Infrared Studies of Solvent Effects on Hydrogen Bonding in Some Pyridine Trifluoroacetates

Zofia Dega-Szafran,* Ewa Dulewicz, and Mirosław Szafran
Department of Chemistry, A. Mickiewicz University, 60780 Poznań, Poland

The i.r. spectra are reported for the trifluoroacetates of five substituted pyridines in five dry solvents of different activity with respect to proton transfer, aggregation, and triple ion effects. Four broad absorption regions (bands B—E) may be distinguished in the spectra. The intensity variation of these bands with solvent is very similar to that predicted by theory, and may provide evidence that the dipole of the hydrogen bond interacts with the reaction field from the environment. The shift of the centre of gravity, $\bar{\nu}_H$, as the reaction field increases can be explained either by a change of symmetry of the potential surface or by a change of hydrogen bond length. The centre of gravity, $\bar{\nu}_H$, is correlated with $(\varepsilon - 1)/(2\varepsilon + 1)$ and E_T parameters and discussed with respect to specific and nonspecific interactions.

A reaction between acid (AH) and base (B) in aprotic solvents is represented in general by the equilibria in the Scheme. The equilibria between various acid–base species in solutions depend mainly on (i) the proton-donor and proton-acceptor properties of the interacting components expressed by $pK_a^{B^+H}$ and pK_a^{AH}, (ii) the nature of organic solvents, and (iii) the concentration of solute.[1-3]

In the case of complexes of pyridines with carboxylic acids the following species were recognized: $A{-}H \cdots B \rightleftharpoons A^- \cdots HB^+$ (from i.r.[4-8] and u.v.[9] spectra), $(AHB)_n$ (from vapour pressure osmometry measurements,[10-12]), and triple ions (from conductance[13]). Indirect evidence for the equilibrium $A{-}H \cdots B \rightleftharpoons A^- \cdots HB^+$ was obtained from dielectric measurements,[14] ^{35}Cl n.q.r.,[15,16] and ^1H n.m.r.[17-20] spectra.

Interactions of molecules with the environment can be explained on the basis of (i) quantum chemical calculations (electrostatic approximations),[21] (ii) classical calculations based on modern theories of nonelectrolytes (dipole–dipole or reaction field approximations),[22] and (iii) empirical parameters of solvent polarity.[23]

Various authors[22,24,25] have stressed the importance of the reaction field for the position of the proton in the complex and thus for the mean dipole moments and continuous absorption of the hydrogen bonds. Theoretical calculations demonstrate that the reaction field as well as the bond length distributions are necessary conditions for the occurrence of the i.r. continua.[24-26]

Recently we have investigated the solvent effect on the chemical shift of hydrogen-bonded protons in complexes of pyridines with trifluoroacetic acid.[20] A plot of δ *versus* $(\varepsilon - 1)/(2\varepsilon + 1)$ consists of straight lines with a positive slope for weak pyridines ($pK_a < 4$) and a negative slope for strong pyridines ($pK_a > 5$). Points for benzene solution deviate from the correlation lines. We believe that these variations of chemical shift with solvent reflect a change of hydrogen bond strength.

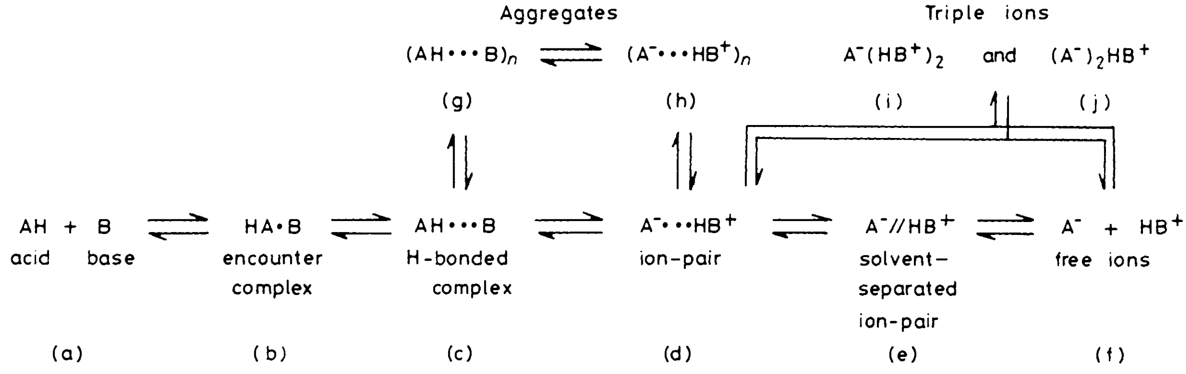
In this paper we extend investigation of solvent effect on i.r. spectra in order to get new independent evidence of this effect on the strength of hydrogen bond. Nuclear magnetic shielding is described by a multi-term expression[27] and is very sensitive to protonation (effect of charge[28,29]). The position of the i.r. absorption band is more directly correlated with the hydrogen bond length.[30]

Experimental

Complexes and solvents were prepared as previously.[20] Since trifluoroacetic acid interacts with acetonitrile, in two cases, *i.e.* 4-cyano- and 3-bromo-pyridine complexes, spectra were measured with an excess of bases ($C_B : C_{AH} = 4:1$).

