Spectroscopic Differences between Molecular (O–H $\cdots$ N) and Ionic Pair (O$^-$ $\cdots$ H–N$^+$) Hydrogen Complexes

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The centre of gravity ($\bar{\nu}_H$) and chemical shifts (δ_H) of hydrogen-bonded protons in 55 complexes of pyridines with acetic acids have been measured in dichloromethane. If $\bar{\nu}_H$ and δ_H are plotted against the aqueous pK_a values for protonation of these bases general scatter diagrams are obtained which may be resolved into separate trends for different acids. We noted that this behaviour is controlled by the equilibrium between the molecular complex and the ion pair. Strong overlap of the carbonyl and carboxy stretching bands of the molecular complex and the hydrogen-bonded ion pair leads in most cases to a single band. Characteristic variations of the bandwidth were found. A plot of δ_H against $\bar{\nu}_H$ can be resolved into a series of straight lines for molecular complexes, hydrogen-bonded ion pairs and their mixtures, respectively. A straight line for molecular complexes consists of data for the monomeric acids. The chemical shifts for N$^+$–H proton of the 'free' pyridine cation was estimated from the line of protonated pyridines and compared with the calculated value.

It is generally accepted that complexes of pyridines with acetic acids can be described by a tautomeric equilibrium (1) between molecular and H-bonded ionic-pair species.[1] For a given acid–base pair, the degree of proton transfer depends primarily on the solvation of the ion pair, and the effects of the delocalization charge.

$$\text{A–H} \cdots \text{B} \rightleftharpoons \text{A}^- \cdots \text{HB}^+ \qquad (1)$$

A detailed analysis of vapour pressure osmometry data in low polar solvents is consistent with the presence of aggregates[2,3] [equation (2)]. Strong evidence may also be cited for the presence of various kinds of ionic species [equation (3)].[4]

$$n\text{AHB} \rightleftharpoons (\text{AHB})_m \qquad (2)$$

$$\text{Free ions} \rightleftharpoons \text{H-bonded ion pairs} \rightleftharpoons \text{Triple ions} \qquad (3)$$

In previous investigations,[5–7] we have studied the variations in the chemical shifts of hydrogen-bonded protons, δ_H, and the centre of gravity, $\bar{\nu}_H$, of strong and broad absorption in the i.r. spectra of complexes of trifluoroacetic acid with 12 pyridines in benzene and dichloromethane. A plot of δ_H against $\bar{\nu}_H$ consists of two intersecting straight lines. It was suggested that the principal cause for the difference between the two lines lies in the charge derived by protonation of the pyridine ring. Since most of the complexes investigated so far involve both species of equation (1), it seems interesting to extend research on complexes which form only one species.

Previously[8] we have drawn attention to the effect of the reaction field (caused by solvent or concentration) on δ_H and $\bar{\nu}_H$, which was correlated with equations (1) and (2). Thus, all complexes were measured at the same concentration (0.2M).

Experimental

4-n-Nonylpyridine, b.p. 122—123 °C at 0.4 mmHg, and 4-n-undecylpyridine, b.p. 176 °C at 0.2 mmHg, were prepared from 4-picoline, n-octyl and n-decyl chloride, respectively, and phenyl-lithium.[9]

Complexes were prepared by adding stoicheiometric amounts of acetic acids in ether solutions of pyridines and cooled in a CO_2–acetone bath. The resulting precipitates were recrystallized from ether.

Complexes of 4-n-undecylpyridine with mineral acids were prepared according to the method described by Cook[10] and recrystallized from ethyl acetate. All complexes were dried over P_2O_5.

Dichloromethane was purified and dried as previously.[7] All solutions were prepared and all transfers of nonaqueous solutions were made in a dry-box.

I.r. spectra were recorded on Perkin-Elmer 580 and 377 spectrophotometers using cells with KBr (0.23 and 0.124 mm windows) and CaF_2 (3.1 mm windows). ^{1}H N.m.r. spectra were measured on a Tesla BS 467 spectrometer. All chemical shifts were taken downfield relative to the resonance of the solvent and then converted into δ values by adding 5.3.

Both i.r. and ^{1}H n.m.r. spectra of complexes of acetic, 3-bromopropionic, and chloroacetic acids were measured with 2—4-fold excess of base.

Centres of gravity of the reconstructed bands were obtained as $\bar{\nu}_H = \int A(\nu)\nu d\nu / \int A(\nu) d\nu$, where $A = \log_{10} T_{bl}/T$. T_{bl} and T are the transmittance of base line and complex, respectively. Compensation of solvent in the 4 000—1 600 cm^{-1} region and broad absorption of acids in the 1 600—400 cm^{-1} region were used as a base line. The reproducibility of $\bar{\nu}_H$ obtained was ± 75 cm^{-1}.

