-bond effect on C-4 has been estimated as the difference in the chemical shift between aqueous and chloroform solutions [$\Delta_1 = \delta(\text{D}_2\text{O}) - \delta(\text{CDCl}_3)$], and the protonation effect as a difference in the chemical shift between perchloric acid and aqueous solutions [$\Delta_2 = \delta(\text{HClO}_4) - \delta(\text{D}_2\text{O})$]. Data listed in Table 1 show that substituents alter appreciably both H-bonds and protonation effects. Some substituents increase (4-Me, 4-Bu^t, 4-Cl) while other decrease (4-NMe₂, 4-OMe, 4-NO₂, 4-COMe) Δ_1 and Δ_2 in comparison with reference data (X=H). Substituent like 4-CN increases one effect but decreases another. Substituents at C-3 change Δ_1 and Δ_2 in a way different from substituents at C-4. The chemical shifts of H-bonded protons (δ_{H}) (eqn. 8) and the centre of gravity, (ν') (eqn. 9) of pyridine *N*-oxide complexes with dichloroacetic acid (DCA) correlate well with the relative ¹³C chemical shift difference [$(\Delta_3 - \Delta_4)/\Delta_3$]; [$\Delta_3 = \delta(\text{HClO}_4) - \delta(\text{CDCl}_3)$] and [$\Delta_4 = \delta(\text{DCA}) - \delta(\text{D}_2\text{O})$]

$$\delta_{\text{H}} = 19.576 - 11.182(\Delta_3 - \Delta_4)/\Delta_3; r=0.994, \text{SD}=0.510, n=15 \quad (8)$$

$$\nu' = 877.14 + 2072.2(\Delta_3 - \Delta_4)/\Delta_3; r=0.926, SD=105.5, n=15 \quad (9)$$

Table 1. Differences and relative ^{13}C chemical shift for C-4 in complexes of substituted pyridine *N*-oxides.⁶⁹

R	pK _a ^a	Δ_1	Δ_2	Δ_3	Δ_4	δ_{H}^a	ν'^a
4-NO ₂	-1.70	4.83	7.70	12.53	6.15	13.56	2011
4-CN	-1.17	9.19	5.78	17.81	8.84	13.70	1927
4-COMe	-	6.85	9.47	16.28	9.79	-	-
4-Cl	0.36	7.64	12.79	20.43	13.83	15.62	1639
H	0.79	7.25	11.21	18.46	13.56	16.33	1522
3-Me	1.08	8.62	11.19	19.81	13.90	16.58	1471
4-Me	1.29	8.26	13.06	21.32	17.28	17.09	1390
4-Bu ⁱ	-	9.39	11.77	20.94	18.13	-	-
3,4-Me ₂	1.48	7.64	12.11	19.75	16.86	17.22	1303
2,4,6-Me ₃	1.99	6.26	16.84	23.10	18.68	16.98	1209
4-OEt	1.97	5.44	6.83	12.27	10.55	17.97	1169
4-OMe	2.05	5.16	7.75	12.91	10.63	17.88	1205
4-OMe-2-Me	2.41	4.35	7.63	12.16	10.83	17.96	1175
4-OMe-2,6-Me ₂	3.45	4.11	10.28	14.39	11.36	17.95	1151
4-NMe ₂	4.05	4.28	4.11	8.39	6.79	17.85	1250
4-NMe ₂ -2-Me	4.35	2.99	5.05	8.82	6.80	17.55	1291
4-NMe ₂ -2,6-Me ₂	4.75	5.63	7.97	13.60	9.36	16.98	1304

a - data from ref. 57.

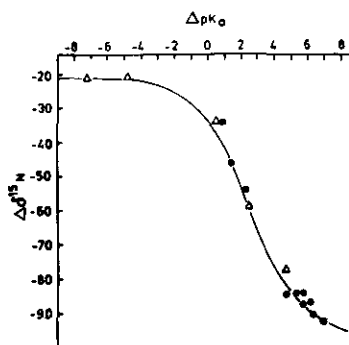
Nitrogen-15 Nmr Spectra

The ^{15}N nmr spectra of pyridines have been widely investigated.⁷³⁻⁸¹ Pyridine chemical shifts depend strongly on the substituent,⁷⁷ solvent⁷⁸⁻⁸⁰, protonation and *N*-alkylation.⁷⁷ Both protonation and *N*-alkylation shift the nitrogen resonance position more than 100 ppm upfield from its value in the free base.^{77,80,81} In the case of

pyridine *N*-oxides variation of the nitrogen resonance reach *ca.* 20 ppm.⁷⁴

The ¹⁵N nmr chemical shifts of ten substituted pyridines (R-Py ≡ B) and their complexes with trifluoroacetic acid (R-Py·TFA ≡ AHB) were measured at the natural abundance level in dichloromethane.⁸² The plot of the relative chemical shifts $\Delta\delta(^{15}\text{N}) = \delta(\text{AHB}) - \delta(\text{B})$ against $\Delta\text{p}K_a$ gives a titration curve (Figure 9), which reflects a protometric equilibrium (eqn. 1). These data were used to determine the constants of the overall proton transfer reaction (K_{exp}). A linear relationship holds between $\log K_{\text{exp}}$ and $\Delta\text{p}K_a$. This gives the 50% of the proton transfer at $\Delta\text{p}K_a = 4.4$, which is similar to that obtained by dielectric and ir methods.

