Infrared and ^{1}H Nuclear Magnetic Resonance Studies of Hydrogen Bonds in Some Pyridine Trifluoroacetates and their Deuteriated Analogues in Dichloromethane

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I.r. and ^{1}H n.m.r. spectra are reported for the trifluoroacetates of 12 substituted pyridines in dry dichloromethane. The carbonyl–carboxylate region shows that the weakest and strongest pyridines form, respectively, hydrogen-bonded complexes ($B \cdots HA$) and hydrogen-bonded ion pairs ($B^+H \cdots A^-$). The intermediate-strength pyridines form a mixture of both species. Dichloromethane, as a more polar solvent than benzene, slightly shifts the equilibrium between these species to the ion-pair form. If the centres of gravity ($\tilde{\nu}_H$ or $\tilde{\nu}_D$) and the chemical shifts of hydrogen-bonded protons (δ) are plotted *versus* ΔpK_a, the points fall on two intersecting straight lines. The correlations reflect changes in the hydrogen bond strength and the equilibrium between the molecular complex and the ion pair with ΔpK_a. The centres of gravity in dichloromethane are compared with those in benzene and discussed with respect to variations of hydrogen bond strength. A plot of δ *versus* $\tilde{\nu}_H$ gives again two intersecting straight lines, which reflects the effect of a positive charge caused by the proton transfer on the chemical shift. The effect of the solvent on the correlation of δ *versus* $\tilde{\nu}_H$ is examined and discussed. The isotope frequency ratio ($\tilde{\nu}_H/\tilde{\nu}_D$) varies from 1.07 to 1.21.

In previous investigations,[1,2] we have studied the variations of the chemical shifts of hydrogen-bonded protons and the centre of gravity of the strong and broad absorption in the i.r. spectra of complexes of trifluoroacetic acid with a number of pyridines in benzene. It was possible to correlate quite quantitatively the n.m.r. and i.r. results. This allowed us to estimate the shielding of hydrogen-bonded protons due to the charge effect produced by protonation of the pyridine ring.

It is well known that when a polar molecule is dissolved in an aromatic solvent (*e.g.* benzene) the solute proton absorptions are usually shifted relative to their position in an inert solvent, such as neopentane, hexane, or even chloroform, due to the ASIS effect.[3] In this paper we have extended previous studies to dichloromethane in order to eliminate the ASIS effect on screening of the hydrogen-bonded protons.

Experimental

Complexes were prepared as previously.[1] Dichloromethane was passed through alumina, stored over Linde 4 Å molecular sieves, and used after ten days of purification. Dichloromethane for deuteriated complexes was washed with D_2O, distilled, and then dried. The percentage of the deuterium in complexes was monitored by ^{1}H n.m.r. spectra, and was greater than 90%. Complexes were prepared and cells were filled in a dry box.

^{1}H N.m.r. spectra were measured at 60 MHz on a Varian EM 360 spectrometer at 24 ± 2 °C. All chemical shifts are reported downfield relative to the solvent signal and then converted into δ values.

I.r. spectra were recorded on a Perkin-Elmer 180 spectrophotometer, using cells with KBr windows 0.062 mm thick. The concentration was 0.5M.

Centres of gravity of the reconstructed bands were obtained as $\tilde{\nu} = \int A(\nu)\nu d\nu / \int A(\nu) d\nu$ by numerical integration described previously.[4] Since some investigated compounds exist as an equilibrium of neutral and ionised complexes, both ν(OH) and ν(NH) vibrations are present and overlap in their spectra. Thus $\tilde{\nu}_H$ denotes $\tilde{\nu}$(OH), $\tilde{\nu}$(NH), or $\tilde{\nu}$(OH) + $\tilde{\nu}$(NH). In deuteriated compounds $\tilde{\nu}_D$ has a similar meaning.

Results and Discussion

Figure 1 shows the spectra of the investigated complexes and their deuteriated analogues in the carbonyl–carboxylate region. Although the absorption in this region is perturbed by the $\tilde{\nu}$(OH) [$\tilde{\nu}$(OD)] and/or $\tilde{\nu}$(NH) [$\tilde{\nu}$(ND)] vibrations (Figures 2 and 3), it is quite obvious that the complexes investigated in CH_2Cl_2 solution exist as a tautomeric equilibrium between the molecular form and the ion pair. The ν(C=O) band observed in the spectra of the complexes of the weakest bases (1 775 cm^{-1}) is close to the ν(C=O) band of the $(CF_3COOH)_2$ dimer (1 780 cm^{-1}). The bandwidth is three or more times greater than that in the dimer (Table 1). The observed increase of the bandwidth is caused partly by superposition of the OH stretching vibration (Figure 1). In the spectra of the strongest bases (Figure 1i—l) the absorption feature characteristic of the $\nu_{as}(COO^-)$ vibration appears at *ca.* 1 680 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 $CF_3COO^-M^+$ (M = Na or R_4N).[5] In the case of complexes of medium-strong bases both the ν(C=O) and $\nu_{as}(COO^-)$ frequencies are observed (Figure 1e—h). The frequency of the ν(C=O) band strongly decreases with increasing acceptor properties of bases, while the frequency of the $\nu_{as}(COO^-)$ band shows much smaller variations: Deuteriation results in lowering the frequency and reduces the bandwidth of absorption in the carbonyl and carboxylate region (Figure 1 and Table 1).