I.r. spectra were recorded on Perkin-Elmer 580 and 180 spectrophotometers, using cells with KBr windows, 0.11 mm thick. The concentration was 0.3M

A continuous proton absorption was separated graphically from sharp bands ascribed to other internal vibrations. To correct the subtracted continuous absorption, spectra of complexes with trifluoroacetic [^{2}H]acid were used, in some intricate examples, as a reference. Centres of gravity of the reconstructed graphically bands were obtained as $\bar{\nu} = \int A(\nu)\nu d\nu / \int A(\nu) d\nu$ by numerical integration. The largest uncertainty in determining



Scheme.

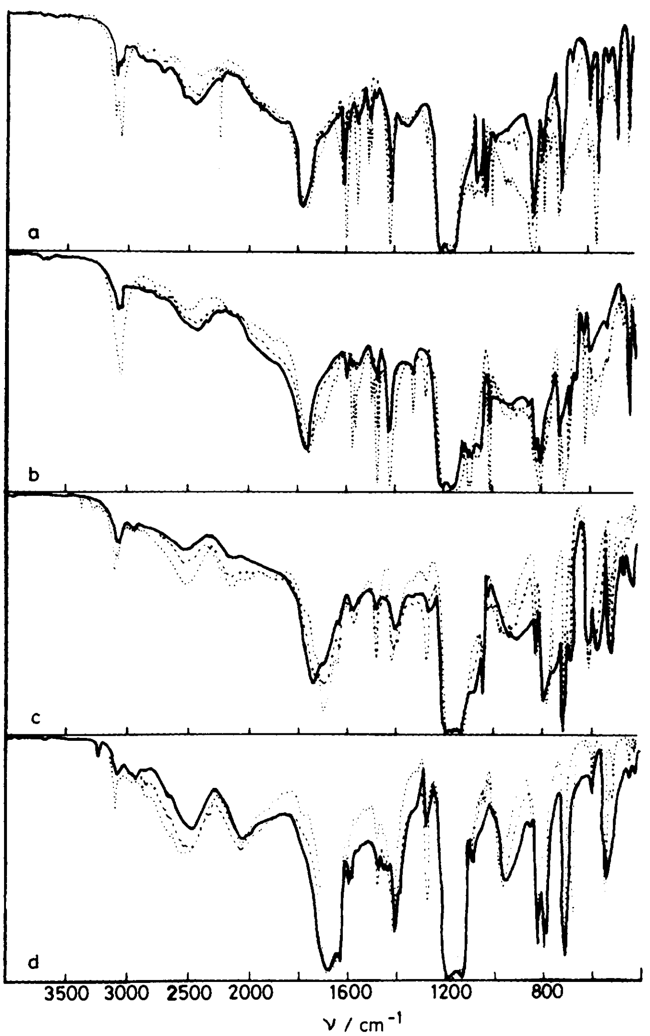


Figure 1. I.r. spectra of complexes of substituted pyridines with CF_3COOH: a, 4-cyanopyridine; b, 3-bromopyridine; c, 3-methylpyridine; d, 2,6-dimethylpyridine. —— C_6H_6 and C_6D_6, - - - CH_2Cl_2, ····· CH_3CN and CD_3CN

the centre of gravity is connected with separation of the continuous absorption from ν(C=O) or $\nu_{as}(COO^-)$ and $\nu(CF_3)$ absorptions in the regions of 1 800—1 650 and 1 200—1 100 cm^{-1}. This can cause a systematic error. The standard deviation in the $\bar{\nu}$ values is of the order of ±75 cm^{-1}.

Results and Discussion

The spectra of the investigated pyridine trifluoroacetates exhibit continuous absorption over the frequency region from 3 000 to 400 cm^{-1}. Within this range there are usually five overlapping absorption bands (A >2 800, B *ca.* 2 500, C *ca.* 1 900, D *ca.* 1 100, and E *ca.* 850 cm^{-1}). All these bands are poorly resolved and exhibit several subpeaks resulting from superposition of sharp bands ascribed to other internal vibrations and to the Fermi resonance. Additionally, the spectra of these complexes contain, as a rule, several strong Evans holes (transmission windows) which deform the contours of the corresponding bands (Figure 1). Hence, the centre of gravity is used to characterise this complex absorption. The structure and intensity of the bands A—E depend strongly on the proton-acceptor properties of the pyridine bases.