Results

Both i.r. frequencies (ν_{OH}[11] and $\bar{\nu}_H$[8]) and chemical shifts (δ_H)[12] due to hydrogen bonding are generally concentration dependent. Nevertheless, the frequencies and the chemical shifts have usually been determined at only one concentration. Discrepancies between ν and δ reported in the literature are often not due to experimental error but are results from different concentrations employed by different investigators. It has been proposed that ν can be determined by extrapolation to infinite dilution to obtain 'a concentration-independent measurement'. This procedure cannot be applied to ^{1}H n.m.r. spectra, since the chemical shift of hydrogen-bonded protons is very sensitive to traces of water.[12,13] Thus, Figures 1 and 2 show an example of spectra and Table 1 lists values of $\bar{\nu}_H$ and δ_H determined at the same concentration (0.2M).

In Table 1 our results (corrected by base line) are compared with published values (without base-line correction) for 14 complexes with acetic acids. They are almost identical within

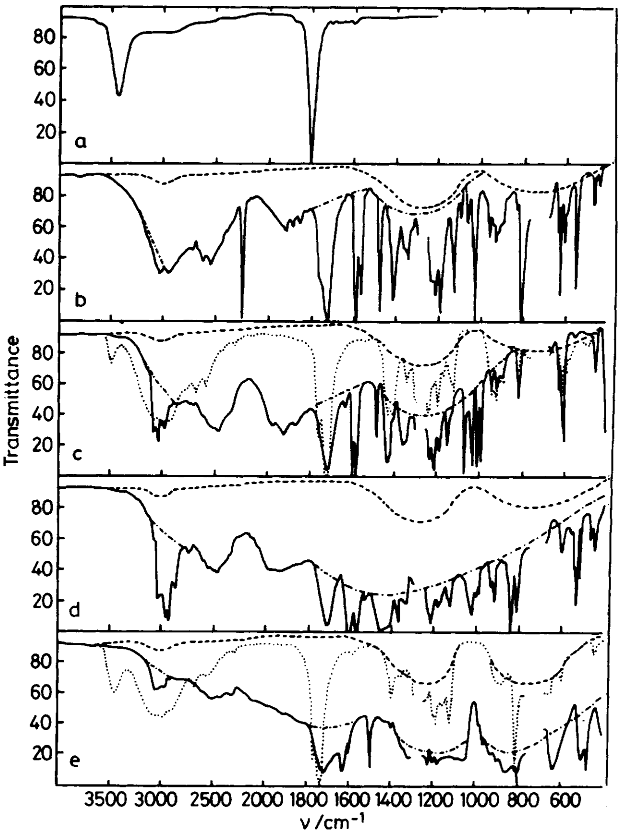

Figure 1. I.r. spectra of: a, CF_3COOH; b, 3-cyanopyridine•$HOOCCH_2CH_2Br$; c, pyridine•$HOOCCH_2CH_2Br$ (———), CH_2BrCH_2COOH (• • • • •); d, 2,4,6-trimethylpyridine•$HOOCCH_2CH_2Br$; e, 4-methylpyridine•$HOOCCHCl_2$ (———), $CHCl_2COOH$ (• • • • •) in CH_2Cl_2. Concentration (a) 0.0165M, (b—e) 0.2M. Continuous absorption (• — • — •); base line (— — —)

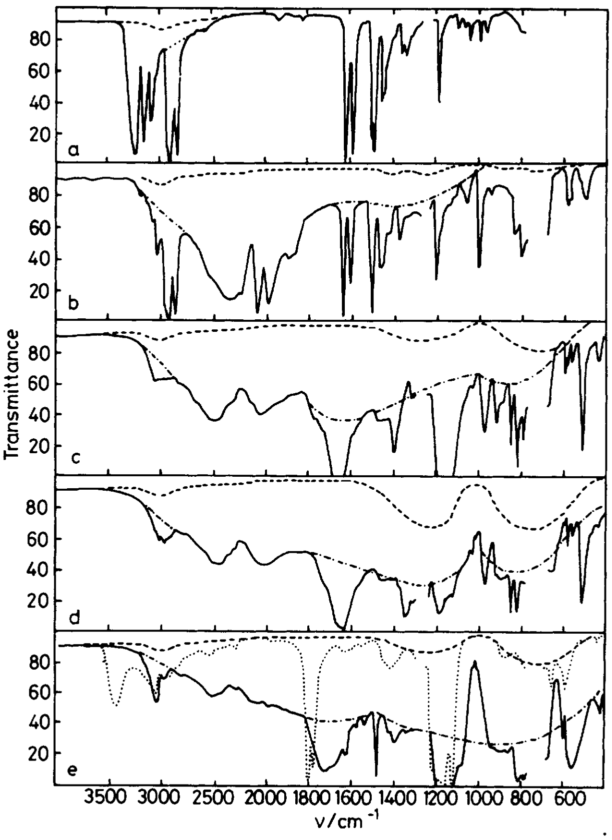

Figure 2. I.r. spectra of: a, 4-nonylpyridine–$HSbCl_6$; b, 4-n-nonylpyridine–HCl; c, 2,4,6-trimethylpyridine–$HOOCCF_3$; d, 2,4,6-trimethylpyridine–$HOOCCHCl_2$; e, pyridine–$HOOCCF_3$ (———), CF_3COOH (• • • • •) in CH_2Cl_2 (0.2M). Continuous absorption (– • – • – •); base line (– – –)

experimental error for all complexes except two with trifluoroacetic acid (points 38 and 44).