Figure 9. Plot of $\Delta\delta(^{15}\text{N}) = \delta(\text{R-Py} \cdot \text{TFA}) - \delta(\text{R-Py})$ against $\Delta\text{p}K_a$; data ● from ref 82 and Δ from ref 80.

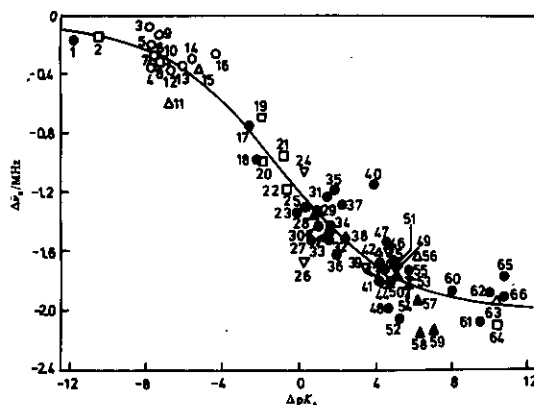


Nuclear Quadrupole Resonance (nqr) Spectroscopy

Changes in the electron density distribution in both the donor and acceptor molecules are one of the consequences of H-bond formation. The nqr spectroscopy, being particularly sensitive to subtle changes in electron density is a valuable tool in studies of H-bonds in solids. A proper selection of proton donor and acceptor enables one to modified the position of the proton inside the bridge which reveals itself as a change in nqr frequency. This effect had been reported first by Biedenkapp and Weiss in 1966.⁸³ Studies by numerous authors showed a direct relation between the nqr frequency and the degree of the proton transfer in the H-bonded complexes.^{41,84-94} Although the PT mechanism in the solid state and solution is usually different.⁹⁵ The shape of a plot of the mean ³⁵Cl nqr frequency shift, $\Delta\nu_{\text{NQR}} = \nu_{\text{NQR}} - 40.124 \text{ MHz}$ against $\Delta\text{p}K_a$ (Figure 10)

is similar to a titration curve and the degree of the proton transfer is near 0 or 100% in the plateau regions.

Figure 10. Plot of ^{35}Cl nqr mean frequency shift ($\Delta\nu_{\text{NQR}}$) against ΔpK_a for base-trichloroacetic acid systems. Numbers refer to Figure 1 in ref. 90.



The relation between the average frequency ν_{NQR} and ΔpK_a is given by eqn. (10), where ν_{HB} and ν_{PT} are the average resonance frequencies for $\text{A-H}\cdots\text{B}$ and $\text{A}\cdots\text{HB}^+$ species, respectively; ξ and C' are constants, listed in Table 2..

$$\log(\nu_{\text{HB}} - \nu_{\text{NQR}})/(\nu_{\text{NQR}} - \nu_{\text{PT}}) = \xi\Delta\text{pK}_a + C' \quad (10)$$

Table 2. Values of ξ and C' from eqn. (10) and ΔpK_a

Donor	ξ	C'	ΔpK_a	ref
Trichloroacetic acid	0.15	0.17	-1.1	90
Dichloroacetic acid	0.42	-0.70	1.67	40
2,6-Dichlorobenzoic acid	0.92	-3.86	4.2	91
2-Chlorobenzoic acid	0.82	-4.00	4.9	91
2-Chloro-4-nitrobenzoic acid	1		3.6-3.7	92
2-Chloro-5-nitrobenzoic acid			3.77	93
2,6-Dichloro-3-nitrobenzoic acid			3.77	93
2-Chloro-3,5-dinitrobenzoic acid			3.77	93

In solutions, complexes of pyridines and pyridine N-oxides form two different series (compared Figures 5a with 5b and 7a with 7b), but in the solid state they work up into one class (Figure 10).

Since the frequency of molecular vibration is much greater than that of a nuclear quadrupole precision, the

electric field gradient at the chlorine nucleus will be an average over all positions of the proton, so that it is not possible within further evidence to distinguish between a single minimum ($A \cdots H \cdots B$) or a symmetric double minimum ($A-H \cdots B \leftrightarrow A^- \cdots HB^+$) potential function. The field gradient at chlorine nucleus arises predominantly from the electrons in the C-Cl bond, and the proton or carbon contributed only a small part to the gradient, through the charge density of the neighboring carboxylate oxygen atoms. The oxygen charge density can influence the chlorine field gradient by (i) a direct, "through space" effect acting on the Cl atom and (ii) by an indirect, polarization effect acting on the C-Cl bond.

