The Basicity of 2,3,4,5,6-Pentafluorodiphenylamine. The Use of ^{19}F NMR Chemical Shifts in Protonation Studies

ROLF KOPPANG,[a] CHARLES G. RUSSELL [b] and DONALD G. LEE [b]

[a] Department of Dental Technology, University of Oslo, Geitmyrsveien 69, Oslo, Norway and
[b] Department of Chemistry, University of Regina, Regina, Saskatchewan, S4S 0A2 Canada

The pK_{BH^+} of 2,3,4,5,6-pentafluorodiphenyl-amine, as determined by use of UV spectroscopy in aqueous methanesulfonic acid solutions, is -4.35 ± 0.13. The use of ^{19}F NMR spectroscopy for this purpose was less satisfactory because the chemical shifts appeared to be subject to solvent effects in highly concentrated acid solutions.

A variety of techniques (including both spectrometric and electrochemical methods) have been used to determine the extent of protonation of organic compounds.[1-3] In general, it appears that UV-VIS spectroscopy is the most reliable method for compounds that contain a suitable chromophore. Hence the extent of protonation of almost all aromatic compounds may be determined by this method; however, aliphatic compounds which often lack suitable chromophores may more easily be studied by the use of NMR spectroscopy.[4] In this paper we report on the determination of the basicity of 2,3,4,5,6-pentafluorodiphenylamine (1) by use of UV spectroscopy and describe some interesting results that were obtained when an attempt was made to use ^{19}F NMR spectroscopy for the same purpose.

EXPERIMENTAL

2,3,4,5,6-Pentafluorodiphenylamine. This compound was prepared as previously described.[5]

Methanesulfonic acid solutions. Commercially available methanesulfonic acid was dried over phosphorus pentoxide and vacuum distilled (b.p. 115 – 116 °C/0.07 kPa) under a nitrogen atmosphere.[6] Portions of this acid were then diluted with distilled water and standardized by titration against sodium hydroxide.

Determination of the pK_{BH^+} *value of 2,3,4,5,6-pentafluorodiphenylamine by UV spectroscopy.* 2,3,4,5,6-Pentafluorodiphenylamine (0.136 g) was dissolved in 25.0 ml of acetonitrile. A portion of this solution (16 μl) was transferred to a volumetric flask containing 5.0 ml of standardized methanesulfonic acid. Three ml of the acid solution was then transferred to a 1.00 cm cell which was placed in the thermostated (25.0 °C) cell compartment of a Unicam SP500 spectrophotometer. The maximum absorbance in the region of 260 – 268 nm was recorded and tabulated (Table 1). The wavelength of the

Table 1. Absorbance data for 0.0210 M 2,3,4,5,6-pentafluorodiphenylamine in aqueous solutions of methanesulfonic acid.

Methane-sulfonic acid/wt. %	$-H_0$[a]	Absorbance	log I[b]
49.2	1.96	0.717	
51.1	2.02	0.712	
57.5	2.53	0.706	
60.1	2.72	0.695	
66.0	3.22	0.666	−1.07
69.4	3.54	0.616	−0.74
71.8	3.77	0.568	−0.53
74.5	4.04	0.489	−0.27
76.2	4.16	0.420	−0.08
78.2	4.32	0.341	0.14
80.0	4.53	0.274	0.33
81.8	4.81	0.204	0.57
84.0	5.18	0.147	0.85
89.0	6.13	0.085	
93.2	6.92	0.068	
96.5	7.52	0.068	
98.6	7.74	0.066	

[a] Bascombe, K. N. and Bell, R. P. *J. Chem. Soc.* (1959) 1096. [b] $I = [BH^+]/[B] = (0.717 - \text{Absorbance})/(\text{Absorbance} - 0.066)$.

Table 2. ^{19}F NMR chemical shift data for 2,3,4,5,6-pentafluorodiphenylamine in aqueous solutions of methanesulfonic acid.

