Infrared Investigation of Hydrogen Bonding and Proton Transfer of Some Pyridine Trifluoroacetates in Benzene

By **Zofia Dega-Szafran** and **Mirosław Szafran,*** Institute of Chemistry, A. Mickiewicz University, 60780 Poznań, Poland

I.r. spectra are reported for the trifluoroacetates of ten substituted pyridines in dry benzene. 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. A plot of the gravity centre ($\bar{\nu}_H$) of ν_{AH} complex absorption against ΔpK_a consists of two intersecting straight lines. This correlation is considered in the light of the previously reported similar relationship between the chemical shift of hydrogen-bonded protons (δ) and ΔpK_a. If δ is plotted *versus* $\bar{\nu}_H$, again two intersecting straight lines are found. The correlation reflects the effect of a positive charge caused by the proton transfer on the chemical shift. All these results confirm the long-held assumption that no general correlation exists for hydrogen-bonded complexes and hydrogen-bonded ion-pairs.

ALIPHATIC amines and pyridines are able to form both hydrogen-bonded complexes ($B \cdots HA$) and hydrogen-bonded ion pairs ($B^+H \cdots A^-$) with carboxylic acids in the solid state,[1] solvents,[2-11] and an argon matrix.[12] In the vapour phase the formation of a hydrogen-bonded complex only is suggested.[13] The two forms appear simultaneously in some solutions and can be observed by means of their i.r. spectra in the carbonyl and carboxylate regions. This is the main experimental evidence supporting a double minimum potential–energy curve.[14] The separation of carbonyl and carboxylic bands strongly depends on the nature of the acid and base and reflects variations of both hydrogen-bond strength and the symmetry of the carboxylate group. The largest differences between carbonyl and carboxylate bands are observed in complexes of aliphatic amines with monohalogenoacetic acids, $\nu(C{=}O) - \nu_{as}(COO^-)$ *ca.* 90—140 cm^{-1}.[5,10] The interaction of pyridines with carboxylic acids forms stronger hydrogen bonds and the difference between $\nu(C{=}O)$ and $\nu_{as}(COO^-)$ strongly decreases.[4,11] The spectra of complexes of some pyridines with trichloroacetic acid contain only one broad band in the 1 755—1 675 cm^{-1} region, with or without submaxima.[11] In this paper we investigate complexes of trifluoroacetic acid (pK_a 0.23) with various pyridines ($1.45 \leqslant pK_a \leqslant 7.44$) in benzene in order to obtain more information on the evolution of carbonyl and carboxylate bands and other spectral features (*e.g.* continuous absorption) with the change of the acceptor properties of bases. Trifluoroacetic acid with some pyridines forms one of the strongest (NHO) intermolecular hydrogen bonds.[15]

EXPERIMENTAL

Solvents and complexes were prepared as previously.[15] I.r. spectra were recorded on Perkin-Elmer 580 and 180 spectrophotometers, using cells with KBr windows (*d* 0.11 and 0.247 mm). Measurements were performed in benzene and $[^2H_6]$benzene which were used as solvents. Concentrations varied from 0.15 to 0.3M. Since the solubility of pyridine trifluoroacetate in benzene is limited, its spectrum was obtained in a benzene solution containing a two-fold excess of pyridine. Complexes were prepared and cells were filled in a dry-box.

Centres of gravity of the reconstructed bands were obtained as $\bar{\nu}_H = \int A(\nu)\cdot\nu \, d\nu / \int A(\nu) \, d\nu$ by numerical integration. The reproducibility of $\bar{\nu}_H$ obtained in different cells and concentrations was ± 40 cm^{-1} (*ca.* 5% of band width values).

RESULTS AND DISCUSSION

Several authors [16-18] have discussed the vibrational spectra of trifluoroacetic acid and its salts and complexes. Denisov *et al.*[18] provide a detailed analysis of frequency variations of the $\nu_{as}(COO^-)$ band with symmetry.