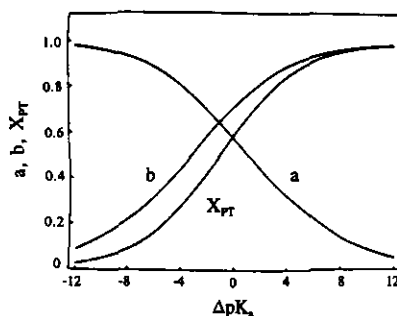
The charge distribution in H-bonded complexes can also be analyzed in term of the Mulliken charge-transfer formalism.⁹⁶ In this model, when asymmetry parameter of the electric field gradient tensor is small ($\eta \leq 0.2$), ν_{NQR} may be expressed through resonance frequencies (eqn. 11), where ν_0 and ν_1 are the average frequencies of the two boundary states, ν_{ex} is the average frequency contributing from the molecular lattice field and S is the overlapping integrals and a and b are parameters.

$$\nu_{\text{NQR}} = \nu_0 (b^2 + abS)(\nu_1 - \nu_0) + \nu_{\text{ex}}; \quad a^2 + b^2 + 2abS = 1 \quad (11)$$

When eqn. 11 was used with $S=0.2$, $\nu_0 = \nu_{\text{HB}}$, $\nu_1 = \nu_{\text{PT}}$, and $\nu_{\text{ex}}=0$, a and b were determined as a function ΔpK_a and are shown in Figure 11. The inversion point at which $a=b=0.645$ is equivalent to that indicated on the X_{PT} scale. Both formalism (the proton transfer equilibrium and the charge-transfer effect) describe the intermediate range of ΔpK_a in a similar way, where the complex should show a nearly symmetrical proton-density distribution within the bridge.⁴¹ This is in agreement with *ab initio* calculations that predict that H-bonds are strongly electrostatic in nature with an essential charge-transfer contribution.⁹⁷

Since the N^+-O^- group in pyridine *N*-oxides is strongly polarizable, it can act either as an electron-attracting or as an electron-donating group, facilitating both electrophilic and nucleophilic substitutions in the aromatic compounds.^{98,99} The effect of such a polarizable group on the electron densities at different sites of substitution of the pyridine was studied by ^{35}Cl nqr¹⁰⁰ and ^{14}N nqr.¹⁰¹ The change in the nqr frequencies in *N*-oxides as compare to their parent compounds are interpreted in terms of the conjugative effect and the inductive effect of the N^+-O^- group.

Figure 11. X_{PT} , a and b coefficients of the Mulliken equation plotted against ΔpK_a ; from ref. 90.



Calorimetric Studies

Guryanova *et al.*¹⁰² have collected ΔH° and ΔS° values for the formation of H-bonded complexes. Most of the literature results have been obtained from the temperature variation of the equilibrium constants using a spectroscopic method (uv, ir, raman, and nmr). The standard free energy, ΔG° , enthalpies, ΔH° , and entropies, ΔS° , are determined from the relations (12) and (13).

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T \Delta S^\circ \quad (12)$$

$$\ln K = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (13)$$

ΔH° and ΔS° were usually found by a graphical procedure based on eqn (12) from the shape of the linear plot of $\ln K$ against $1/T$ and from the intercept on the ordinate axis.

A systematic calorimetric studies have been done for pyridine complexes with trifluoroacetic acid in CCl_4 ¹⁹ and CHCl_3 ,¹⁰³ for reaction of equal amount of base and acid, $\Delta H^\circ_{1:1}$, and for the stoichiometry of 2:1 base to acid, $\Delta H^\circ_{2:1}$, and 1:2 base to acid, $\Delta H^\circ_{1:2}$. In all cases ΔH° increases with ΔpK_a of pyridines. This suggest that ΔH° is a sum of the heat of formation of the complex and the heat of the proton transfer (eqn. 14).

$$\Delta H^\circ = \Delta H^\circ_{HB} + \Delta H^\circ_{PT} \quad (14)$$

Values of $\Delta H^\circ_{1:2}$ are ca. 60% larger than the $\Delta H^\circ_{1:1}$, suggesting that both $\text{B} \cdot \text{HA} \cdot \text{HA}$ and $\text{B}^+ \text{H} \cdot \text{A}^- \cdot \text{HA}$ are more stable than $\text{B} \cdot \text{HA}$ and $\text{B}^+ \text{H} \cdot \text{A}^-$. Values of $\Delta H^\circ_{2:1}$ are slightly larger (from 0.2 to 0.4 kcal/mol) than the $\Delta H^\circ_{1:1}$ values, which indicate that $(\text{BHB})^+ \text{A}^-$ species are present in a small amount.

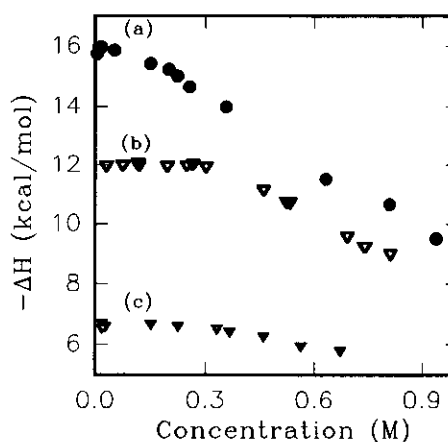
Enthalpies can also be obtained from the semiempirical relationship (eqn. 15) introduced by Iogansen,⁵⁴

$$-\Delta H^{\circ} = 2.91 \cdot \Delta A^{1/2} \quad (15)$$

where $\Delta A^{1/2} = A_{\text{AHB}}^{1/2} - A_{\text{AH}}^{1/2}$; A_{AHB} and A_{AH} are the integrated intensities of the protic vibration and monomeric acid, respectively. Enthalpies reproduced by eqn. (15) contain mainly the heat of H-bond formation.^{57b}

Figure 12 shows the variation of $\Delta H^{\circ}_{1:1}$ for pyridine complexes with trifluoroacetic acid as a function of concentration, due to formation of higher aggregates $(\text{BHA})_n$.