Methane-sulfonic acid/wt. %	$-H_0{}^a$	δ meta— δ ortho/ ppm	δ meta— δ para/ ppm	log I
46.2	1.75	13.93	0	
50.0	2.00	13.77	0	
62.4	2.90	13.72	0	
64.6	3.10	13.73	0	
69.7	3.57	13.78	1.36	− 0.77
74.3	4.00	13.26	2.94	− 0.34
76.2	4.16	12.99	4.07	− 0.12
78.2	4.32	12.77	4.88	0.03
80.1	4.52	12.53	5.86	0.22
81.1	4.66	12.42	6.46	0.34
82.9	4.98	12.20	7.21	0.52
84.2	5.20	12.11	7.62	0.63
85.0	5.34	12.00	8.08	0.79
87.5	5.84	11.87	8.51	
90.4	6.40	11.45	8.87	
93.7	7.04	11.68	9.17	
97.0	7.56	11.62	9.24	
101.0	7.92	11.54	9.34	
101.0	7.92	11.51	9.30	

 [a] Bascombe, K. N. and Bell, R. P. *J. Chem. Soc.* (1959) 1096.

maximum found at 268 nm in 50 % methanesulfonic acid decreased with increasing acid concentration until it was 260 nm in 98 % methanesulfonic acid.

Attempted use of ^{19}F NMR for studying the basicity of 2,3,4,5,6-pentafluorodiphenylamine. A stock solution of *1* in dimethyl sulfoxi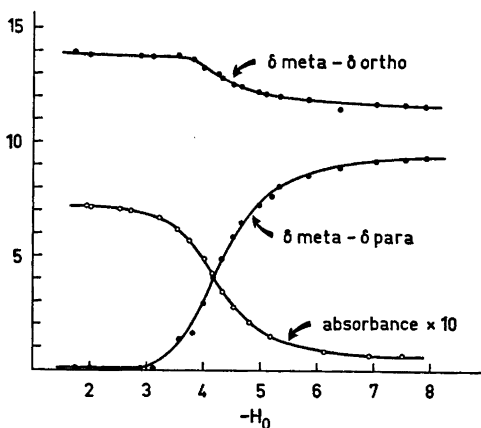de (DMSO) was prepared. Twenty μl of the solution was added to 1.0 ml of standardized methanesulfonic acid and the ^{19}F spectrum obtained using a BRUKER HX-90 NMR spectrometer. Since we were interested only in the relative differences in chemical shifts, no internal standard was added. Instead the chemical shifts of the *ortho-* and *para-*fluorines were measured relative to those of the *meta-*fluorines. The results presented in Table 2 were obtained.

RESULTS

The results obtained are summarized in Tables 1 and 2. That the observed changes correspond to a protonation reaction can be seen from the sigmoidal curves found in Fig. 1. The inflection points for all of these curves are at about − 4.4 thus confirming that the changes in the ultraviolet spectrum and in the chemical shifts are likely due to the same cause.

DISCUSSION

Determination of the basicity of 1. The protonation of a weak organic base may be described in terms of eqns. (1) and (2) where log $I =$ log ([BH$^+$]/[B]) and H_x is an acidity function

$$\text{BH}^+ \xrightleftharpoons{K_{\text{BH}^+}} \text{B} + \text{H}^+ \qquad (1)$$

$$\text{p}K_{\text{BH}^+} = H_x + \log I \qquad (2)$$

that is appropriate for the base under investigation.[3] The applicability of a particular acidity function is most easily evaluated by plotting log I *vs.* $-H_x$; the observance of a linear plot of near unit slope may be taken as an indication that a satisfactory function has been found. In the case of *1* the H_0 acidity function appears to be quite satisfactory (see Fig. 2). This is not surprising since the H_0 function was developed by use of aromatic amine indicators[7] and subsequent work has shown that substituted diphenylamines conform to this function in their protonation behaviour.[8] Furthermore, Yates and Shapiro[9] have shown that the function is also applicable to fluorinated anilines.