Solvent effect on the centre of gravity ($\bar{\nu}_H$/cm^{-1}) of complexes of stituted pyridines with trifluoroacetic acid

	Substituent						
Solvent	4-CN	3-Br	H	3-Me	2,6-Me$_2$	ε^3	$E_T{}^3$
C_6H_6–C_6D_6	1 680	1 610	1 310	1 425	1 720	2.27	34.5
C_6H_5Cl	1 665	1 585	1 370	1 445	1 740	5.61	37.5
CH_2Cl_2	1 615	1 535	1 450	1 550	1 870	8.93	41.1
$ClCH_2CH_2Cl$	1 600	1 540	1 465	1 570	1 890	10.36	41.9
CH_3CN–CD_3CN	1 555	1 510	1 590	1 690	2 035	37.5	46.0

Figure 1 shows solvent effects on i.r. spectra. In complexes of 4-cyano- and 3-bromo-pyridine, the dominant species is a molecular complex (AH ··· B).[28] In these two cases, when the electric permittivity of the solvent increases a systematic decrease in the intensity of the bands B and C is observed. Simultaneously the intensity of the bands D and E increases (Figure 1a and b). In the spectra of complexes of 3-methyl- and 2,6-dimethyl-pyridine, where the dominant species is the ion-pair (A^- ··· HB^+),[28] intensities of the bands B—E change on the reverse side on increasing the electric permittivity (Figure 1c and d). The observed intensity variations of bands B—E with solvent are very similar to those predicted by *ab initio*[24] and SCF[25] calculations and a stochastic model,[26] and observed in some homoconjugated cations $(NH \cdots N)^+$ when the temperature is changed.[31] According to theoretical calculations, the observed variations in absorption as the field increases can be explained either by a change of symmetry in the potential surface or a change in the hydrogen bond length. A strong increase in band E intensity with the solvent polarity in complexes of 4-cyano- and 3-bromo-pyridine may be evidence that the potentials become more symmetrical or hydrogen bonds become shorter. Similarly, a decrease in intensity of band E in the other complexes implies weaker hydrogen bonds or an increase in the asymmetry of the potential surface. The observed variation of intensity caused a change of the $\bar{\nu}_H$ values, which is directly related to the hydrogen bond distance.[30] The linear correlations of δ *versus* $\bar{\nu}_H$ observed previously for benzene[28] and dichloromethane [29] indicate that contribution of the bond length to variation in absorption is important.

The Table lists the centres of gravity ($\bar{\nu}_H$) of continuous absorption. Figures 2 and 3 show the relationship between the centre of gravity and the $(\varepsilon - 1)/(2\varepsilon + 1)$ and E_T parameters, respectively. Similar correlations have been obtained previously[20] between the chemical shifts of the hydrogen-bonded protons and $(\varepsilon - 1)/(2\varepsilon + 1)$ and E_T.

A reaction field model also predicts a linear relation between free energy, ΔG, and the reaction field parameter $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ in a case of electrostatic solvation.[22] The slope of these correlations is positive for weakly polar (AH ··· B) and negative for strongly polar (A^- ··· HB^+) complexes.

The observed linear correlations between $\bar{\nu}_H$ [32] and $(\varepsilon - 1)/(2\varepsilon + 1)$ shown in Figure 2 for some solvents reflect electrostatic solvation. The deviation of benzene points from the straight lines (Figure 2) is caused by specific interactions.

Pyridine trifluoroacetates in benzene form aggregates, $(AHB)_n$.[11] The aggregation constant strongly decreases with an increase in solvent electric permittivity.[33] The centre of gravity $\bar{\nu}_H$ is sensitive to aggregation, *e.g.* for 2,4,6-timethylpyridinium trifluoroacetate $\bar{\nu}_H$ = 1 760 cm^{-1} (0.068M) and $\bar{\nu}_H$ = 1 923 cm^{-1} (0.604M).[34]

Since aggregation shifts $\bar{\nu}_H$ values to higher frequency, correlations of $\bar{\nu}_H$ values reduce (about twice) the deviation of points from lines in the case of complexes with negative slope, but slightly increase it for a case with positive slope.