Dichloromethane (ε 8.9) is a more polar solvent than benzene (ε 2.3), hence its solvation power is greater. This effect caused variations in the absorption in the carbonyl–carboxylate region. In dichloromethane the bands due to the ν(C=O) and $\nu_{as}(COO^-)$ frequencies are shifted *ca.* 5 cm^{-1} to lower frequencies relative to their position in benzene.[1,2]

Of interest is the change in relative intensities of the ν(C=O) and $\nu_{as}(COO^-)$ bands with change of solvent. In the spectra of complexes of medium-strong bases the intensity of the ν(C=O) band in dichloromethane decreases, and $\nu_{as}(COO^-)$ band increases, with respect to their intensities observed in benzene. This indicates that the tautomeric equilibrium between the molecular complex and the ion pair is shifted to the ion-pair form with increasing solvent polarity. A similar trend was observed for other complexes.[6,7]

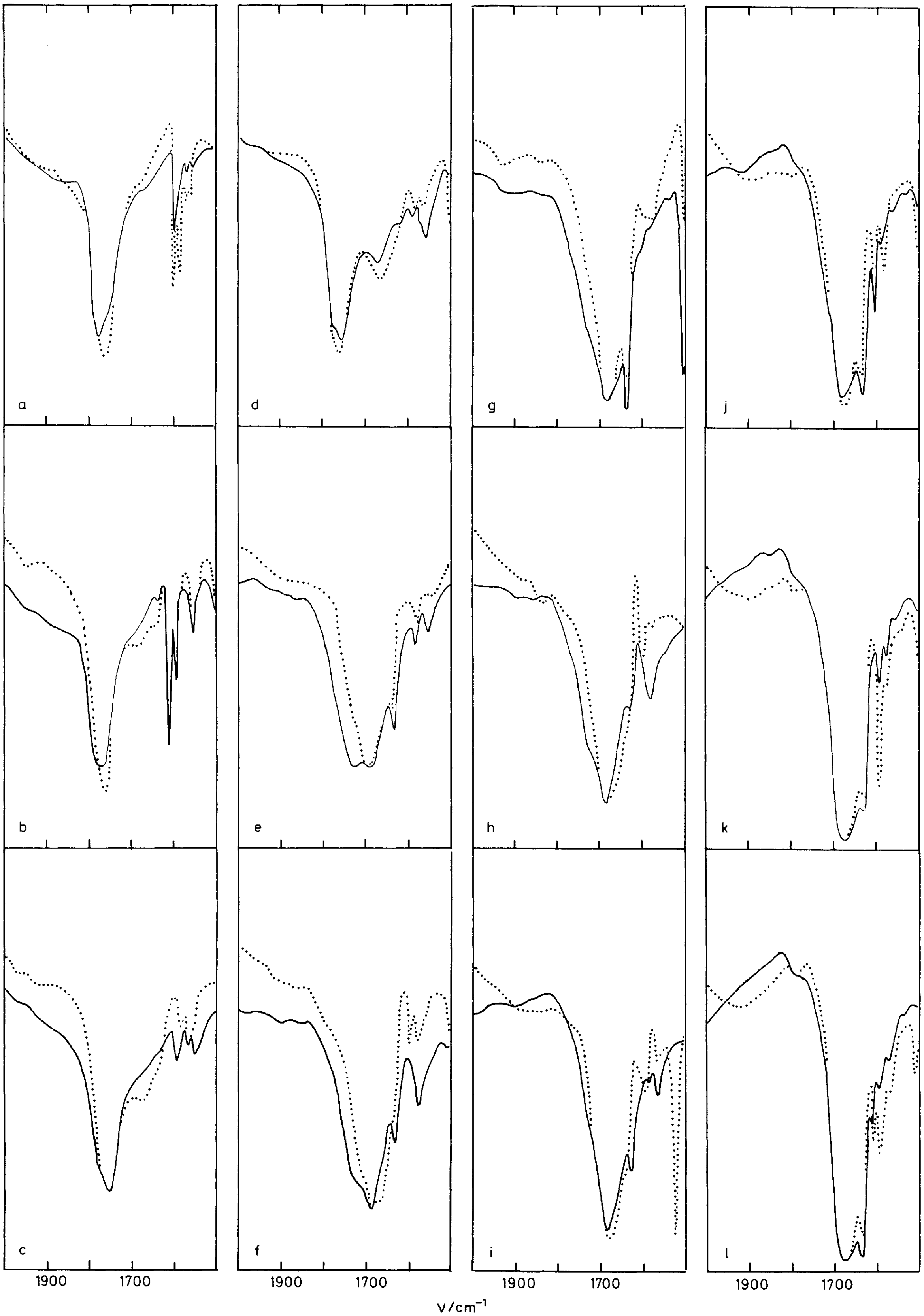

Figure 1. I.r. spectra of complexes of substituted pyridines with CF_3COOH (——) and CF_3COOD (· · ·) in dichloromethane: a, 3-cyanopyridine; b, 4-cyanopyridine; c, 3-bromopyridine; d, 3-methoxypyridine; e, pyridine; f, 3-methylpyridine; g, 4-methylpyridine; h, 3,5-dimethylpyridine; i, 2,5-dimethylpyridine; j, 2,4-dimethylpyridine; k, 2,6-dimethylpyridine; l, 2,4,6-trimethylpyridine