Figure 12. Effect of concentration on enthalpies for complexes of trifluoroacetic acid with (a) 2,4,6-trimethylpyridine, (b) pyridine, (c) 4-cyanopyridine; data from ref. 103.



Colligative Properties

The principles of osmometric measurements of vapour pressure lowering and practical application of the method have been reported in the literature.¹⁰⁴⁻¹¹⁰ When a non-volatile solute is dissolved in a solvent, the vapour pressure of the solvent is lowered. The temperature difference is determined by matched thermistors and is measured by imbalance V in the Wheatstone bridge. It can be shown that V values depend linearly on the osmotic concentration ($\phi \cdot m$) of the solute, so that the relation (16) is valid if no dissociation of the solute in the solvent occurs. In eqn. (16) V is the measured imbalance (μV), k is the calibration constant, ϕ is the practical molal osmotic coefficient, p and p_0 are the partial pressures of the solvent over the solutes and the pure solvent, respectively, a_1 is the thermodynamic activity of the solvent, M_1 is the molecular weight of the solvent, m is the stoichiometric (analytical) solute concentration (in $\text{mol} \cdot \text{kg}^{-1}$).

$$10^3 V/kM_1 = 10^3 \phi \cdot m M_1 = -\ln a_1 = -\ln p/p_0 \quad (16)$$

Table 3. Aggregation constants

Compounds	Solvent	Temp °C	Constant kg · mol ⁻¹	Ref
3-Br-Py · HOCCF ₃	benzene	27	K=0.63±0.10	112
Py · HOCCF ₃	benzene	25	K=5.48±0.38	112
3-Me-Py · HOCCF ₃	benzene	27	K=4.69±0.40	112
4-Et-Py · HOCCF ₃	benzene	30	K ₂ =36.0±2.50	113
4-Me-Py · HOCCF ₃	benzene	30	K ₂ =13.1±0.60	113
2,4,6-Me ₃ -Py · HOCCF ₃	benzene	27	K=7.72±0.22	112
2,4,6-Me ₃ -Py · HOCCCHCl ₂	benzene	27	K=2.06±0.08	114
2,4,6-Me ₃ -Py · HOCCCl ₂ CH ₃	benzene	27	K=0.77±0.03	114
Py→O	benzene	25	K=1.52±0.17	10
4-Cl-Py→O · HOCCF ₃	benzene	27	K=0.99±0.13	111
4-Me-Py→O · HOCCF ₃	benzene	27	K=4.37±0.44	111
4-PhO-Py→O · HOCCF ₃	benzene	27	K=2.36±0.17	111
4-MeO-Py→O · HOCCF ₃ *	benzene	27	K=7.93±0.28	111
		35	K=7.58±0.16	
		40	K=6.95±0.27	
		45	K=5.80±0.14	
		50	K=5.30±0.13	
4-MeQNO · HOCCCH ₂ Cl	benzene	27	K ₂ =1.78±0.47	115
4-MeQNO · HOCCCH ₂ Cl	chlorobenzene	27	K ₂ =0.99±0.20	115
4-MeQNO · HOCCCH ₂ Cl	1,2-dichloroethane	27	K ₂ =0.04±0.02	115
4-MeQNO · HOCCCH ₂ Cl	acetone	27	K ₂ ~0	115
Q · HOCCF ₃	benzene	33	K=3.34±0.19	116

Py - pyridine, Py→O - pyridine *N*-oxide, QNO - quinoline *N*-oxide, Q - quinoline; * $\Delta H^\circ = -12.15 \pm 0.26$ kJ, $\Delta S^\circ = -24.16 \pm 0.59$ J/molK.

The experimental values $\phi \cdot m$ and m are the quantities which are utilized to obtain equilibrium constants for aggregation. Two models were considered.¹¹¹ In model I, the monomer is in an equilibrium with other polymeric species of degree of aggregation n , and K_n is given by eqn. (17). Model II assumed that an extended

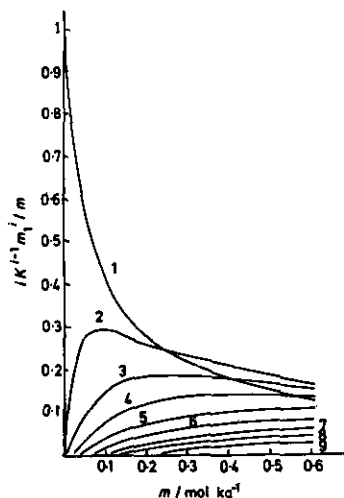
series of multimers (dimers, trimers, tetramers, etc) are formed. Assuming for simplicity that a series of equilibrium constants are equal and not dependent on n (eqn. 18).

$$K_n = [(m-\phi m)(n-1)^{n-1}] / [(n\phi m)^n] \quad (17)$$

$$K = (m-\phi m)/(\phi m)^2 \quad (18)$$

Examples of the equilibrium constants are given in Table 3. Figure 13 presents the distribution of dominant aggregates of 4-methoxypyridine *N*-oxide trifluoroacetate.