The pK_{BH^+} value obtained from a statistical analysis of the plot presented in Fig. 2 is − 4.35 ± 0.13. Such a result is not unreasonable when comparison is made with the basicities of other diphenylamines.[8]
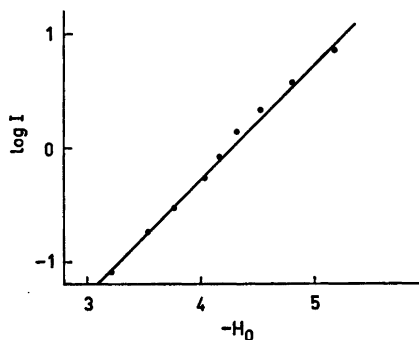

Fig. 1. Titration curves for the protonation of *1* in methanesulfonic acid.

Fig. 2. Plot of log I vs. $-H_0$ based on ultra-violet measurements. Slope = 1.02 ± 0.03. Intercept = 4.43 ± 0.13.

Table 3. Comparison of pK_{BH^+} values of substituted anilines and the corresponding diphenylamines.

Substituent	Aniline	Diphenyl-amine	Difference
4-Methyl	5.08 [a]	1.20 [c]	3.88
4-Methoxy	5.34 [a]	1.36 [c]	3.98
3-Methoxy	4.23 [a]	0.40 [c]	3.83
None	4.63 [a]	0.78 [c]	3.85
3-Chloro	3.46 [a]	−0.45 [c]	3.91
4-Chloro	4.15 [c]	0.01 [c]	4.14
3-Nitro	2.50 [e]	−1.61 [c]	4.11
4-Nitro	1.02 [e]	−3.13 [c]	4.12
2-Nitro	−0.29 [e]	−4.12 [c]	3.83
Pentafluoro-	−0.36 [b]	−4.35 [d]	3.99
		Average	3.96 ± 0.12

[a] *Handbook of Chemistry and Physics*, Forty-ninth Ed., The Chemical Rubber Publishing Co., Cleveland 1969, p. D-87. [b] Yates, K. and Shapiro, S. A. *Can. J. Chem. 50* (1972) 581. [c] Dolman, D. and Stewart, R. *Can. J. Chem. 45* (1967) 903. [d] This work. [e] Bascombe, K. N. and Bell, R. P. *J. Chem. Soc.* (1959) 1096.

Further evidence for the reliability of this result comes from a consideration of the differences in basicities between substituted anilines and the corresponding substituted diphenylamines. As the data presented in Table 3 indicate the diphenylamines are approximately 4 units less basic; *i.e.*, introduction of a phenyl group decreases the pK_{BH^+} values by about 4 acidity units. Since the pK_{BH^+} of pentafluoroaniline is known [9] to be -0.36 ± 0.02 it is consistent to find that the value for 2,3,4,5,6-pentafluorodiphenylamine is -4.35 ± 0.13. Consequently it appears as if this result may be accepted with considerable confidence.

The use of ^{19}F NMR spectroscopy for basicity determinations. Several examples are known where both ^1H [4] and ^{13}C NMR spectroscopy [10] have been used for basicity measurements. In order to further expose the use of this potentially important technique the ^{19}F NMR spectra of *1* in various methanesulfonic acid solutions have been examined and an attempt has been made to use the chemical shifts for basicity measurements.

In order to minimize solvent effects on the chemical shifts no internal standard was used. Instead the chemical shifts of the *ortho-* and *para*-fluorines were compared with those for the *meta*-fluorines (Table 1). This method rests on the assumption that the chemical shifts of

different fluorines will be affected differently by protonation and that these variations can be taken as a measure of the extent of protonation. Since all of the atoms in a simple molecule will be in approximately the same environment macroscopic solvent effects on the chemical shifts should be minimized.

All of the fluorine atoms would be expected to exert a substantive electron acceptor polar effect (I), thus accounting for the observed decrease in basicity.[11] However, as indicated by eqn. (3), some of the fluorines could also exert an electron donor π delocalization effect (R) which would stabilize the positive charge on the conjugate acid and thus tend to increase the basicity of these compounds. Pushkina, Stepanov, Zhukov and Naumov [12] have developed correlation equations between fluorine shifts and the Taft [13] constants for *ortho-*, *para-* and *meta*-fluorines in pentafluorophenyl amines (eqns. 4 – 6). Similar correlations have also been observed by other workers.[14]
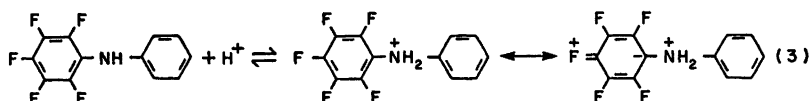
$$\delta(ortho) = 73.82\sigma_I - 24.35\sigma_R^\circ - 177.63 \qquad (4)$$