The average difference in chemical shifts for five complexes between our values and literature values is 0.6 p.p.m.

Figure 5 shows the evolution of the absorption in the carbonyl–carboxylate region.

Discussion

Correlation of $\bar{\nu}_H$ *and* δ_H *with* pK_a.—In hydrogen-bond complexes formation between Brönsted acids (AH) and bases (B), the proton is magnetically deshielded and the A–H (or B^+–H) stretching frequency decreases. Both the change in the A–H (or B^+–H) stretching frequency ($\Delta\nu$) and the change in proton shielding constant (Δ) in hydrogen-bond complex formation have been correlated with pK_a, proton affinities, bond lengths, i.r. intensities, polarity of hydrogen bonds ($\Delta\bar{\mu}$), heats of hydrogen bonding (ΔH_f), heats of protonation (ΔH_i), *etc.*[14–16] There is now almost unanimous agreement that no general linear correlation exists. However, for closely related compounds (such as those of a single functional group) interacting with the same AH or a single base B with a series of similar AH, good linear correlations are found. An exception is the good linear correlation between ΔH_i and pK_a for 56 various bases with HSO_3F.[15]

Figure 3 shows a plot of the centre of gravity ($\bar{\nu}_H$) against the pK_a values of pyridine bases. As expected each acid forms its own series of complexes. The various straight lines drawn in Figure 3 are least-squares fits of the data. It is worth noting that there is a single line for complexes of acetic and 3-bromopropionic acids and there are two lines for complexes of dichloroacetic and trifluoroacetic acids. Two-line correlations between $\bar{\nu}_H$ and pK_a have been observed previously for several complexes.[7,17–19]

Absorption in the carbonyl–carboxylate region (see below) confirms the tautomeric equilibrium (1) in complexes of pyridine bases with carboxylic acids. Thus the point of intersection corresponds to equimolar equilibrium of the molecular complex and hydrogen-bonded ion pairs. The observed gradual shift of $\bar{\nu}_H$ to higher wavenumbers with decreasing pK_a values on the first line is caused by the molecular complexes, whereas the gradual shifts to higher wavenumbers with increasing pK_a values on the second line reflect an increase in the hydrogen-bonded ion pairs.

A number of authors have found, for pyridine bases with methanol,[11] phenol,[11] and *p*-fluorophenol,[15] a linear correlation between the change of frequency ($\Delta\nu$) and pK_a values of the base [equation (4)]. Table 2 lists values of parameters *a* and *b*. When the proton-donor properties of acids increase, both the intercept and slope increase. The systematic increase in the intercept undoubtedly contributes to the increase in hydrogen-bond strength with the acid. On the other hand the observed increase in the slope may reflect an increase in the contribution of hydrogen-bonded ion pairs with an increase in the proton-donor properties of acids.

$$\Delta\nu_H = a + b\mathrm{p}K_a \qquad (4)$$

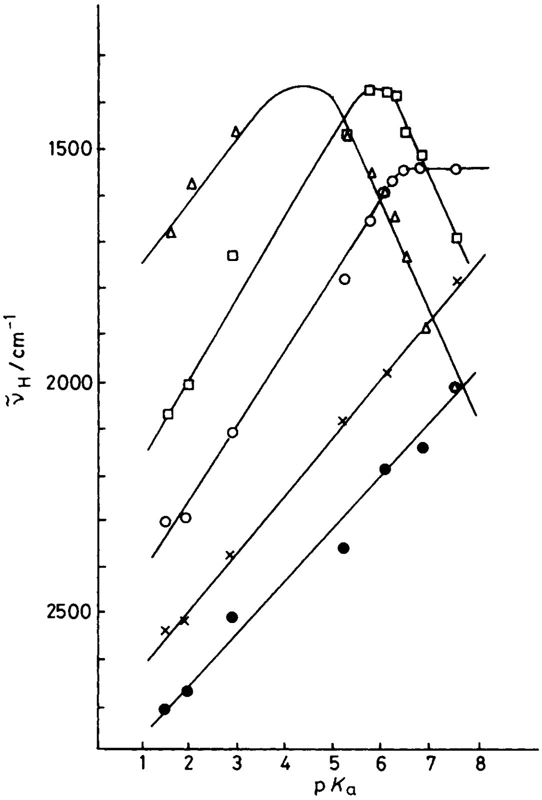

Figure 3. Plot of the centre of gravity ($\tilde{\nu}_H$) of the broad absorption against aqueous pK_a values of pyridine bases. Complexes with: ●, CH_3COOH; ×, CH_2BrCH_2COOH; ○, $CH_2ClCOOH$; □, $CHCl_2COOH$; △, CF_3COOH