Figure 13. The distribution of the major associated species for the 4-methoxypyridine *N*-oxide - trifluoroacetic acid complex in benzene at 27 °C; form ref. 111.

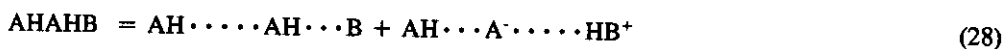
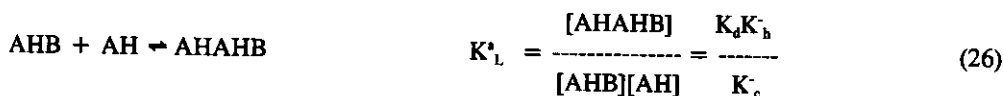
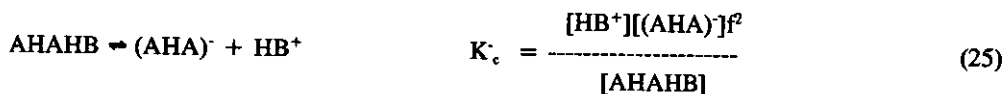
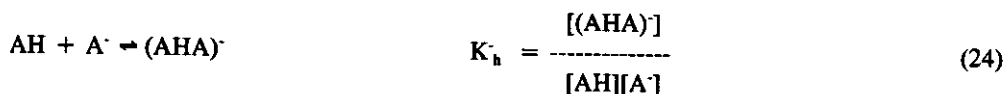
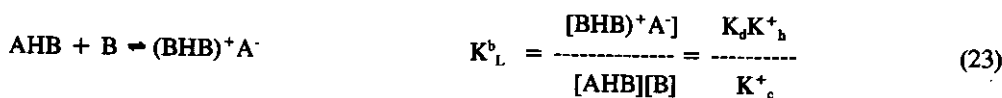
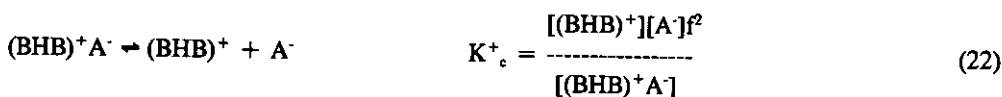
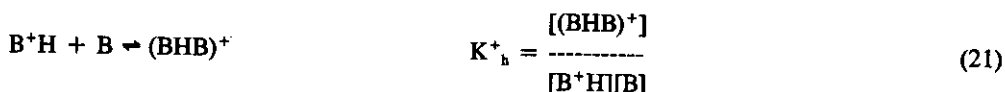
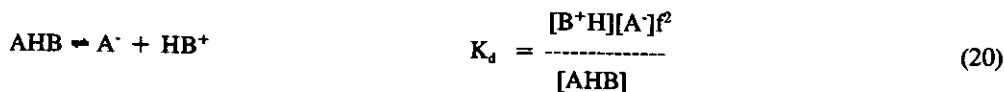
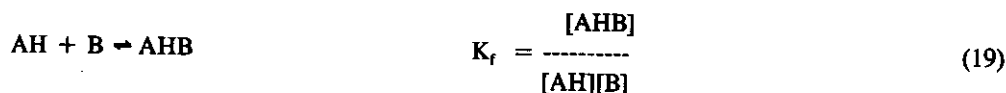


Pyridinium salts in chlorobenzene solution form aggregates and the association constants increases with the planarity of the cation.¹¹⁷

Conductance Studies

The best information about ions come from conductance.⁴⁻⁶ Several conductometric acid-base titrations in organic solutions have been reported in the literature,^{33,118-120} also for complexes of pyridines¹²¹⁻¹²³, and 4-methoxy-2,6-dimethylpyridine *N*-oxide with trifluoroacetic acid.¹²⁴

The following equilibria (19)-(28) were considered in order to explain the measured conductivity.



where f is the mean activity coefficient of ions.

The molar conductivities were analyzed using equations (29) and (30) derived by Fuoss and Kraus,³² and by Witschonke and Kraus,¹²⁵ respectively.