In our spectra of complexes of the strongest bases (Figure 1h, i, Table 1) the absorption feature characteristic of the $\nu_{as}(COO^-)$ vibration appears at *ca.* 1 685 cm^{-1}, proving that hydrogen-bonded ion pairs are

TABLE 1

Characteristic i.r. bands and chemical shifts of hydrogen-bonded protons of substituted pyridine trifluoroacetates in benzene (0.3M)

No.	Substituent	ΔpK_a	$\nu(C{=}O)/cm^{-1}$	$\nu_{as}(COO^-)/cm^{-1}$	$\bar{\nu}_H/cm^{-1}$	δ^{15}
1	3-CN	1.22	1 780		1 830	17.32
2	4-CN	1.67	1 775		1 705	17.73
3	3-Br	2.64	1 760		1 605	18.43
4	H	4.94	1 745 *	1 700 *	1 310	20.33 *
5	3-Me	5.45	1 740	1 700	1 380	20.40
6	3,5-Me_2	5.92	1 730	1 700	1 455	20.03
7	2,5-Me_2	6.17	1 715	1 700	1 500	19.83
8	2,4-Me_2	6.40	1 720	1 690	1 640	19.52
9	2,6-Me_2	6.52		1 685	1 720	19.33
10	2,4,6-Me_3	7.21		1 685	1 870	18.82

* 0.15M with a two-fold excess of pyridine.

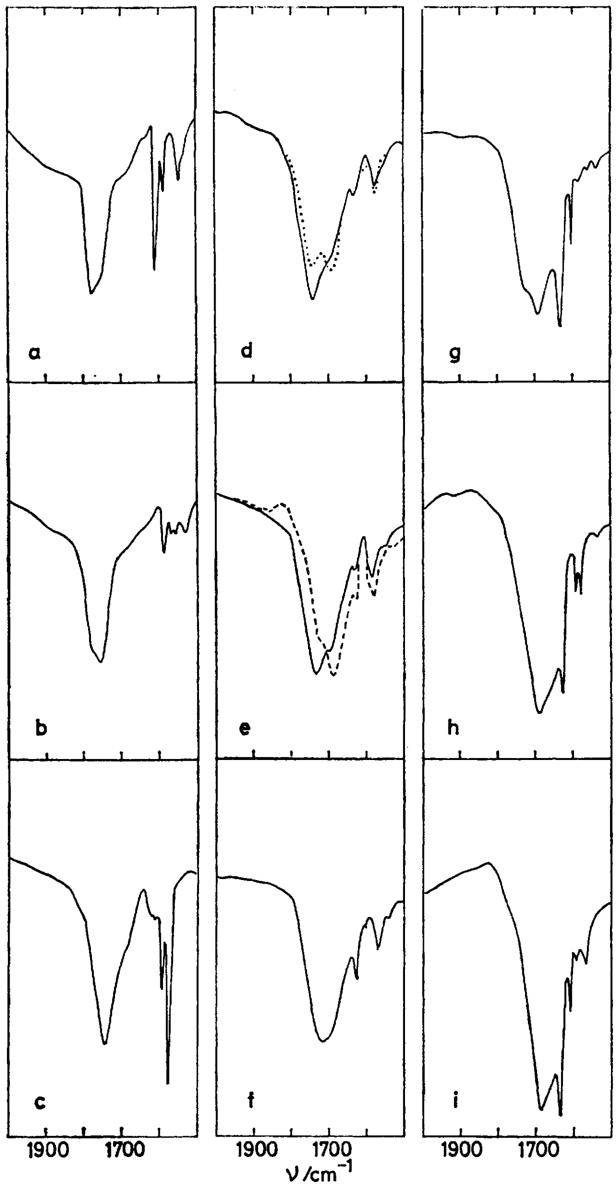

FIGURE 1 I.r. spectra of complexes of substituted pyridines with trifluoroacetic acid in benzene: a, 4-cyanopyridine; b, 3-bromopyridine; c, pyridine; d, 3-methylpyridine (···· the same with addition of H_2O); e, 3,5-dimethylpyridine (— — — the same in CH_2Cl_2); f, 2,5-dimethylpyridine; g, 2,4-dimethylpyridine; h, 2,6-dimethylpyridine; i, 2,4,6-trimethylpyridine

present. 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), but it is noticeably higher than $\nu_{as}(COO^-)$ of $CF_3COO^-\cdot(HOOCCF_3)_2$.[16,18] The spectra of complexes of the weakest bases show a strong band at *ca.* 1 780 cm^{-1} due to the $\nu(C=O)$ vibration. The frequency of this band is close to the frequency of the dimer, which is typical for an acid molecule forming strong hydrogen bonds without proton transfer. In the case of complexes of medium-strong bases both $\nu(C=O)$ and $\nu_{as}(COO^-)$ frequencies are observed. The frequency of the $\nu(C=O)$ band strongly decreases with increasing acceptor properties of bases, while the frequency of the $\nu_{as}(COO^-)$ band shows much smaller variations. Upon addition of an equimolar amount of water to the complex, the $\nu_{as}(COO^-)$ band shifts to a lower frequency (Figure 1d). In a more polar solvent, *e.g.* CH_2Cl_2, the intensity of the carbonyl component decreases but the carboxylate component increases (Figure 1e). These spectral features indicate that both ($B\cdots HA$) and ($B^+H\cdots A^-$) species are present in the investigated solutions.