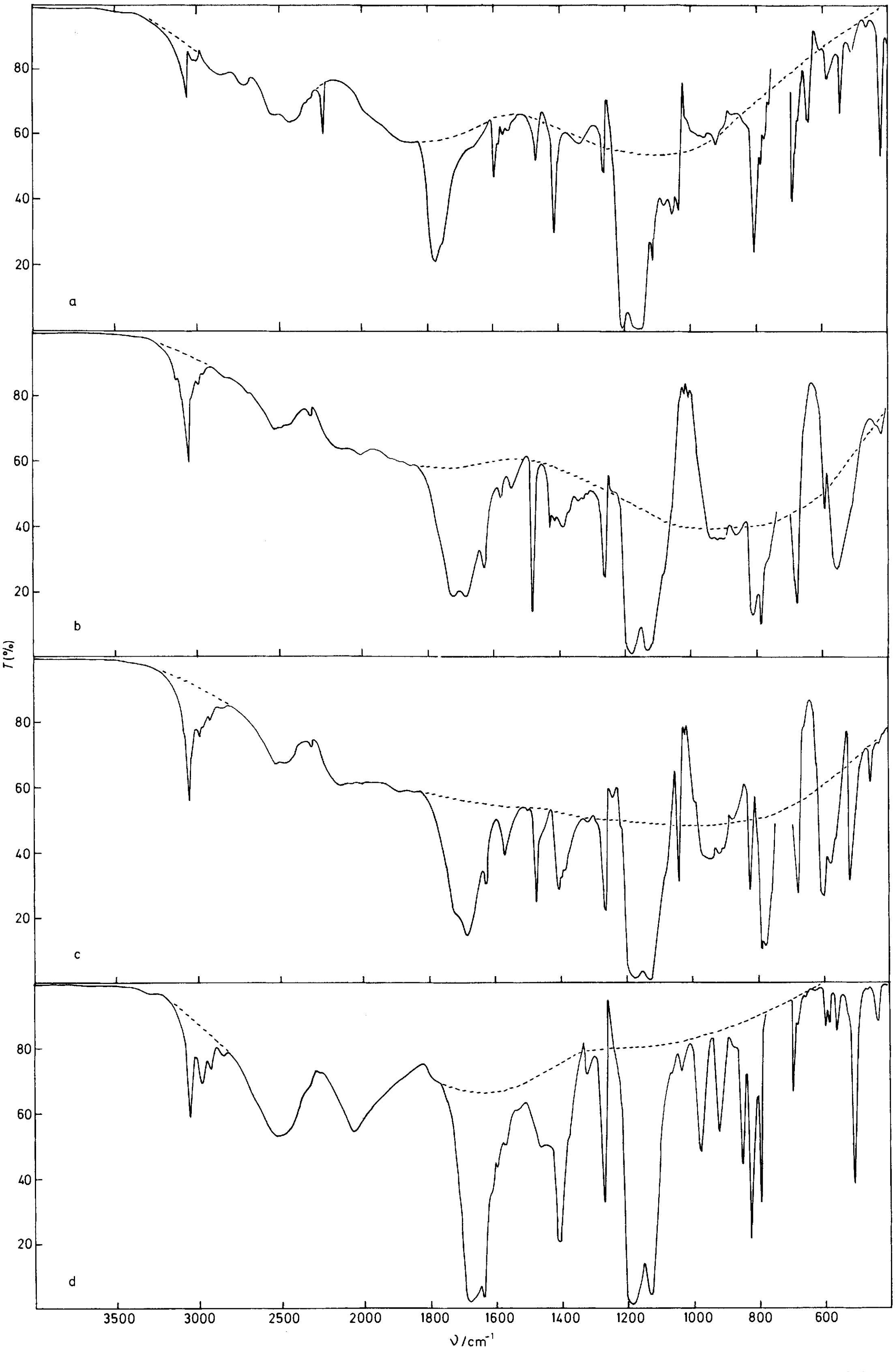

Figure 2. I.r. spectra of complexes of substituted pyridines with CF_3COOH in dichloromethane: **a**, 3-cyanopyridine; **b**, pyridine; **c**, 3-methylpyridine; **d**, 2,4,6-trimethylpyridine. – – – –, Continuous absorption