$$F(z)/\Lambda_c = 1/\Lambda^\infty + 1/(\Lambda^\infty)^2 K + \Lambda_c C^\circ f^2 / F(z) \quad (29a)$$

$$F(z) = (4/3) \{ \cos^2[(1/3) \arccos(-3 \sqrt{3/2z})] \} \quad (29b)$$

$$z = S (\Lambda_c C^\circ)^{1/2} / (\Lambda^\infty)^{3/2} \quad (29c)$$

$$\alpha = \Lambda_c / \Lambda^\infty F(z) \quad (29d)$$

$$F(z)/\Lambda_c = 1/\Lambda^\infty + f/\Lambda^\infty (K_d K_f)^{1/2} + \Lambda_c C^\circ f^2 / K_d F(z) (\Lambda^\infty)^2 \quad (30)$$

where $F(z)$ is a function of variable z and is related to the degree of dissociation, α , by the equation (29d), Λ_c is the measured molar conductivity, Λ^∞ is the molar conductivity at infinite dilution, K is the dissociation constant, S is the Onsager coefficient, f is the mean activity coefficient calculated from the Debye-Hückel theory, and C° is the concentration. A plot of $F(z)/\Lambda_c$ against $\Lambda_c C^\circ f^2 / F(z)$ should be linear and Λ^\pm and K can be determined from the intercept and slope, respectively. Several linear plots were obtained and the resulting Λ^∞ and K values are listed in Table 4. Figure 14 presents the distribution of the species at $C = 1 \cdot 10^{-4}$

The main difference between complexes of pyridine and pyridine *N*-oxide is visualized in K^+_{h} constants. The homoconjugated symmetric cation $(\text{BHB})^+$, where B is pyridine or substituted pyridines show a doublet for $\nu_s(\text{NHN})$ at *ca.* 2000 and 2500 cm^{-1} , which is thought to arise from a double-minimum low barrier potential well.¹²⁶ When B is pyridine *N*-oxide, the homoconjugated cation consists of two crystallographic equivalent residue joined by very short H-bonds ($\text{O} \cdots \text{H} \cdots \text{O}$ distances of 2.345-2.40 Å). The available X-ray, ir, and ^1H nmr data are consistent with a symmetrical single minimum potential.²⁸ The H-bonds in homoconjugated cations of pyridine *N*-oxides are much stronger than that in pyridines and hence K^+_{h} is *ca.* three order bigger.

Figure 14. Distribution of major species in complexes of trifluoroacetic acid with 2,4,6-trimethylpyridine (filled chart) and 4-methoxy-2,6-dimethylpyridine *N*-oxide (open chart). (1) B; (2) HB^+ ; (3) AHB ; (4) A^- ; (5) $(\text{AHA})^-$; (6) AH (data from ref. 123, 124).

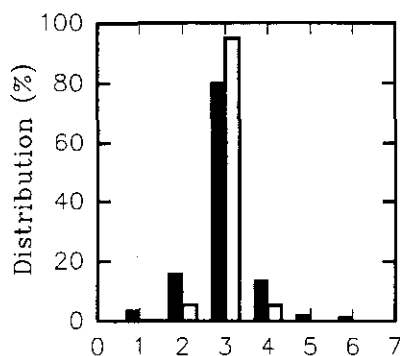


Table 4. Molar conductivities of complexes, Λ^∞ , or ions, λ^∞ , and equilibrium constants, K_i , of various competing equilibria occurring in nitrobenzene solutions of trifluoroacetic acid (TFA) complexes with 2,4,6-trimethylpyridine (2,4,6-Me₃-Py) and 4-methoxy-2,6-dimethylpyridine *N*-oxide (4-MeO-2,6-Me₂-Py→O).

	2,4,6-Me ₃ -Py · TFA ¹²³	4-MeO-2,6-Me ₂ -Py→O · TFA ¹²⁴
Equilibrium constants		
K_f	$(1.3 \pm 0.1) \times 10^7$	$> 10^{30}$
K_d	$(2.64 \pm 0.03) \times 10^{-6}$	$(2.7 \pm 0.1) \times 10^{-7}$
$K^+_{h_1}$	24.4 ± 1.4	$(1.5 \pm 0.3) \times 10^4$
$K^+_{c_1}$	$(5.8 \pm 1.1) \times 10^{-5}$	$(1.2 \pm 0.1) \times 10^{-3}$
$K^b_{L_1}$	1.09 ± 0.38	3.70 ± 0.7
$K^-_{h_1}$	$(1.05 \pm 0.08) \times 10^5$	$(1.03 \pm 0.08) \times 10^5$
$K^-_{c_1}$	$(7.4 \pm 0.4) \times 10^{-2}$	$\gg 1$
$K^b_{L_2}$	3.7 ± 0.3	$\ll 1$
Conductance		
Λ^∞_{AHB}	39.2 ± 0.3	38.9 ± 0.2
Λ^∞_{AHAHB}	33.46 ± 0.02	33.2 ± 0.1
Λ^∞_{BHBA}	36.22 ± 0.1	35.1 ± 0.4
$\lambda^\infty_{A^-}$	23.0	23.0
$\lambda^\infty_{(HB)^+}$	16.2	15.9
$\lambda^\infty_{(AHA)^-}$	17.3	17.3
$\lambda^\infty_{(BHB)^+}$	13.3	12.2

X-Ray Studies

Only structures of few complexes have been solved by X-ray.^{25,26,127,128} In complexes of trifluoroacetic acid with 4-NMe₂- and 4-Me-pyridines the N-H···O bonds are 2.724(3) and 2.702(4) Å, respectively, proton is bonded to pyridine N(1) atom,¹²⁸ and the H-bonds are nearly linear, 177(4)°. Shorter H-bond is in the complex of trifluoroacetic acid with 4-CN-pyridine, the N···O distance is 2.552(4) Å and the H(1) atom is located near the middle of N···H···O bridge. The difference Fourier map and the refinement process have shown, that

its position is slightly shifted toward the N(1) atom.¹²⁸

Two asymmetric hydrogen bonds are present in 4-picolinium hydrogen malonate.²⁶ The intermolecular O...N bond of 2.639(3) Å, connecting 4-picolinium and hydrogen malonate ions, is nearly linear (170(3)°), while the intramolecular bond is bent (159(4)°) and short, O...O = 2.493(3) Å.

