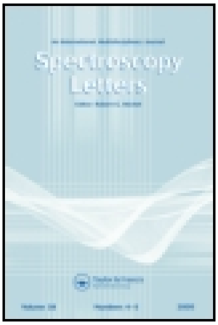


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lstl20

NMR Study of Pentafluoroaniline - Hydrogen Bonding and Proton Exchange

I. Wawer [a], Z. Kecki [a] & G. S. Denisow [b]

[a] Laboratory of Molecular Interactions, Department of Chemistry, University of Warsaw, 02-093, Warsaw, Poland

[b] Institute of Physics, Leningrad State University, Leningrad, Petrodvorez, 198904, USSR

To cite this article: I. Wawer, Z. Kecki & G. S. Denisow (1991): NMR Study of Pentafluoroaniline - Hydrogen Bonding and Proton Exchange, Spectroscopy Letters, 24:10, 1363-1372

To link to this article: http://dx.doi.org/10.1080/00387019108021767

SPECTROSCOPY LETTERS, 24(10), 1363-1372 (1991)

NMR STUDY OF PENTAFLUOROANILINE - HYDROGEN BONDING AND PROTON EXCHANGE

Key Words: pentafluoroaniline, hydrogen bonds, ^{1}H NMR

I. Wawer, Z. Kęcki

Laboratory of Molecular Interactions, Department of Chemistry, University of Warsaw, 02-093 Warsaw, Poland

G.S. Denisow

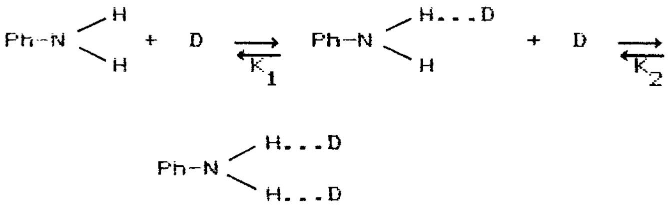
Institute of Physics, Leningrad State University, Leningrad, Petrodvorez, 198904 USSR

ABSTRACT

The temperature and concentration dependence of ^{1}H NMR chemical shifts of pentafluoroaniline and aniline in acetone (Ac), dimethylsulphoxide (DMSO) and hexamethylphosphortriamide (HMPA) indicate that the effect of hydrogen bond formation, $\Delta = \delta_{obs} - \delta_{A}$, is similar for both anilines. The analysis of ^{1}H NMR spectra showed, that proton exchange of t-butyl alcohol (tBA) and 2,6-di-t-butylphenol (DTBPh) with pentafluoroaniline is slower than that with aniline.

INTRODUCTION

Static and dynamic properties of hydrogen bonds formed by aniline (A) have been widely studied, but the data concerning its pentafluoro-analog are few. Earlier IR studies[1,2] established that equilibrium constants for the hydrogen bonded complex of pentafluoroaniline (pFA) with DMSO and HMPA are higher than the respective ones of aniline (A). Denisow et.al[2]. showed by the analysis of ν NH bands of pFA, that the complexes 1:1 and 1:2 are formed. In the presence of strong electron-donor such as HMPA the complexes with one NH proton dominate and the existence of second hydrogen bond is disfavoured.



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It seemed worth to compare (A) and pFA applying multinuclear and dynamic NMR.

EXPERIMENTAL

Pentafluoroaniline and aniline were commercial products (Aldrich).

Aniline and the solvents used were freshly distilled.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer, equipped with a variable temperature probe, at 89.55 and 22.50 MHz, respectively, with TMS as an internal reference. ^{15}N spectra were recorded on Bruker AM 500 spectrometer at 50.7 MHz and chemical shifts were referenced to $CH_3{}^{15}NO_2$.

TABLE. 1

Chemical shifts (δ, ppm) and pK_a values for pFA and A

	$C_6F_5NH_2$	$C_6H_5NH_2$
^1H NMR (δ_M, in CCl_4)	3.47	2.70
^{13}C NMR (Ci,aromatic, in $CDCl_3$)	125.5	147.8
^{15}N NMR, (in C_6D_6)	-324.2	-347.5
pK_a (in 95.6% ethanol)	2.1	4.1

RESULTS AND DISCUSSION

Some NMR chemical shifts and the basicity of both compounds A and pFA are presented in Table 1.

In the temperature range 20-70°C the signal of NH_2 protons of pFA shifts upfield with increasing temperature and decreasing concentration in CCl_4 (Fig.1). The value of 3.47 ppm, at the infinite dilution, δ_M, is characteristic of the pFA monomer.