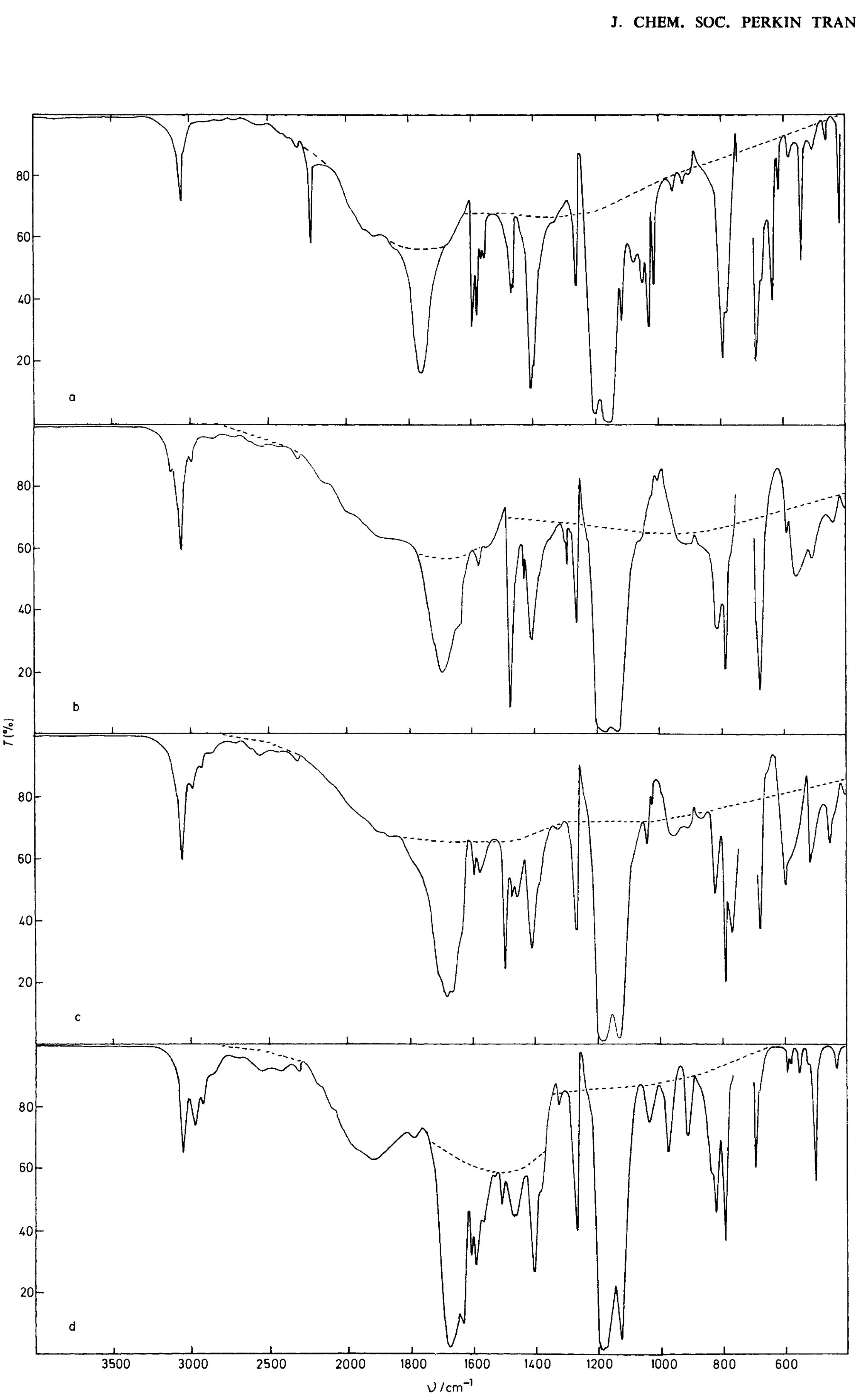

Figure 3. I.r. spectra of complexes of substituted pyridines with CF_3COOD in dichloromethane: a, 3-cyanopyridine; b, pyridine; c, 3-methylpyridine; d, 2,4,6-trimethylpyridine. - - - -, Continuous absorption