A considerable scattering of corrected points from lines

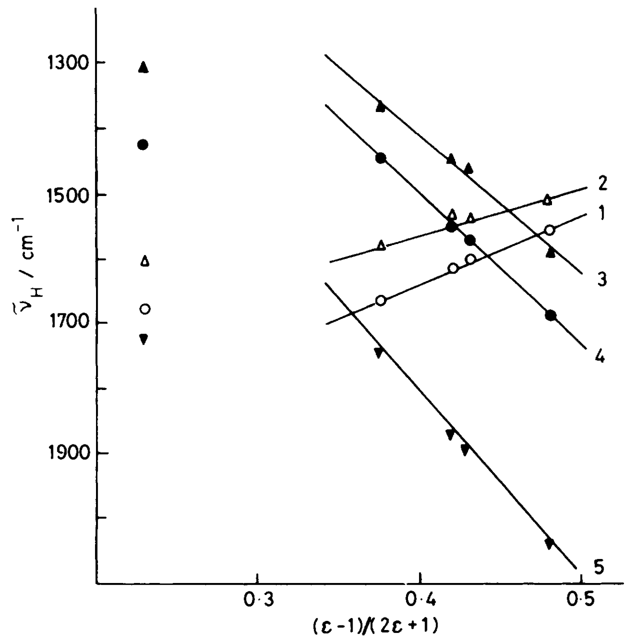


Figure 2. The plot of the centre of gravity ($\tilde{\nu}_H$) *versus* (ε − 1)/(2ε + 1) of complexes of substituted pyridines with CF_3COOH: 1, 4-cyanopyridine; 2, 3-bromopyridine; 3, pyridine; 4, 3-methylpyridine; 5, 2,6-dimethylpyridine (*r* 0.96—0.99)

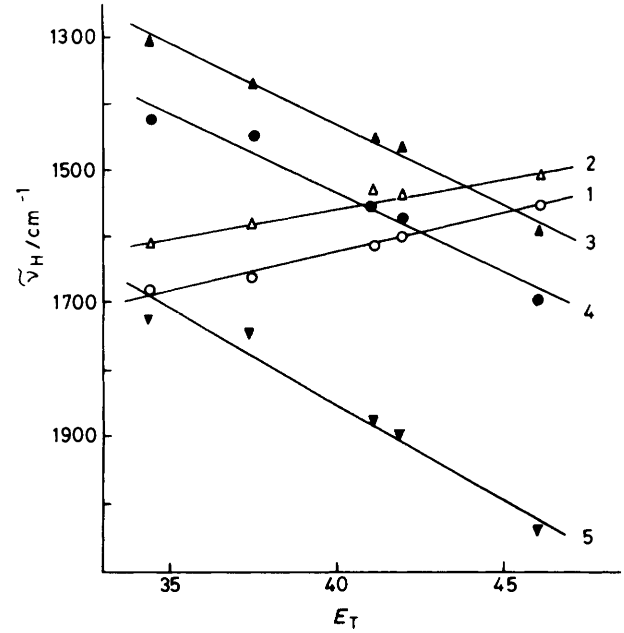


Figure 3. The plot of the centre of gravity ($\tilde{\nu}_H$) *versus* E_T of complexes of substituted pyridines with CF_3COOH: 1, 4-cyanopyridine; 2, 3-bromopyridine; 3, pyridine; 4, 3-methylpyridine; 5, 2,6-dimethylpyridine (*r* 0.98—0.99)

suggests the contribution of other specific interactions. Triple ions could be one of them, but this is not the case.[13] The amount of triple ions depends on the concentration and nature of the solvent. Since aggregation also varies with concentration i.r. spectra include both effects, formation of aggregates and triple ions.

Mehta and Chawla[13] estimated the amount of the ionic species in dilute solution (9×10^{-2}M) of 2,4,6-trimethylpyridinium trifluoroacetates in chloroform to be *ca.* 2—7%; this gives $\bar{n} = 1.03$. Benzene is a less active solvent than chloroform, the value of $\bar{n} = 1.53$ (for 9×10^{-2}M)[11] indicating an increase in the concentration of non-ionic aggregates and triple ions. It seems that the concentration of non-ionic aggregates is larger than that of triple ions, since the dissociation constant of ion-pairs to free ions ranges from 10^{-18} to 10^{-21}.[35]

E_T parameters include polar and specific interactions, hence in the plot of $\tilde{\nu}_H$ *versus* E_T all points are on the lines (Figure 3).

Acknowledgements

We acknowledge financial support from the Polish Academy of Sciences (project MR.I.9.4.4.4).