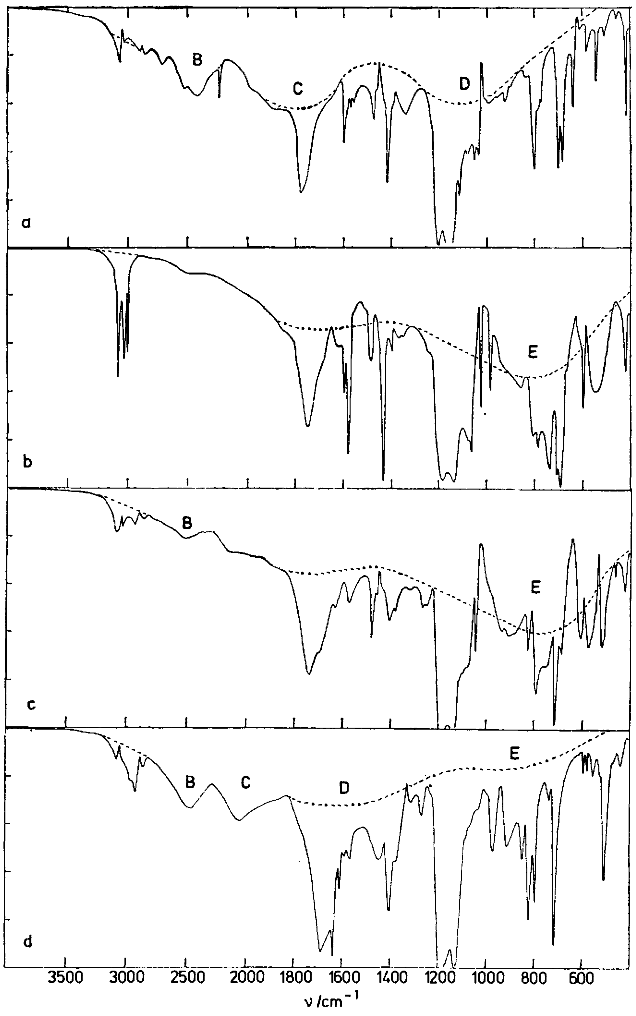

FIGURE 2 I.r. spectra of complexes of substituted pyridines with trifluoroacetic acid in benzene: a, 3-cyanopyridine; b, pyridine; c, 3-methylpyridine; d, 2,4,6-trimethylpyridine (- - - - continuous absorption)

More recently, Hadži and Bratos[19] have reviewed the literature data and have concluded that the quintet of bands (A >2 800, B *ca.* 2 500, C *ca.* 1 900, D *ca.* 1 100, and E *ca.* 850 cm^{-1}) in the i.r. spectra of compounds with strong hydrogen bonds are caused by Fermi resonance interaction of the fundamental tone of ν_{AH} with combinations and overtones. Hence, the frequencies and intensities of the $\nu(OH)$ or $\nu(N^+H)$ bands in strong hydrogen-complexes could be considered as corresponding to the centre ($\bar{\nu}_H$) of all the components of the complex absorption of ν(OH) or $\nu(N^+H)$, and not to the frequency and intensity of the principal maximum; ($\bar{\nu}_H$) is independent of Fermi resonances.[20] Theoretical study supports this inference.[21]

Examples of i.r. spectra are shown in Figure 2. Following Odinokov *et al.*,[6-8] we calculated data for $\bar{\nu}_H$ (Table 1) by numerical integration of the i.r. spectra. In Figure 3 their correlation with ΔpK_a is tested. In several previous publications we have reported the same type of correlation between the chemical shift of hydrogen-bonded protons and ΔpK_a.[11,12,16,22] Arnett and Chawla[23] have reported a good linear correlation between pK_a and the heats of reaction of substituted pyridines with trifluoroacetic acid in CCl_4 ($\Delta H_{1:1}$). Hopkins *et al.*[24] found a good linear correlation for pyridines between the gas-phase proton affinities (PA) and pK_a values. Thus we expect that the chemical shift of hydrogen-bonded protons and the centre ($\bar{\nu}_H$) of the i.r. absorption would correlate in a similar way with PA and $\Delta H_{1:1}$.