Table 1. Characteristic i.r. bands and ^1H n.m.r. chemical shifts of hydrogen-bonded protons of substituted pyridine trifluoroacetates and their deuteriated analogues in dichloromethane (0.5M)

No.	Substituent	ΔpK_a	$\nu(C=O)/cm^{-1}$ H	$\nu(C=O)/cm^{-1}$ D	$\nu_{as}(COO^-)/cm^{-1}$ H	$\nu_{as}(COO^-)/cm^{-1}$ D	$\Delta\nu_{3/4}(C=O)-(COO^-)$ */ cm^{-1} H	$\Delta\nu_{3/4}(C=O)-(COO^-)$ */ cm^{-1} D	$\bar{\nu}_H/cm^{-1}$	$\bar{\nu}_H/\bar{\nu}_D$	δ
(1)	3-CN	1.22	1 775	1 770			65	50	1 699	1.120	17.20
(2)	4-CN	1.67	1 770	1 760			70	55	1 637	1.105	17.92
(3)	3-Br	2.61	1 755	1 755			80	85	1 570	1.098	18.63
(4)	3-OMe	4.65	1 755	1 750			80	70	1 474	1.071	19.79
(5)	H	4.94	1 730	1 725sh	1 690	1 690	140	110	1 452	1.072	20.05
(6)	3-Me	5.45	1 730sh	1 720sh	1 685	1 685	115	100	1 528	1.098	19.94
(7)	4-Me	5.79	1 725sh	1 720sh	1 685	1 685	120	100	1 636	1.116	19.60
(8)	3,5-Me_2	5.92	1 725sh	1 720sh	1 685	1 685	100	90	1 661	1.116	19.47
(9)	2,5-Me_2	6.17			1 685	1 675	90	85	1 752	1.138	19.25
(10)	2,4-Me_2	6.40			1 680	1 675	95	80	1 847	1.162	18.97
(11)	2,6-Me_2	6.52			1 680	1 680	85	90	1 883	1.173	18.77
(12)	2,4,6-Me_3	7.21			1 680	1 680	80	70	2 041	1.208	18.15

* The values of $\Delta\nu_{3/4}(C=O)$ are 17 and 16 cm^{-1}, respectively, for $(CF_3COOH)_2$ and $(CF_3COOD)_2$.

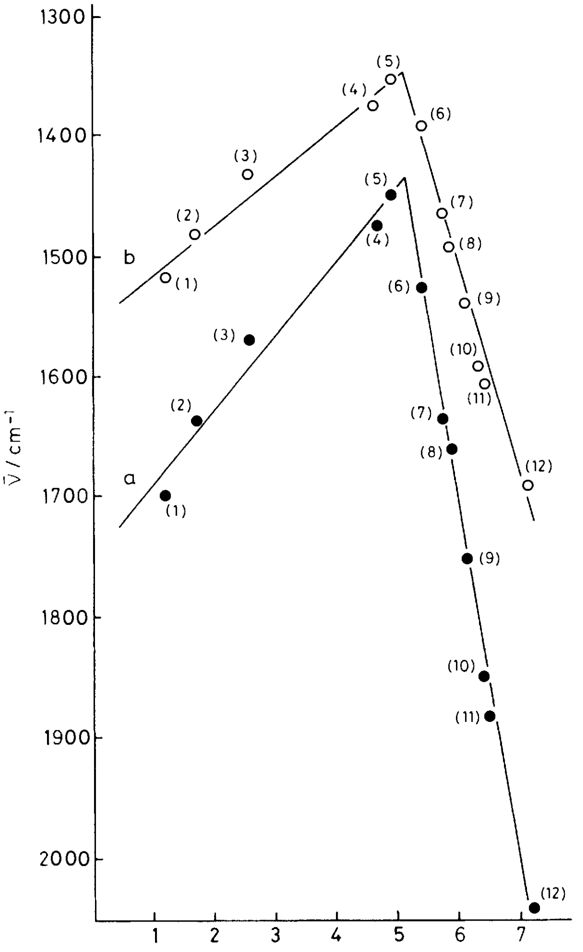

Figure 4. The plot of the centre of gravity ($\bar{\nu}_H$) (a) and ($\bar{\nu}_D$) (b) of the broad absorption against ΔpK_a (numbers refer to Table 1)