A brief report of X-ray work gives the O...O distance as 2.41 Å in complex of trichloroacetic acid with pyridine *N*-oxide.¹²⁷ Two molecules of 3-Me-pyridine *N*-oxide are bonded by a short O...O distance of 2.517(6) Å with one molecule of fumaric acid.¹²⁹ Position of H-bonded proton is not localized.

Other Methods

Ultraviolet and visible spectroscopy is very fruitful method to investigate H-bonds and proton transfer in complexes of phenols with various non-aromatic bases. This method confirmed the existence a mixture of tautomers (eqn. 1) in solution of phenols with alkylamines.^{3,130} In the case of pyridines uv spectroscopy is less useful due to the problem of separation $\pi \rightarrow n^*$ and $n^* \rightarrow \pi$ transitions.¹³¹

Kreevoy and Chong¹³² have shown that the uv spectra of complexes formed by pyridine *N*-oxide with various carboxylic and sulfonic acids of various strength are not combinations of the spectra of the protonated and unprotonated base. Rather, the complexes with acids of intermediate strength show bands in intermediate positions. Neither fully protonated nor unprotonated base is present. Instead, these complexes have two partial O-H bonds, the relative strength of which varies continuously with the strength of the acid.

These results do not indicate whether there is one or two minima between the two basis oxygens in the potential function for the hydrogen. However, if there are two, the residence time of the hydrogen in one of them can be no more than about 10^{-15} s. Such a residence time is of no chemical significance. If there is a double minimum potential function, the barrier between the two minima must be almost entirely below the first allowed vibrational level.

Potentiometric measurements may be used to study formation of homoconjugated cations (BHB)⁺ and anions

(AHA):¹³³⁻¹³⁵

An ion cyclotron resonance mass spectrometry is a fairly new technique for studying an ion-molecule reaction in the gas phase. Protonated pyridine interacts with pyridine to form (BHB)⁺ cation.¹³⁶

Theoretical Calculations

Experiment and theory are equally fundamental in any branch of science that has reached a rigorous stage. Complexes with H-bonds are investigated by both *ab initio*¹³⁷ and semiempirical¹³⁸ methods. *Ab initio* calculations are still obtained to relative small molecules, e.g. HCOOH · OH₂ or HCOO⁻ · HOH.¹³⁹ Complexes like RCOOH · NCCH₃ or pyridine-alcohol are studied by semiempirical methods.¹⁴⁰

It is well known, that the widely used semiempirical methods MNDO/3 and MNDO do not reproduced the geometrical structure and energies of H-bonded systems well. Therefore, several modifications of these methods have been designed with the aim of correcting these drawbacks, e.g. AM1¹⁴¹ and PM3.¹⁴² Both method (AM1 and PM3) reproduced correctly geometry of many H-bonded complexes. The AM1 overestimates H-bond interactions through decreases core repulsion function (CRF) and favours bifurcated (two H atom with one lone pair) H-bonds over linear ones, whenever possible (i.e. it tends to maximize the number of H-bonds interactions) and also cyclic structures over open ones.^{143,144}

For several complexes of trifluoroacetic acid with pyridines in the gas phase, PM3 predicts two minima, the deeper one for the A-H ··· B complex and the shallower one for the A ··· HB⁺ form.¹²⁸ The higher energy minimum it is at least partly due to an overestimation of the attraction interaction between O(1') from COO group and proton H(6) from pyridine ring.

In solution complexes of pyridines with trifluoroacetic acid exist in a tautomeric equilibrium (eqn. 1) and the amount of the ionic form increases with increasing dielectric constant of the solvent. This behaviour is qualitatively reproduced by PM3 method. For the most probable cavity radius ($a=4.0$), the ionic form is predicted to be more stable than the molecular one which agree well with the ir^{20} and $^1\text{H nmr}^{145}$ spectra. The

interaction energies predicted by PM3 are about two times larger than those predicted by the AM1 method, but they are probably half of the experimental values.

Solvent Effect

The solvent effect on H-bonded complexes are most frequently investigated and reviewed.¹⁴⁶⁻¹⁴⁹ Figures 15 and 16 show solvent effect on the centre of gravity (ν') and the chemical shifts of H-bonded proton (δ_H) in complexes of pyridine and pyridine *N*-oxides with trifluoroacetic acid. The pyridine complexes are very sensitive to solvent effect, while the complexes of pyridine *N*-oxides are resistant.

The variation of ν' and δ_H with solvent in the complexes of pyridines is very similar to that predicted by theory and may provide evidence that dipole of the hydrogen bond interacts with the reaction field from the environment.¹ These variations reflect that the equilibrium (1) is shifted toward the polar form with increasing solvent polarity.