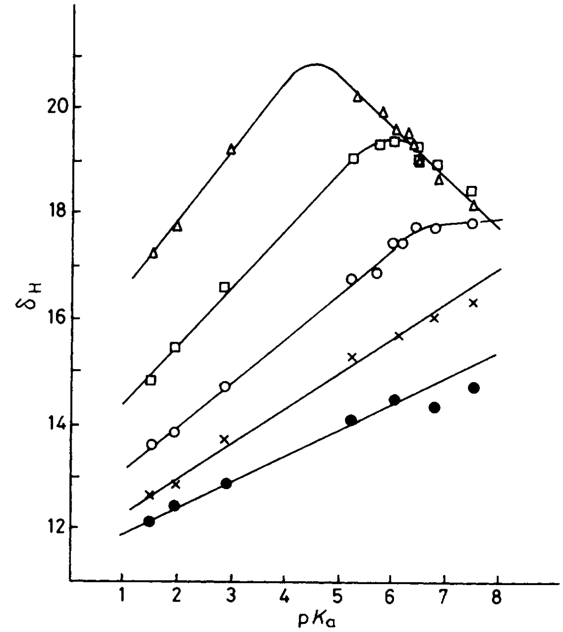

Figure 4. Plot of the chemical shift of hydrogen-bonded protons (δ_H) against aqueous pK_a values of pyridine bases. Complexes with: ●, CH_3COOH; ×, CH_2BrCH_2COOH; ○, $CH_2ClCOOH$; □, $CHCl_2COOH$; △, CF_3COOH

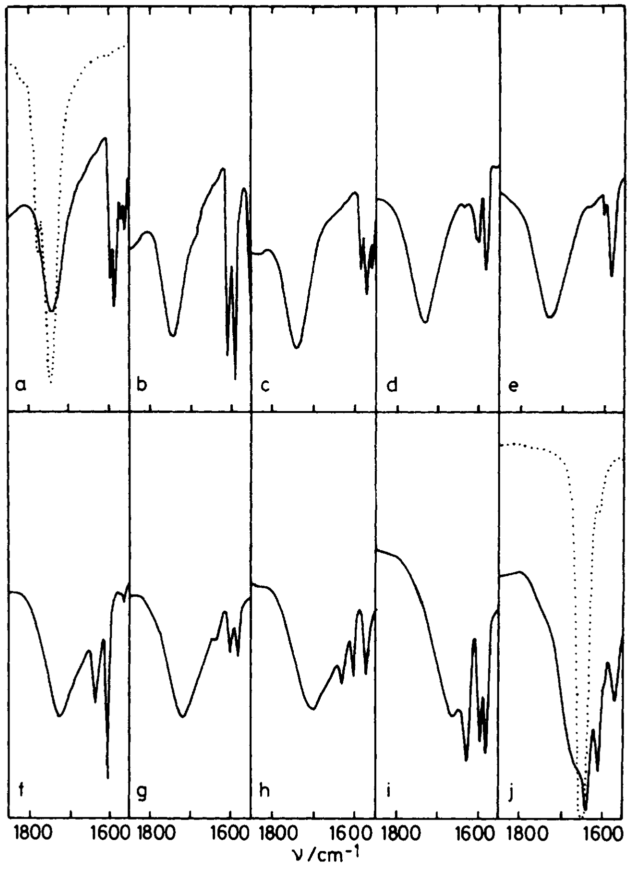

Figure 5. I.r. spectra of complexes of substituted pyridines with $CHCl_2COOH$ in CH_2Cl_2: a, 3-cyanopyridine; b, 4-cyanopyridine; c, 3-bromopyridine; d, pyridine; e, 3-methylpyridine; f, 4-methylpyridine; g, 3,5-dimethylpyridine; h, 2,5-dimethylpyridine; i, 2,6-dimethylpyridine; j, 2,4,6-trimethylpyridine. (····): a, $CHCl_2COOH$; j, $CHCl_2COO^-N^+(Bu)_4$

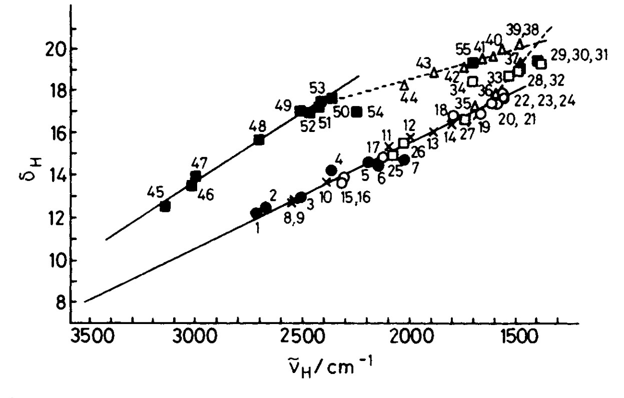

Figure 6. Plot of the chemical shift of hydrogen-bonded protons (δ_H) against the centre of gravity ($\tilde{\nu}_H$) of the complex absorption (numbers refer to Table 1)

Arnett *et al.*[15] concluded that the limitation of correlations mentioned so far to a series of similar B with a single AH arises from different responses of different classes of bases to two processes, hydrogen-bonding and protonation. Our results confirm this opinion. Thus the dispersal shown in Figure 3 indicates the difference between the ability of AH to form hydrogen-bonding and protonation.