The concentrations of pFA (or A) in further experiments were kept constant, 0.2 M, and the concentration of electron-donor D in CCl_4 was varied. The NH_2 signal shifts downfield (Fig.2,3) with lowering the temperature and increasing concentration of D which is characteristic for the hydrogen bonded complex formation, according to (1). The downfield shift increases with increasing electron-donor abilities of D: Ac <DMSO <HMPA. The observed chemical shift of NH_2 protons is the weighed average of δ_M, δ_{MD}, δ_{MD_2}, i.e. chemical shifts of monomer, 1:1 and 1:2 complex, respectively. NMR yields no accurrate data of

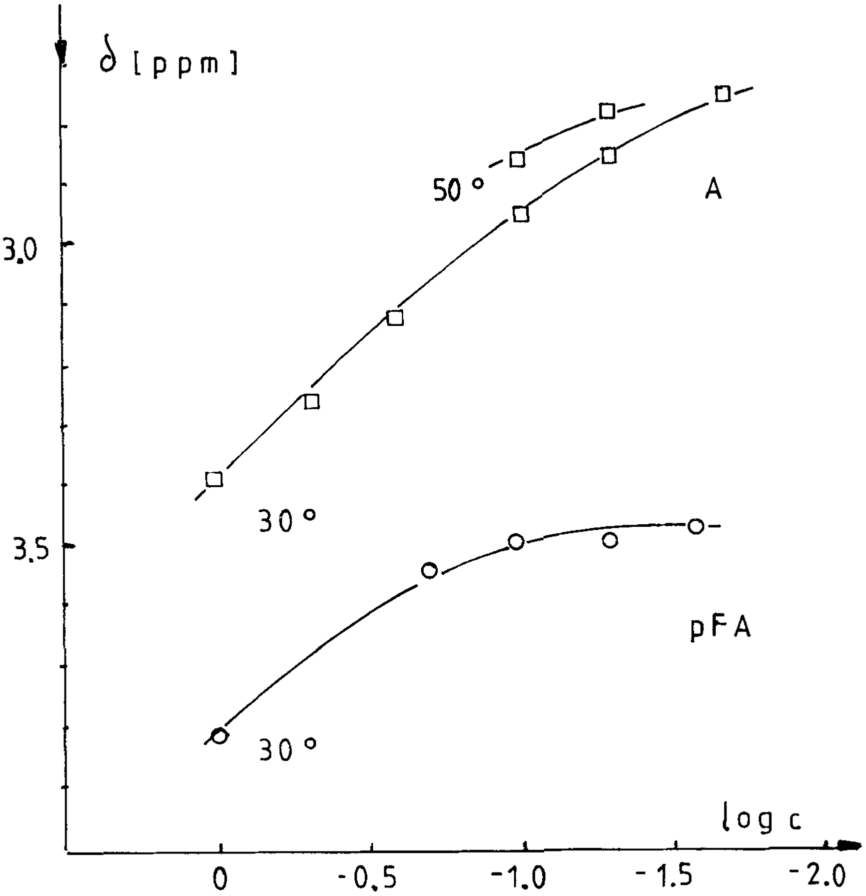


FIG. 1 The dependence of chemical shifts of NH_2 protons on concentration (logarithmic scale) in CCl_4

equilibrium constants for molecular complexes in such a case; the more suitable method is IR where separate bands of 1:1 and 1:2 complexes can be observed[2]. Some estimation, however, can be made concerning the δ_{MD} and δ_{MD_2} values. The NMR spectrum of solution pFA : HMPA