Table 2. Comparison of data at the intersecting points

Correlation	ΔpK_a	δ	$\bar{\nu}_H/cm^{-1}$	$\bar{\nu}_D/cm^{-1}$
$\delta = f(\Delta pK_a)$	5.17	20.23		
$\delta = f(\bar{\nu}_H)$		20.30	1 429	
$\bar{\nu}_H = f(\Delta pK_a)$	5.12		1 438	
$\bar{\nu}_D = f(\Delta pK_a)$	5.10			1 349

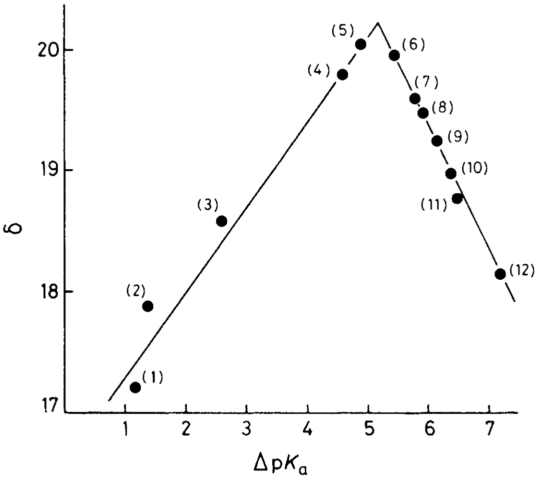

Figure 5. Correlation of the chemical shift of hydrogen-bonded protons (δ) with ΔpK_a (numbers refer to Table 1)

The i.r. spectra of pyridine trifluoroacetates in dichloromethane show, similar to those in benzene and other compounds with a strong hydrogen bond,[8] an extremely broad absorption that extends from 3 000 down to 400 cm^{-1} and is topped by some poorly expressed maxima. This absorption is assigned to the OH and/or N^+H stretching vibrations of the strongly hydrogen-bonded pyridine trifluoroacetates (Figure 2). Deuteriation reduces this absorption (Figure 3). Table 1 lists the centres of gravity ($\bar{\nu}_H$ and $\bar{\nu}_D$) of the very broad stretching vibration and the isotope frequency ratios ($\bar{\nu}_H/\bar{\nu}_D$). Figure 4 shows a generally good correlation between the centre of gravity ($\bar{\nu}_H$ and $\bar{\nu}_D$) and ΔpK_a. A similar correlation exists between the chemical shift of the hydrogen-bonded protons and ΔpK_a (Figure 5). Table 2 lists data of points of intersection. Similar correlations have been obtained previously in benzene.[1,2] The characteristic alterations of both the centre of complex absorption and the chemical shift reflect the variations of the hydrogen bond strength. The strongest hydrogen

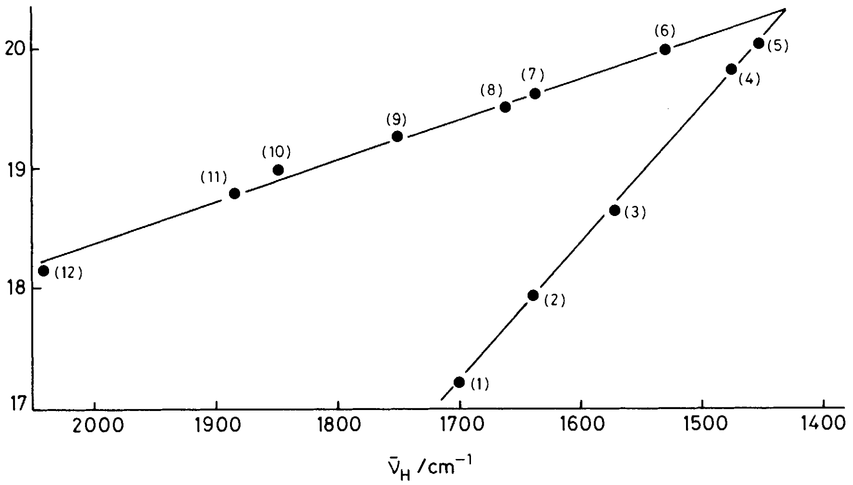

Figure 6. The plot of the chemical shift of hydrogen-bonded protons (δ) against the gravity centre ($\bar{\nu}_H$) of the complex absorption (numbers refer to Table 1)