The observed resistance of ir and ¹H nmr spectra of pyridine *N*-oxides with trifluoroacetic acid to solvent effect confirms that these complexes show a single minimum potential.^{49,132}

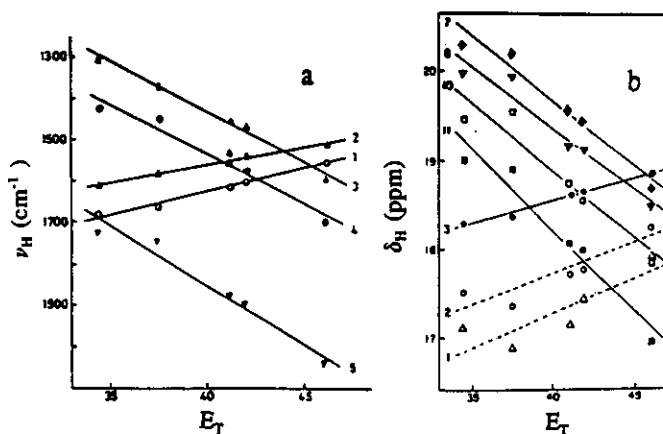


Figure 15. Plot of the centre of gravity (a) and the chemical shift of H-bonded proton (b) against E_T of complexes of trifluoroacetic acid with pyridines; from ref. 20, 145.

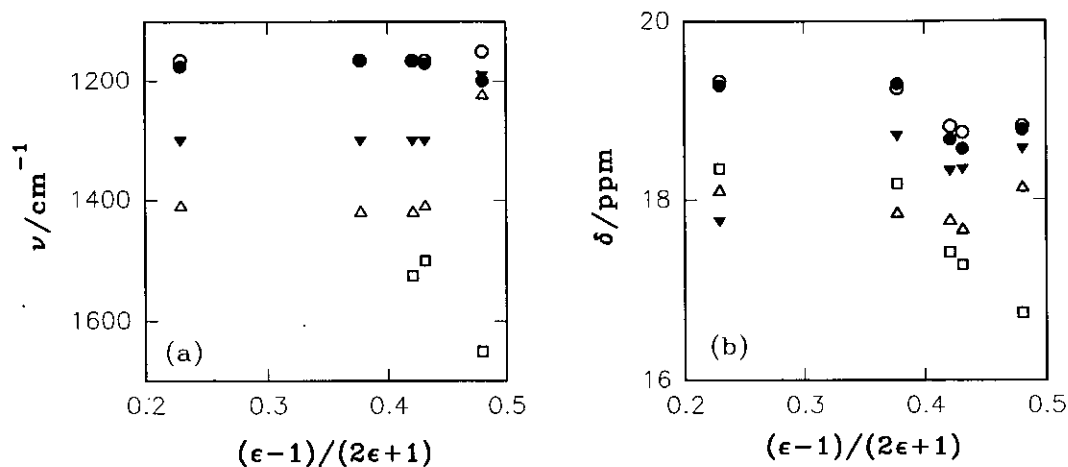
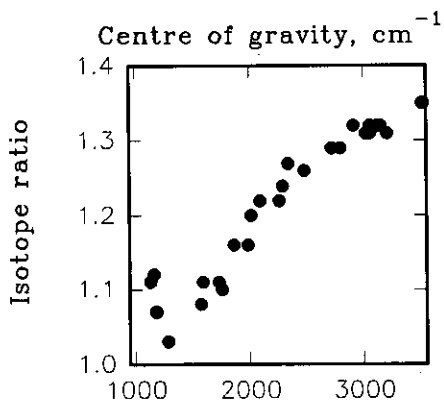


Figure 16. Plot of the centre of gravity (a) and the chemical shift of H-bonded proton (b) against $(\epsilon-1)/(2\epsilon+1)$ of complexes of trifluoroacetic acid with pyridine *N*-oxides; from ref. 150

Isotope Effect

Replacing the H of an H-bond by D may be expected to cause changes in some or all of the physical properties of the bond. Sing and Wood¹⁵¹ calculated that in ir spectrum the isotope frequency ratio ν_{AH}/ν_{AD} would vary significantly from the expected $2^{1/4} \approx 1.35$ of non-hydrogen-bonding models. The ir changes are dealt by Novak¹⁵² who shows graphically how this ratio first decreases with strong H-bonds to a nil isotope effect, e.g. $\nu_{AH}/\nu_{AD} = 1$, but then for very short H-bonds again increases. Figure 17 illustrates the variation of ν'_{AH}/ν'_{AD} versus ν'_{AH} for various complexes of pyridines and pyridine *N*-oxides.

Figure 17. Plot of the isotope ratio (ν'_{H}/ν'_{D}) as a function of the centre of gravity (ν'_{H}) for various complexes; data from ref. 55.



The theoretical results obtained by Guissani and Ratajczak¹⁵³ suggest that some indication on the potential energy curve of the H-bonds can be acquired from the study of $\nu\text{AH}/\nu\text{AD}$ ratio. The results plotted in Figure 17 do not indicate whether there is one or two minima in the potential function for the hydrogen.

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