In Figure 4 the chemical shift of the hydrogen-bonded protons is plotted against pK_a values of pyridines. In general the correlations shown in Figure 4 are very similar to those in Figure 3. The differences are observed for complexes of di- and

Table 1. Data and results for hydrogen bonding of various acids to substituted pyridines in CH_2Cl_2

No.	Complex AH	Substituent	M.p. (°C)	νC=O/ cm^{-1}	$\nu_{as}COO^-$/ cm^{-1}	$\Delta\nu_{3/4}$ νC=O + $\nu_{as}COO^-$/ cm^{-1}	δ_H	δ_H^{lit}	$\bar{\nu}_H$/ cm^{-1}	$\bar{\nu}_H^{lit}$/ cm^{-1}	pK_a
1	CH_3COOH	3-CN		1 713		10	12.18		2 710		
2		4-CN		1 713		12	12.42		2 670		
3		3-Br		1 713		11	12.90		2 510		
4		H		1 710		16.5	14.11	13.42^{a}	2 360	2 470^{b}	
5		4-Me		1 709		19	14.50		2 190		
6		2,6-Me_2		1 708		19	14.33		2 145		
7		2,4,6-Me_3		1 707		25	14.71		2 020		
8	CH_2BrCH_2COOH	3-CN		1 722		15	12.65		2 545		
9		4-CN		1 720		16	12.85		2 525		
10		3-Br		1 719		21	13.70		2 380		
11		H		1 718		30.5	15.23		2 095		
12		4-Me		1 717		33	15.70		1 995		
13		2,6-Me_2		1 717		30	16.00		1 890		
14		2,4,6-Me_3		1 715		36	16.30		1 795		
15	$CH_2ClCOOH$	3-CN		1 740		30	13.60		2 310		1.45
16		4-CN		1 735		32	13.86		2 300		1.90
17		3-Br		1 735		35	14.74		2 120		2.84
18		H		1 728		37	16.69	17.10^{c}	1 790	1 790^{a} 1 730^{d}	5.17
19		3-Me		1 727		39	16.85		1 665		5.68
20		4-Me	~18	1 727		39.5	17.41		1 605		6.02
21		3,5-Me_2		1 727		41	17.42		1 580		6.15
22		2,5-Me_2		1 725		46	17.68		1 555		6.40
23		2,6-Me_2		1 723		48	17.67	16.85^{c}	1 550		6.75
24		2,4,6-Me_3		1 721		61	17.82		1 555	1 510^{f}	7.44
25	$CHCl_2COOH$	3-CN	~14	1 744		42	14.85		2 080		
26		4-CN	68—69	1 744		42	15.47		2 020		
27		3-Br	~18	1 743		44	16.62		1 740		
28		H	50—51	1 732		55	18.98	19.65^{a}	1 480	1 430^{a,f}	
29		3-Me	~10	1 727		57	19.27		1 380		
30		4-Me	72—75	1 725		65	19.38		1 385		
31		3,5-Me_2	56—58	1 717		71	19.39		1 385		
32		2,5-Me_2	39—40	1 700	1 665sh	91	19.12		1 470		
33		2,6-Me_2	28		1 662	74	18.64		1 530		
34		2,4,6-Me_3	66—67		1 650	59	18.38		1 705	1 570^{d-f}	
35	CF_3COOH	3-CN	48—49	1 769		52	17.22	17.20^{g}	1 685	1 699^{g}	
36		4-CN	74	1 763		55	17.73	17.92^{g}	1 580	1 637^{g}	
37		3-Br	~10	1 758		49	19.20	18.63^{g}	1 470	1 570^{g}	
38		H	74—75	1 735	1 700sh	90	20.17	18.27^{a} 20.05^{g}	1 475	1 650^{a} 1 600^{e} 1 452^{g}	
39		3-Me	31—32	1 725sh	1 696	81	19.89	19.94^{g}	1 560	1 528^{g}	
40		4-Me	101	1 725sh	1 692	80	19.54	19.60^{g}	1 605	1 636^{g}	
41		3,5-Me_2	~15	1 720sh	1 690	55	19.45	19.47^{g}	1 655	1 661^{g}	
42		2,5-Me_2			1 690	45	19.00	19.25^{g}	1 740	1 752^{g}	
43		2,6-Me_2	24—26		1 680	42	18.77	18.77^{g}	1 885	1 883^{g}	
44		2,4,6-Me_3	44—45		1 680	42	18.15	18.15^{g}	2 020	2 200^{f} 2 041^{g} 1 994^{h} 2 069^{h}	
45	$HSbCl_6$	4-n-C_9H_{19}	76—77				12.50		3 140	3 060^{i}	
46	HBF_4	4-n-$C_{11}H_{23}$	95—96				13.50		3 010	3 080^{i}	
47	$HClO_4$		109				13.90		3 000	3 060^{i}	
48	HI		137				15.67		2 700	2 700^{i}	
49	HBr		138				17.04		2 510	2 480^{i}	
50	HCl		126				17.61		2 355	2 240^{e} 2 290^{i}	
51	Picric		110				17.26		2 490		
52	*p*-$MeC_6H_4SO_3H$		105—107				16.92		2 455		
53	HNO_3		96—97				17.47		2 410		
54	HSCN		110				16.98		2 245		
55	1/2 $HClO_4$						19.30	18.50^{a}	1 700	1 770^{a,d}	