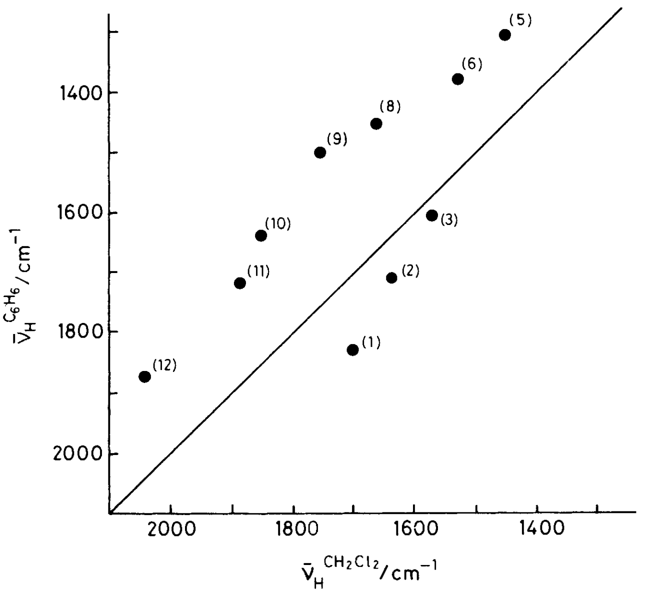

Figure 7. $\bar{\nu}_H^{benzene}$ *versus* $\bar{\nu}_H^{dichloromethane}$ (numbers refer to Table 1). ——, The unit slope

bond appears in complexes which are close to the intersecting point.

In Figure 6 the chemical shift the of hydrogen-bonded protons, δ, is plotted against the centre ($\bar{\nu}_H$) of complex absorption. Exactly the same type of correlation has been reported for benzene solution.[4] The two different straight lines drawn in Figure 6 reflect the effect of a positive charge caused by proton transfer on the chemical shift. The slopes of the lines in benzene differ from those shown in Figure 6. Thus, the difference in the chemical shift between the two lines [in the region of complex (1)] increases from *ca.* 1.8 in benzene to *ca.* 2.2 p.p.m. in dichloromethane. This observation may be interpreted in at least two ways: (1) in terms of the benzene–solute collision complex (the ASIS effect) [3] or alternatively (2), by the change of hydrogen bond strength. Evidence supporting the second explanation comes from the relationship shown in Figure 7, which reflects the variation of the hydrogen bond strength caused by the solvent. In the case of complexes (1)—(3) the values of $\bar{\nu}_H$ in dichloromethane are shifted to lower frequencies in comparison to benzene. This indicates that the hydrogen bond becomes stronger (shorter) in dichloromethane. The reverse situation is observed for the other complexes; these hydrogen bonds are weaker (longer) in dichloromethane. The effect of charge (both positive and negative) on the chemical shift strongly decreases with distance; hence, as the separation of the negative charge in hydrogen-bonded ion pairs seems to be greater in dichloromethane than in benzene, the shielding effect of an anion in the former solution would be smaller. Assuming that the deshielding effect of the positive charge on the chemical shift in both solutions is similar, the net effect of the charge would thus increase, and the difference in the chemical shift between the molecular complex and the ion pair would also increase.

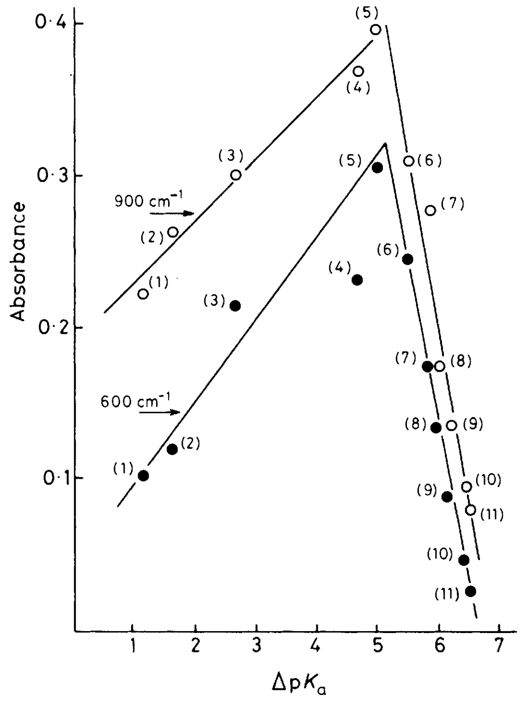

Figure 8. Correlation of the absorbance at 650 and 900 cm^{-1} with ΔpK_a (numbers refer to Table 1)

An i.r. absorption band is characterized by several parameters including frequency, intensity, and half-width. The absolute intensity is a difficult quantity to obtain experimentally and it is usually the relative integrated intensity that is measured and reported in chemical spectroscopy.[9] The absorption coefficient at the band maximum is also reported. In this paper we correlated the frequency with ΔpK_a and chemical shift. Previously, Lindemann and Zundel [10] investigated complexes of substituted pyrazine, pyridine, pyrazole, and imidazole with formic, acetic, monochloro-, and dichloroacetic acids as pure liquids and correlated the intensity of the broad absorptions at *ca.* 700 and *ca.* 2 200 cm^{-1} with ΔpK_a.