References

1 B. H. Robinson, in 'Aprotic Solvents in Proton Transfer Reactions,' eds. E. Caldin and V. Gold, Chapman and Hall, London, 1975, p. 121.
2 R. F. Fouss and F. Accascina, 'Electrolytic Conductance,' Interscience, New York, 1959.
3 C. Reichardt, 'Solvent Effect in Organic Chemistry,' Verlag Chemie, Weinheim, New York, 1979.
4 G. M. Barrow, *J. Am. Chem. Soc.*, 1956, **78**, 5802.
5 G. V. Gusakova, G. S. Denisov, and A. L. Smolyansky, *Zh. Prikl. Specktrosk.*, 1971, **5**, 860.
6 G. V. Gusakova, G. S. Denisov, A. L. Smolyansky, and V. M. Schreiber, *Dokl. Akad. Nauk SSSR*, 1970, **193**, 1065.
7 S. E. Odinokov and A. V. Iogansen, *Spectrochim. Acta*, 1972, **28A**, 2343.
8 R. Lindemann and G. Zundel, *J. Chem. Soc., Faraday Trans. 2*, 1972, 979; 1977, 788.
9 J. Nasielski and E. V. Donckt, *Spectrochim. Acta*, 1963, **19**, 1989.
10 Z. Dega-Szafran, E. Grech, M. Z. Naskret-Barciszewska, and M. Szafran, *J. Chem. Soc., Perkin Trans. 2*, 1975, 250.
11 Z. Dega-Szafran, *Adv. Mol. Relax. Interact. Processes*, 1980, **18**, 61.
12 Z. Dega-Szafran and M. Szafran, *J. Mol. Liquids*, 1983, **25**, 109.
13 S. K. Mehta and B. Chawla, *Electrochim. Acta*, 1982, **27**, 9.
14 L. Sobczyk and Z. Pawełka, *J. Chem. Soc., Faraday Trans. 1*, 1974, 832.
15 H. Chihara and N. Nakamura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1980.
16 J. Pietrzak, B. Nogaj, Z. Dega-Szafran, and M. Szafran, *Acta Phys. Polon.*, 1977, **A52**, 779.
17 K. Toyoda, T. Ikenone, and T. Isobe, *J. Chem. Phys.*, 1958, **28**, 356.
18 Z. Dega-Szafran and J. Kunzendorf, *Pol. J. Chem.*, 1979, **53**, 623.
19 J. A. Gowland and R. A. McClelland, *Can. J. Chem.*, 1979, **57**, 2140.
20 Z. Dega-Szafran and E. Dulewicz, *Org. Magn. Reson.*, 1981, **16**, 214.
21 J. Tomasi, in 'Molecular Interactions,' eds. H. Ratajczak and W. J. Orville-Thomas, Wiley, Chichester, 1982, vol. 3, p. 119.
22 J. Małecki, in 'Molecular Interactions,' eds. H. Ratajczak and W. J. Orville-Thomas, Wiley, Chichester, 1982, vol. 3, p. 183.
23 C. Reichardt, in 'Molecular Interactions,' eds. H. Ratajczak and W. J. Orville-Thomas, Wiley, Chichester, 1982, vol. 3, p. 241.
24 A. Janoschek, E. G. Weidemann, and G. Zundel, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 505.
25 A. Hayd, E. G. Weidemann, and G. Zundel, *J. Chem. Phys.*, 1979, **70**, 86.
26 H. Romanowski and L. Sobczyk, *Chem. Phys.*, 1977, **19**, 361.
27 W. T. Raynes, R. Ditchfield, and R. B. Mallion, ' Nuclear Magnetic Resonance,' Chem. Soc. Specialist Periodical Reports, 1972—1978, vols. 1—7, ch. 1.
28 Z. Dega-Szafran and M. Szafran, *J. Chem. Soc., Perkin Trans. 2*, 1982, 195.
29 Z. Dega-Szafran and E. Dulewicz, *J. Chem. Soc., Perkin Trans. 2*, 1983, 345.
30 A. Novak, *Struct. Bonding (Berlin)*, 1974, **18**, 177.
31 E. Grech, Z. Malarski, and L. Sobczyk, *Spectrosc. Lett.*, 1976, **9**, 749.
32 There is a linear correlation between frequency and ΔG for a few limited series of closely similar compounds, see *e.g.* M. D. Joesten and L. J. Schaad, 'Hydrogen Bonding,' Dekker, New York, 1974.
33 Z. Dega-Szafran and M. Szafran, *J. Mol. Struct.*, 1978, **45**, 33.
34 Z. Dega-Szafran and M. Szafran, *J. Chem. Soc., Chem. Commun.*, 1984, 1470.
35 C. A. Kraus, *J. Chem. Educ.*, 1958, **35**, 324.

Received 3rd January 1984; Paper 4/006