[a] Ref. 23. [b] S. E. Odinokov, A. V. Iogansen, and A. K. Dzizenko, *Zh. Prikl. Spektrosk.*, 1971, **14**, 418. [c] S. E. Odinokov, A. A. Mashkovsky, and A. K. Dzizenko, *Dokl. Akad. Nauk SSSR*, 1975, **220**, 1130. [d] S. E. Odinokov, A. A. Nabiullin, A. A. Mashkovsky, and V. P. Glazunov, *Spectrochim. Acta*, 1983, **39A**, 1055. [e] V. P. Glazunov, A. A. Mashkovsky, and S. E. Odinokov, *Spectrosc. Lett.*, 1976, **9**, 391. [f] V. P. Glazunov, A. A. Mashkovsky, and S. E. Odinokov, *Zh. Prikl. Spektrosk.*, 1975, **23**, 469. [g] Ref. 7. [h] Ref. 8. [i] V. P. Glazunov and S. E. Odinokov, *Spectrochim. Acta*, 1982, **38A**, 409, for pyridine complexes in CD_3CN.

Table 2. Values of regression coefficients *a* and *b* of equation (4) and standard error of estimate $\Delta\bar{\nu}_H$ for complexes of pyridine bases with various proton donors (AH)

AH	*a*	*b*	*r*	Standard error	No. of points
MeOH[11]	173.07	20.39	0.906	18	20
PhOH[11]	332.81	28.61	0.988	9	12
p-FC_6H_4OH[15]	333.91	36.09	0.941	40	8
CH_3COOH	635.80	109.55	0.991	38	7
CH_2BrCH_2COOH	748.33	126.53	0.999	14	7
$CH_2ClCOOH$	907.48	158.77	0.997	28	7
$CHCl_2COOH$	1 171.82	160.85	0.986	60	4
CF_3COOH	1 554.37	148.93	0.982	28	3

Table 3. Frequencies and chemical shifts for acetic acids and their salts in CH_2Cl_2

	$\nu C{=}O/cm^{-1}$			$\bar{\nu}_H/cm^{-1}$		δ	
AH	AH	$[AH]_2$	$A^-N^+(Bu)_4$	CH_2Cl_2	CCl_4	Experimental in CCl_4	Calculated equation (6)
CH_3COOH	1 759 (9)	1 712 (11)	1 578 (13)	3 502	3 527[b] 3 534[f] 3 537[h]	8.66[c] 5.2 ± 0.8[d]	8.11
CH_2BrCH_2COOH	1 760 (12)	1 719 (11)		3 494			8.14
$CH_2ClCOOH$	1 789 1 760	1 735 (18)		3 480	3 534[f] 3 525[g] 3 528[h]	6.94[e]	8.22
$CHCl_2COOH$	1 779 1 760sh (9)	1 745 (14)	1 655 (11)	3 460 3 520[g]	3 509[b]	7.19[e]	8.32
CCl_3COOH	1 781	1 752		3 445	3 516[a] 3 502[b]	7.71[e]	8.39
CF_3COOH	1 805 (9)	1 782 (11)	1 688 (8)	3 440	3 509[a]		8.41

The three-fourth bandwidth is in parentheses. [a] G. S. Denisov, A. L. Smolyansky, A. A. Trusov, and M. I. Sheikh-Zada, *Izv. Vysch. Uchebn. Zaved., Fiz.*, 1974, **17**, 142. [b] S. Bratož, D. Hadži, and N. Sheppard, *Spectrochim Acta*, 1956, **8**, 249. [c] Ref. 30. [d] L. L. Kimtys and V. J. Balevičius, *Adv. Mol. Relax. Interact. Processes*, 1979, **15**, 151. [e] D. Hadži and R. Smerkolj, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1188. [f] S. E. Odinokov, A. V. Iogansen, and A. K. Dzizenko, *Zh. Prikl. Spektrosk.*, 1871, **14**, 418. [g] Ref. 23. [h] I. M. Ginzburg and B. P. Tarasov, *Zh. Obshch. Khim.*, 1972, **42**, 2740.

tri-methylpyridines with dichloroacetic and trifluoroacetic acids; δ_H values are similar for both acids but $\bar{\nu}_H$ differs by *ca.* 300 cm^{-1} (Table 1).