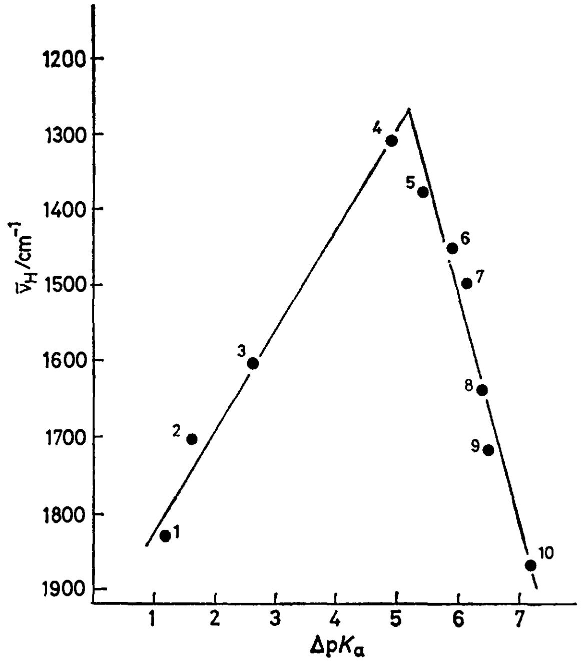

FIGURE 3 The plot of the centre ($\bar{\nu}_H$) of the ν(AH) complex absorption against ΔpK_a (numbers refer to Table 1)

An examination of Figure 1 and Table 1 shows that $\bar{\nu}_H$ lowers its frequency as ΔpK_a increases up to the point of intersection, and simultaneously the intensities are 'transferred' from high- to low-frequency components of the ν(AH) band. The reverse effect is observed above the intersection point. Thus the characteristic alterations of both the centre of the complex absorption and the chemical shift reflect the variations of hydrogen-bond strength. The strongest hydrogen bond appears in complexes which are close to the intersection point.

In our opinion it is not surprising that plots of δ and $\bar{\nu}_H$ *versus* ΔpK_a give two different lines. We explain the discrepancy between the behaviour of the two classes of complexes in terms of the most obvious difference between hydrogen bonding and proton transfer processes.[25]

In Figure 4 δ and $\bar{\nu}_H$ values for the investigated complexes are displayed. Again, two straight lines are derived and the values of δ and $\bar{\nu}_H$ obtained at the point of intersection agree within experimental error with those values derived from other correlations (Table 2).

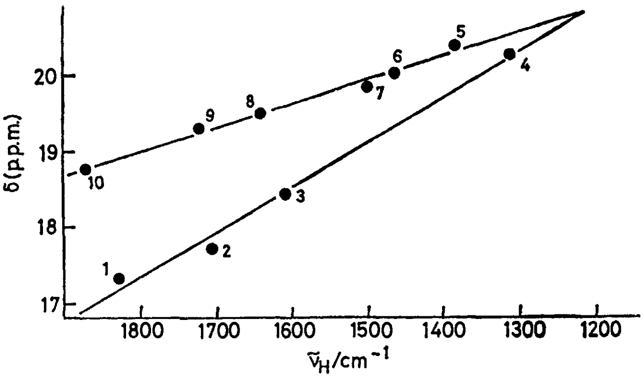

FIGURE 4 The plot of the chemical shift of hydrogen-bonded protons (δ) against the centre ($\bar{\nu}_H$) of the ν(AH) complex absorption. (Numbers refer to Table 1)

TABLE 2

Comparison of data at points of intersection

Correlation	ΔpK_a	$\bar{\nu}_H/cm^{-1}$	δ (p.p.m.)
$\delta = f(\Delta pK_a)$	5.27		20.59
$\bar{\nu}_H = f(\Delta pK_a)$	5.20	1 270	
$\delta = f(\bar{\nu}_H)$		1 225	20.76

^1H N.m.r. studies have established that positive charges on the atom to which hydrogen nuclei are attached generally result in decreased shielding of the hydrogen nuclei.[26] In our case the difference in the chemical shift between complexes of 2,4,6-trimethylpyridine and 3-cyanopyridine is *ca.* 1.8 p.p.m. (derived from Figure 4). This value is consistent with the difference between the chemical shift of tropylium salt and benzene (1.9 p.p.m.).[26] These results support, but of course do not prove, our position that the principal cause for the difference between the two lines shown in Figure 4 lies in the charge derived by protonation of the pyridine ring.