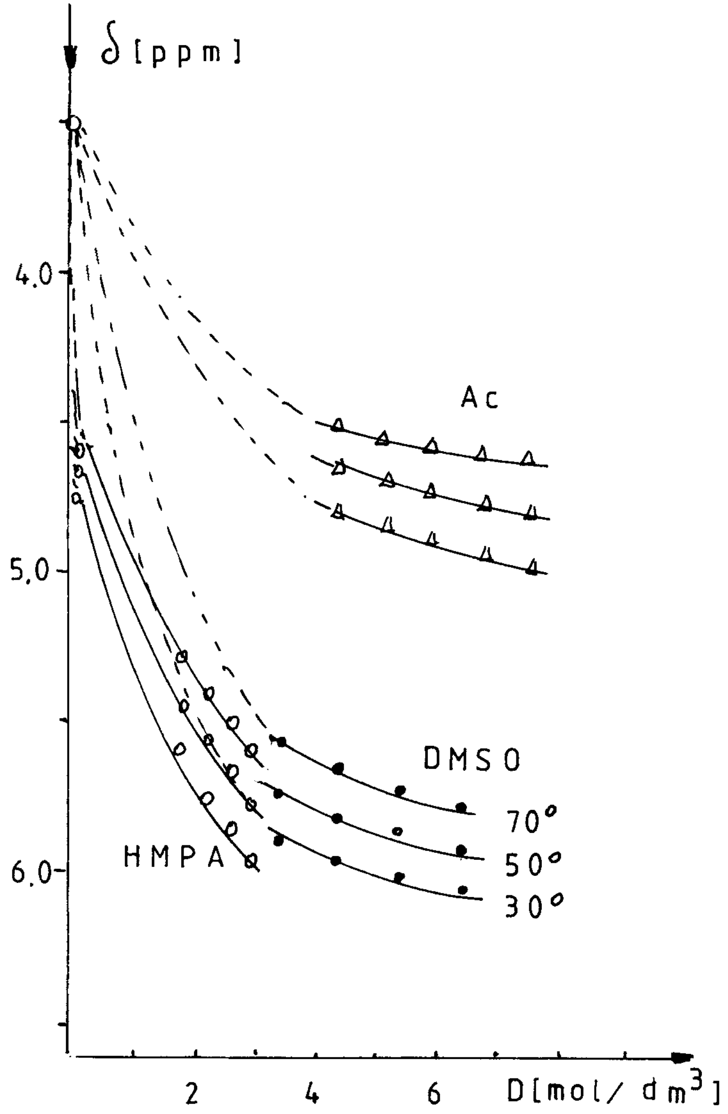


FIG.2 The dependence of δ_{obs} of NH_2 protons in pFA on concentration of electron-donor, D, in CCl_4

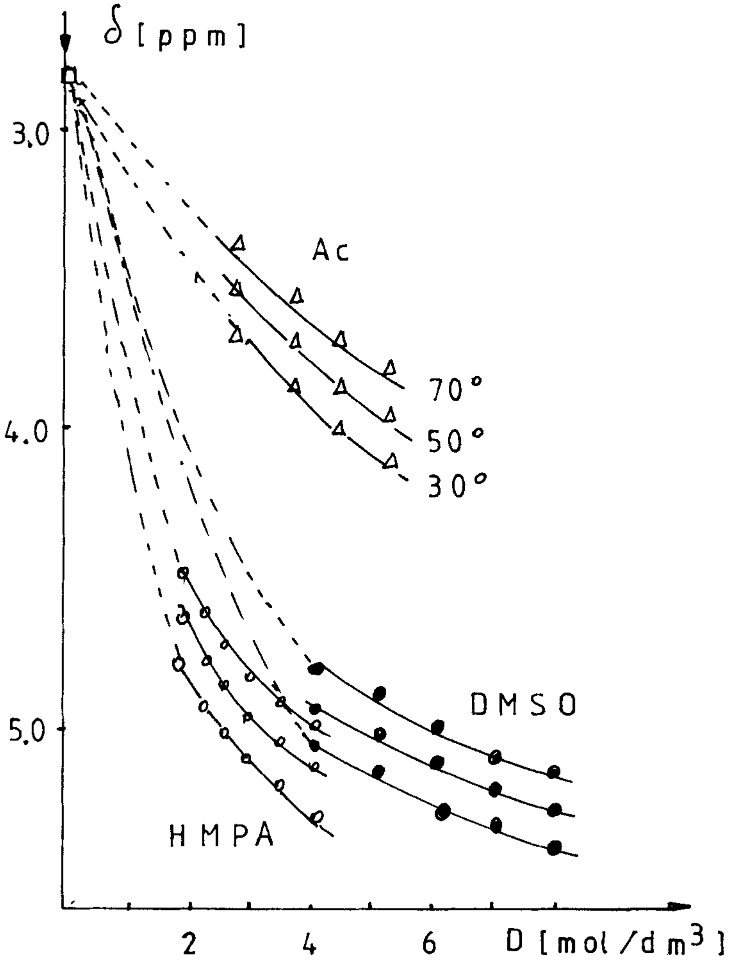


FIG.3 The dependence of δ_{obs} of NH_2 protons in A on concentration of electron-donor, D, in CCl_4

(1:1) in CD_2Cl_2 exhibits δ NH_2 = 5.1 and the chemical shift remains constant in the temperature range -20^o down to -60^o, this value can be taken as δ_{MD}. Simple estimation ($5.1-\delta_M$ = 1.6 ppm per one hydrogen bond formed; for two bonds in MD_2: $3.2+\delta_M$ = 6.7) shows that δ_{MD_2} should amount 6.7 ppm. Chemical shift of NH_2 protons in the spectrum of 1.2 M pFA binary solution in HMPA at 10^oC is 6.5 ppm and is close to the expected δ_{MD_2}.