The $\nu C{=}O$ *and* $\nu_{as}COO^-$ *Stretching Vibrations.*—The simultaneous appearance of the $\nu C{=}O$ and $\nu_{as}COO^-$ bands observed in i.r. spectra of various aliphatic amines with carboxylic acids is a strong experimental proof of tautomeric equilibrium (1).[1,20,21]

In complexes of pyridine bases with acetic acids the hydrogen bond is stronger than that in the complexes of aliphatic amines and absorption in the carbonyl–carboxy region is more complex. When the hydrogen bond becomes stronger the $\nu C{=}O$ band shifts to lower frequency, but the $\nu_{as}COO^-$ band shifts to higher frequency.[22] The difference between $\nu C{=}O$ and $\nu_{as}COO^-$ decreases and a single band with a larger width (Table 3), instead of two bands, is observed (Figure 5). Another difference between i.r. spectra of complexes of aliphatic amines and pyridines is an overlapping of proton vibrations on $\nu C{=}O$ and $\nu_{as}COO^-$ bands in the last complexes.[6,7]

In complexes of pyridines with dichloroacetic acid a single smooth band is observed in the carbonyl–carboxy region (Figure 5). The $\nu C{=}O$ band observed in the spectra of complexes of the weakest bases (1 744 cm^{-1}) is close to the $\nu C{=}O$ band of the $(CHCl_2COOH)_2$ dimer (1 745 cm^{-1}). The three-fourth bandwidth is three or more times greater than that in the dimer (Table 1). In the spectra of the strongest bases (Figure 5) the absorption feature characteristic of $\nu_{as}COO^-$ vibration appears at *ca.* 1 650 cm^{-1}, proving that hydrogen-bonded ion pairs are formed. The observed frequency, $\nu_{as}COO^-$, does not differ from typical values of $\nu_{as}COO^-$ of $CHCl_2COO^-N(Bu)_4^+$ (1 655 cm^{-1}).

The characteristic variation in bandwidth (Table 1) strongly suggests that complexes of the medium-strong pyridines with dichloroacetic acid in CH_2Cl_2 solution exist in a tautomeric equilibrium between the molecular form and the ion pair. [equation (1)].

Odinokov *et al.*[23] postulated the quasi-symmetrical hydrogen bond (A ••• H ••• B) for pyridine dichloroacetate. In complexes with quasi-symmetrical hydrogen-bonds a bandwidth in the carbonyl–carboxy region is practically constant.[18]

Relation between δ_H *and* $\bar{\nu}_H$.—In Figure 6 the chemical shifts of hydrogen-bonded protons, δ_H, are plotted *versus* the centre of gravity, $\bar{\nu}_H$. The data can be resolved into a series of straight lines, each correlating δ_H with $\bar{\nu}_H$ for molecular complexes, hydrogen-bonded ion pairs, and their mixtures.

In the investigated complexes, except complexes with $HSbCl_6$, $HClO_4$, and HBF_4, the signal of hydrogen-bonded protons is narrow, indicating that the exchange process is faster than 10^{-3} s. In complexes of 4-n-undecylpyridine with $HSbCl_6$, $HClO_4$, and HBF_4, the N^+H proton appears as a very broad triplet. On the other hand the total shielding effect is divided into a series of contributions which can be explained in terms of well established 'through-bond' and 'through-space' mechanisms.[24] In this approach, the total distribution in the molecule is partitioned into a 'local' part associated with the nucleus whose shielding is of interest and a 'non-local' part for the rest of the molecule. The types of contribution are $\sigma_{\text{loc}}{}^{\text{d}}$, due to the secondary screening magnetic fields arising from the induced local diamagnetic currents, $\sigma_{\text{loc}}{}^{\text{p}}$, due to the magnetic fields of the local paramagnetic currents, and σ^{m}, arising from magnetic fields associated with currents induced in the 'non-local' electronic distribution. Both $\sigma_{\text{loc}}{}^{\text{d}}$ and $\sigma_{\text{loc}}{}^{\text{p}}$ may be intramolecular electric fields altered by steric effects, and by van der Waals interactions. The value of σ^{m} is usually determined by the magnetic anisotropy of distant bonds or substituent groups but it may also be affected by the existence of ring currents elsewhere in the molecule or by a charge density and pseudocontact (or dipolar) shifts. In general, charges in $\sigma_{\text{loc}}{}^{\text{p}}$ for proton shielding along a series of compounds are negligible due to the large values of ΔE involved. Thus proton chemical shifts are usually determined by changes in $\delta_{\text{loc}}{}^{\text{d}}$ and σ^{m}.