$$\delta(meta) = 17.51\sigma_I - 4.73\sigma_R^\circ - 169.66 \qquad (5)$$

$$\delta(para) = 86.65\sigma_I - 22.30\sigma_R^\circ - 189.89 \qquad (6)$$

The fact that the coefficient for σ_R° is much greater in eqn. (6) than in eqn. (5) indicates that the π delocalization effect is more pronounced for the *para*- than the *meta*-substituents. The correlation coefficient for eqn. (4) was unsatisfactory probably because the *ortho*-position is subject to large steric effects.[12] Consequently the differences between the chemical shifts of the *para*- and the *meta*-fluorines were used in this study.

Examination of the spectra indicated that the *para*-fluorines did indeed shift relative to the *meta*-fluorines as the compound underwent protonation (Table 2, Fig. 1). It was then possible to calculate values of log I as has been done with proton spectra [4] (log $I = [BH^+]/[B] = (\Delta - \Delta_B)/(\Delta_{BH^+} - \Delta)$ where Δ_B is the chemical shift difference between the *meta*- and *para*-fluorines of the unprotonated amine, Δ_{BH^+} is the difference between the chemical shifts of the same fluorines in the completely protonated amine, and Δ the corresponding value when the amine is partially protonated.

A plot of log I vs. $-H_0$ (Fig. 3) proved to be linear with an approximately unit slope up to about 85 % methanesulfonic acid, whereupon it began to exhibit a definite curvature. Nevertheless the intercept (which fell on the linear portion of the curve) gave an accurate estimate of the pK_{BH^+} value (-4.45 ± 0.11).

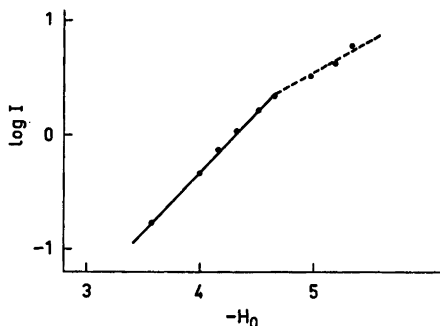The curvature of the plot in Fig. 3 begins at a point where the mol ratio of methane-

sulfonic acid to water is approximately unity. This suggests that the change in slope at higher acidities may be connected with a decrease in the amount of water available for solvation (assuming that each molecule of acid is strongly solvated by one molecule of water as long as sufficient solvent is available). The change in slope of Fig. 3 may thus be associated with a loss of hydrogen bonding to the *meta*-fluorines as the amount of available water decreases. Alternatively it is possible that at lower acidities the *para*-fluorine is solvated extensively by water (as in *2*) which would not

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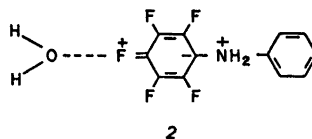
be available at higher acidities. Solvation would then be absent or by methanesulfonic acid as in *3*. Such a change in solvation would likely

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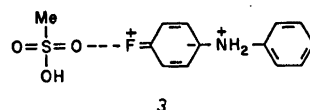
affect the ^{19}F chemical shifts and could be an explanation for the non-linearity of the plot in Fig. 3.

In summary it has been found that (1) the pK_{BH^+} value for 2,3,4,5,6-pentafluorodiphenylamine is -4.35 ± 0.13, (2) the H_0 acidity function adequately describes the protonation behaviour of 2,3,4,5,6-pentafluorodiphenylamine and (3) ^{19}F NMR chemical shifts, while providing a good estimate of the pK_{BH^+} value, are apparently sensitive to solvation effects.

Fig. 3. Plot of log I vs. $-H_0$ based on ^{19}F NMR measurements.

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