In Fig.3. a set of ^1H NMR chemical shifts of NH_2 in aniline solutions is shifted by about 0.8 ppm as compared with those for pentafluoroaniline in Fig.2.

It may be concluded that the effect of hydrogen bond formation by both anilines pFA and A with the electron-donors Ac, DMSO and HMPA, $\Delta = \delta_{obs}-\delta_M$, is about the same, and the difference by about 0.8 ppm is caused by the various shielding of NH_2 protons in the monomers of pFA and A (cf. Table 1). The IR results (ν_{NH}) indicate, that pFA forms stronger hydrogen bonded complexes with electron-donors. The effect of hydrogen bond formation Δ includes contributions from chemical shifts δ_{MD}, δ_{MD_2} and equilibrium constants K_1, K_2 and, therefore, greater value of Δ was expected for pFA than for A.

It seemed interesting to study the rate of proton exchange between pFA (A) and R-OH. As the partners for exchange tertbutylalcohol (tBA) and 2,6-di-tertbutylphenol (DTBPh) were applied. Kinetics of exchange between A and DTBPh was earlier investigated by Sandul et al[3].

The ^1H NMR spectra of pFA (or A) + DTBPh solutions in CCl_4 with various concentrations were recorded in the temperature range $20-70^oC$. As the rough

TABLE 2

Table 2. Kinetic parameters for proton exchange between:

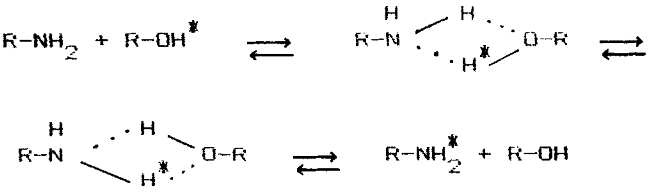
(a) pFA + tBA in $C_6D_5NO_2$
(b) A + tBA in $C_6D_5NO_2$
(c) pFA + DTBPh in CCl_4
(d) A + DTBPh in CCl_4

	T (K)	τ (s)	k (l $mol^{-1}s^{-1}$)	$\Delta G^{\#}$ (kJ mol^{-1})
(a)	453	0.06	41	98.5
	463	0.03	82	98.0
(b)	283	<0.004	>1170	
(c	353	>0.5	<2	
(d)	303	~ 0.1		
	313	0.04	25	68.4
	323	0.02	50	68.8
	333	0.015	67	70.2
	343	0.013	77	72.0
	353	0.008	125	72.7
	T_c	0.00168	595	

Further studies are in progress.

estimations: the line width of TMS was used to calculate relaxation times T_2^{OH} and the broadening of NH_2 due to quadrupolar relaxation: $T_q = T_2^{NH_2}$. The two-site exchange was assumed and the signal shape analysis was carried out by means of computer program[4].

The results obtained indicate that the exchange reaction is bimolecular :



(2)

and runs 1 *via* cyclic complex, and that proton exchange inside it is the rate limiting step.

The kinetic parameters for the exchange between A and DTBPh are given in Table 2. The rate constants were calculated according to the equation:

$$k = \tau^{-1}[RNH_2]^{-1}[ROH]^{-1}$$

In the case of pFA protons the exchange is significantly slower than in A, the broadening of the OH signal up to 75°C was too small for obtaining reliable data by means of d-NMR method.

The exchange between pFA and tBA was studied in $C_6D_5NO_2$ and the kinetic parameters are collected in Table 2.

The kinetics of the exchange process depend on the strength of both NH...O and OH...N bonds i.e on the proton donor and electron-donor abilities of aniline. An increase in proton donor ability of the NH group in pFA should result in the increase in rate of proton exchange. The slow proton transfer indicates the important role of electron donor ability of pFA. Smaller degree of self association in pFA when comparing to A (Fig.1) can also confirm that the nitrogen in pFA forms weaker hydrogen bonds that it is in A without fluorine in aromatic ring.

ACKNOWLEDGMENT

The support with a grant MEN-173 from Ministry of National Education is gratefully acknowledged.

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Date Received: 07/25/91
Date Accepted: 09/03/91