When molecular complexes and hydrogen-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. Thus the separate lines derived for molecular complexes and hydrogen-bonded ion pairs (Figure 6) 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. 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 a single line was derived for the molecular complex and hydrogen-bonded ion pair.[18,19]

The least-squares equations for hydrogen-bonded ion pairs and molecular complexes are, respectively, (5) and (6). These equations can be used to estimate the chemical shift of 'free' pyridinium cation (N^+–H) and monomeric acids. Assuming $\bar{\nu}_{\text{H}} = 3\,400 \pm 100\ \text{cm}^{-1}$[25] for the 'free' N^+–H bond in protonated pyridine and substituting into equation (5), one obtains $\delta_{\text{N}^+\text{H}}$ 11.04 ± 0.65.

$$\delta_{\text{N}^+\text{H}}(\pm 0.24) = 33.174 - 6.501 \times 10^{-3}\bar{\nu}_{\text{H}} \qquad (r = 0.994, n = 9) \quad (5)$$

$$\delta_{\text{OH}}(\pm 0.24) = 25.216 - 4.884 \times 10^{-3}\bar{\nu}_{\text{H}} \qquad (r = 0.992, n = 29) \quad (6)$$

The value of 'free' protonated pyridinium cation obtained is reasonable in comparison with the NH frequency of protonated nitriles (δ 10.5—11.5) and protonated imines (δ 9.5—10.0).[25]

On protonating pyridine there are substantial changes in both the σ- and π-electron distribution. The nitrogen atom becomes a σ-donor but remains a strong π-acceptor and still has an overall net negative charge.[26] In changing from pyridine to

$$\Delta\sigma_E = 12.5 \times 10^{-6} \sum_i \frac{\Delta q_i \cos\theta_i}{R_i^{\,2}} - 17.0 \times 10^{-6} \left(\sum_i \frac{\Delta q_i}{R_i^{\,2}}\right)^2 \quad (7)$$

protonated pyridine the major change in the magnetic anisotropy contribution to the chemical shift arises because of the replacement of $\geqslant$N: by $\geqslant N^+$–H, which has a calculated anisotropy of $\Delta\chi_{\text{N}}{}^{\text{p}} = 1.46$.[27]

To facilitate the calculation benzene is chosen as a reference. The contribution to the distortion of the hydrogen 1*s* orbital by the adjacent electric field can be evaluated from Buckingham's equation related to formal charges by the equation (7)[28] and Emsley's charge densities[26] where $\Delta q_i = q_i\text{N}^+\text{H} - q_i\text{N}$, R_i is the distance (Å) from that atom to the proton in question, and θ_i is the angle between the N^+–H bond and the vector R_i. It is assumed that the rings of pyridine and protonated pyridine are regular hexagons with lengths 1.40 Å, and N^+–H bond length of 1.1 Å. Values of Δq_i were used from Emsley's calculation.[26] The calculated electric field contribution is δ_E −5.2.

The changes in chemical shift due to the magnetic anisotropy of neighbouring atoms when $\geqslant$N is replaced by $\geqslant N^+$–H can be calculated from equation (8). R_{NH} is the vector joining N and

$$\delta_{\text{NH}} = \frac{1}{3NR_{\text{NH}}{}^3} \sum_i (\Delta\chi_{\text{N}}{}^{\text{p}})_i (1 - 3\cos^2\gamma_i) \qquad (8)$$

H, $(\Delta\chi_{\text{N}}{}^{\text{p}})_i = (\chi_{\text{N}}{}^{\text{p}})_i - (\chi_{\text{N}^+}{}^{\text{p}})_i$, γ_i is the angle between the direction of χ_{N} and R_{NH}, N is Avogadro's number. Values of $(\Delta\chi_{\text{N}}{}^{\text{p}})_i$ were taken from Gill and Murrell's paper.[27] The calculated magnetic anisotropy is δ_{NH} 0.5. Taking into account these two effects the N^+–H shift of the 'free' pyridinium cation should be found to be −4.7 p.p.m. from benzene ($\delta_{\text{N}^+\text{H}}$ 7.3 + 4.7 = 12). Shuppert and Angell,[29] using different approaches and neglecting magnetic anisotropy, calculated $\delta_{\text{N}^+\text{H}}$ 12.7. The experimental value for N^+H shift of the 'free' protonated pyridine is found to be in agreement with the theoretical distribution of electrons calculated by Emsley.[26]

In Table 3 values of chemical shift for monomeric acids calculated with equation (6) are compared with the experimental data. The best agreement was found for acetic acid. Since dichloromethane is a more active solvent than carbon tetrachloride, the difference of *ca.* 0.5 p.p.m. seems to be reasonable. For the other acids differences between experimental and calculated values are much larger. Samples of halogenoacetic acids were prepared in a dry-box and the resonance of these acids may be a noticeably spurious upfield shift.[30]

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