Joesten and Schaad[27] have reviewed relationships between chemical shift and other physical properties, *e.g.* ΔpK_a, ΔH, log K, and $\Delta\nu$. Since the chemical shift of hydrogen-bonded protons is very sensitive to the charge of complexes, we conclude that no general relationship between the chemical shift and ΔpK_a, log K, or ΔH exists, although correlations are found in a few limited series of closely similar compounds.

We acknowledge financial support from the Polish Academy of Sciences.

[1/362 *Received*, *3rd March*, 1981]

REFERENCES

[1] S. L. Johnson and K. A. Rumon, *J. Phys. Chem.*, 1965, **69**, 74.

[2] G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, 1954, **76**, 5211.

[3] G. M. Barrow, *J. Am. Chem. Soc.*, 1956, **78**, 5802.

[4] G. V. Gusakova, G. S. Denisov, A. L. Smolyansky, and V. M. Schreiber, *Dokl. Akad. Nauk SSSR*, 1970, **193**, 1065.

[5] G. S. Denisov, G. V. Gusakova, and A. L. Smolyansky, *J. Mol. Struct.*, 1973, **15**, 377.

[6] S. E. Odinokov, A. V. Iogansen, and A. K. Dzizenko, *Zh. Prikl. Spektrosk.*, 1971, **14**, 418.

[7] V. P. Glazunov, A. A. Mashkovsky, and S. E. Odinokov, *Zh. Prikl. Spektrosk.*, 1975, **23**, 469.

[8] V. P. Glazunov, A. A. Mashkovsky, and S. E. Odinokov, *Spectrosc. Lett.*, 1976, **9**, 391.

[9] R. Lindemann and G. Zundel, *J. Chem. Soc., Faraday Trans. 2*, 1972, 979; 1977, 788.

[10] T. Duda and M. Szafran, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1978, **26**, 207.

[11] Z. Dega-Szafran and J. Kunzendorf, *Pol. J. Chem.*, 1979, **53**, 623.

[12] M. Wierzejewska-Hnat, Z. Mielke, and H. Ratajczak, *J. Chem. Soc., Faraday Trans. 2*, 1980, 834.

[13] A. I. Kulbida and V. M. Schreiber, *J. Mol. Struct.*, 1978, **47**, 323.

[14] B. H. Robinson in 'Aprotic Solvents in Proton Transfer Reactions,' eds. E. Caldin and V. Gold, Chapman and Hall, London, 1975, p. 121.

[15] Z. Dega-Szafran and E. Dulewicz, *Org. Magn. Reson.*, 1981, **16**, 214.

[16] E. Spiner, *J. Chem. Soc.*, 1964, 4217.

[17] C. V. Berney, *J. Am. Chem. Soc.*, 1973, **95**, 708.

[18] G. V. Gusakova, G. S. Denisov, and A. L. Smolyansky, *Opt. Spektrosk.*, 1972, **32**, 922.

[19] D. Hadži and S. Bratos, in ' The Hydrogen Bond—Recent Developments in Theory and Experiments,' ed. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, p. 567.

[20] H. R. Zelsmann and Y. Marechal, *Chem. Phys.*, 1977, **20**, 459.

[21] V. P. Sakun and N. D. Sokolov, *Chem. Phys.*, 1980, **50**, 287.

[22] B. Brycki, Z. Dega-Szafran, and M. Szafran, *Adv. Mol. Relax. Interact. Processes*, 1979, **15**, 71; *Pol. J. Chem.*, 1980, **54**, 221.

[23] E. M. Arnett and B. Chawla, *J. Am. Chem. Soc.*, 1978, **100**, 217.

[24] H. P. Hopkins, jun., C. J. Alexander, and S. Z. Ali, *J. Phys. Chem.*, 1978, **82**, 1268.

[25] E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, 1974, **96**, 3875.

[26] J. W. Emsley, J. Feeney, and L. M. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 2, p. 774.

[27] M. D. Joesten and L. J. Schaad, ' Hydrogen Bonding,' Marcel Dekker, New York, 1974.