In Figure 8 plots of the absorbance caused by the hydrogen bond at two frequencies (650 and 900 cm^{-1}) and ΔpK_a are displaced. The various straight lines drawn in Figure 8 are least-squares fits. The intersecting points (ΔpK_a 5.05 and 5.09, respectively, for 650 and 900 cm^{-1}) are slightly lower than the values derived from correlation of the centres of gravity. The absorbance at 2 200 cm^{-1} shows a plateau in the ΔpK_a 5—6.4 region. Absorbance of deuteriated compounds behaves in a similar way.

Lindemann and Zundel [10] have reported a similar type of dispersal of lines in the pure liquids of slightly different complexes. They express the opinion that the absorbance of the broad absorption (continuum) at smaller wavenumbers is much more sensitive to perturbations of the symmetry of the energy surface than the absorbance at higher wavenumbers.

We explain the variation of absorbance with the wavenumber in terms of the stochastic theory developed by Romanowski and Sobczyk.[11] The absorbance at smaller wavenumbers may be assigned mainly to the $0 \longrightarrow 1$ transition, and that at higher wavenumbers to the $1 \longrightarrow 2$ and $0 \longrightarrow 3$ transitions. Indeed, the $0 \longrightarrow 1$ transition seems to be the most sensitive to perturbations of the symmetry of the energy surface.

Though the origin of the broad absorption in the i.r. spectra of compounds with the strong hydrogen bond is so complex, correlation of the centre of gravity of this absorption with the chemical shift allows an estimate of the contribution of charge and ' ring currents ' [12] to hydrogen-bonded shielding. It seems that the experimental correlation $\tilde{\nu}_H = f(\Delta pK_a)$ is less uncertain than absorbance $= f(\Delta pK_a)$.

The isotope frequency ratios ($\tilde{\nu}_H/\tilde{\nu}_D$) decrease from *ca.* 1.21 for the weakest hydrogen bonds to *ca.* 1.07 for the strongest bonds. In some complexes absorption is a composite of the ν(OH) and ν(NH) vibrations. Since the experimental relation ν(OH)/ν(OD) = f[(ν(OH)] is very different from ν(NH)/ν(ND) = f[ν(NH)] [13] nothing useful can be derived from the $\tilde{\nu}_H/\tilde{\nu}_D$ ratio.

Conclusions.—The analysis of the absorption in the carbonyl-carboxylate region and the centre of gravity of the complex absorption of complexes of pyridines with trifluoroacetic acid shows clearly that changes of the solvent from benzene to dichloromethane caused variations, both in the position of the equilibrium between the molecular complex and the ion pair, and in the hydrogen bond strength. The increase in the solvent polarity, as expected, favours the formation of an ion pair. The difference in the chemical shift between the molecular complex and the ion pair depends on the solvent, and is due to the net effect of the charge on the chemical shift.

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References

1 Z. Dega-Szafran and E. Dulewicz, *Org. Magn. Reson.*, 1981, **16**, 214.
2 Z. Dega-Szafran and E. Dulewicz, *Adv. Mol. Relax. Interact. Processes*, 1981, **21**, 207.
3 J. Ronayne and D. H. Williams, in ' Annual Reviews of N.M.R. Spectroscopy,' ed. E. F. Mooney, Academic Press, New York, vol. 2, 1969.
4 Z. Dega-Szafran and M. Szafran, *J. Chem. Soc., Perkin Trans. 2*, 1982, 195.
5 E. Spiner, *J. Chem. Soc.*, 1964, 4217.
6 B. H. Robinson in ' Aprotic Solvents in Proton Transfer Reactions,' eds. E. Caldin and V. Gold, Chapman and Hall, London, 1975, p. 121.
7 J. Jadżyn and J. Małecki, *Acta Phys. Polon.*, 1972, **A41**, 599.
8 D. Hadzi and S. Bratos, in ' The Hydrogen Bond. Recent Developments in Theory and Experiments,' eds. P. Schuster, G. Zundel, and C. Sandorfy, North Holland, Amsterdam, 1976, p. 566.
9 A. S. Waxler, *Appl. Spectrosc. Rev.*, 1967, **1**, 29.
10 R. Lindemann and G. Zundel, *J. Chem. Soc., Faraday Trans. 2*, 1977, 788.
11 H. Romanowski and L. Sobczyk, *Chem. Phys.*, 1977, **19**, 361.
12 M. Szafran and Z. Dega-Szafran, *Spectrochim. Acta*, in the press.
13 A. Novak, *Struct. Bonding*, 1974, **18**, 177.

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