Interactions of 1,8-Bis(dimethylamino)naphthalene with Pentafluorobenzoic Acid in [$^2H_3$]Acetonitrile

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FTIR and ^{1}H, ^{13}C and ^{19}F NMR spectroscopic studies on 1,8-bis(dimethylamino)naphthalene mixtures (1 : 1 and 1 : 2) with pentafluorobenzoic acid and FTIR studies of 1,8-bis(dimethylamino)-naphthalene mixtures (1 : 1 and 1 : 2) with 2,3,5,6-tetrafluorobenzoic acid in acetonitrile have been performed. It was shown that 1,8-bis(dimethylamino)naphthalene with two molecules of acid forms homoconjugated anions and protonated 1,8-bis(dimethylamino)naphthalene. In the case of a 1 : 1 mixture of 1,8-bis(dimethylamino)naphthalene with pentafluorobenzoic acid, decarboxylation of the acid is observed at room temperature.

1,8-Bis(dimethylamino)naphthalene (DMAN) is one of the strongest organic bases ($pK_a = 12.34$)[1] and can be treated as a model for a proton sponge. In the case of DMAN salts (DMANH$^+$) in the solid state a very short intramolecular hydrogen bond (NHN$^+$) is formed.[2,3] The same type of hydrogen bond is also formed in solution. However, deprotonation of DMANH$^+$ and formation of homoconjugated anions has been observed in the presence of some anions such as NCS$^-$ and NO$_3$$^-$.[4–6]

It has recently been shown that protonation of DMAN by various phenols and carboxylic acids in polar solvents proceeds mainly with two molecules of acid which yield DMANH$^+$ and homoconjugated anions.[7] In an acetonitrile solution of a 1:1 mixture of DMAN with phenol or a carboxylic acid a competition between DMANH$^+$ and the acid anion as a proton acceptor occurs. Consequently, a mixture of protonated DMAN (DMANH$^+$), free DMAN, homoconjugated anions and more complicated species is observed.[7] The same effects are observed for mixtures of DMAN with mono-, di-, tri- and tetrafluorobenzoic acids.[8]

A mixture of DMAN with pentafluorobenzoic acid (PFBCOOH) behaves quite differently. Only a very small amount of protonated DMAN is detected in FTIR spectra immediately after mixing the components. Moreover, a decrease in the intensity of the carbonyl band is observed. This surprising observation is not readily explained since PFBCOOH is a strong acid ($pK_a = 1.75$)[9] and decarboxylation of this acid occurs only at high temperatures.[10–13] In order to elucidate the reason for this effect we have undertaken more detailed studies of this mixture by means of ^{1}H, ^{13}C and ^{19}F NMR spectroscopy as well as FTIR spectroscopy.

Experimental

Mixtures of 1,8-bis(dimethylamino)naphthalene (DMAN) with pentafluorobenzoic (PFBCOOH) and 2,3,5,6-tetrafluorobenzoic (TFBCOOH) acids were obtained by mixing a 0.5 mol dm^{-3} solution of the base in [$^2H_3$]acetonitrile with a 0.5 mol dm^{-3} solution of the acid in the same solvent to give the stoichiometry desired.

IR spectra were recorded in [$^2H_3$]acetonitrile solution (0.1 mol dm^{-3}). The solvent was dried over 3 Å molecular sieves. A cell with Si windows and a wedge-shaped layer to avoid interference (mean layer thickness 0.25 mm) was used. The spectra were taken with a Bruker FTIR spectrophotometer IFS 113v at 298 K.

^{1}H NMR spectra were recorded at 298 K at 200 MHz with a Varian XL-200 spectrometer using Me$_4$Si as an internal standard.

^{19}F NMR spectra were recorded by using a Varian XL-200 spectrometer at 188.15 MHz at 298 K with CFCl$_3$ as an internal standard.

^{13}C NMR spectra were recorded at 298 K on a Varian XL-200 spectrometer at 50.32 MHz with full proton decoupling. The spectral window was 10 000 Hz with 32 K data giving a digital resolution of 0.6 Hz per point. The pulse width of 3.3 μs (90°) was used with 0.970 s acquisition time. The number of accumulations varied from 500 to 600 per spectrum.

Results and Discussion

The ^{1}H, ^{13}C and ^{19}F chemical shifts of 1,8-bis(dimethylamino)naphthalene (DMAN) and its mixtures with pentafluorobenzoic acid (PFBCOOH) are given in Tables 1–3, respectively. The protonation of DMAN is manifested in ^{1}H NMR spectra by a signal due to the intramolecularly hydrogen-bonded proton (NHN)$^+$ at *ca.* 18.60 ppm. We have recently shown that the chemical shift of intramolecularly hydrogen-bonded proton in protonated DMAN is not influenced by the nature of the anion used.[6] Hence, we expected the signal of the (NHN)$^+$ proton in the 1:1 mixture of DMAN with pentafluorobenzoic acid to appear in this region. In actual fact, no signal for the intramolecularly hydrogen-bonded proton was detected in the spectrum. On the other hand, the ^{1}H NMR spectrum of the 1:2 mixture of DMAN with PFBCOOH displayed a signal at 18.56 ppm. Traces of water caused this peak to split, one of the signals remaining almost unchanged at 18.70 ppm and the other appearing at *ca.* 16 ppm. It suggests that the peak at 18.56 ppm consists of two signals which correspond to both intramolecular and intermolecular hydrogen-bonded protons in (NHN)$^+$ and (OHO)$^-$ bridges, respectively. The intermolecular (OHO)$^-$ hydrogen bond is much more sensitive to water than that of the intramolecular (NHN)$^+$ one. Therefore, the signal of the (OHO)$^-$ protons shifts to higher fields in wet samples, while that of (NHN)$^+$ remains at almost the same field. This result suggests that the 1:2 mixture of DMAN with PFBCOOH in acetonitrile solution has the structure DMANH$^+$ + (PFBCOO $\cdots$ HOOCBFP)$^-$.

The protonation of DMAN influences the charge distribution in the naphthalene ring and this in turn affects the ^{1}H and ^{13}C NMR chemical shifts. In the case of a 1:1 mixture of DMAN with PFBCOOH the ^{1}H and ^{13}C chemical shifts of ring protons and carbon atoms are comparable to those of free DMAN (Tables 1 and 2). This demonstrates that no protonation of

DMAN occurs in such a mixture. Moreover, no carbonyl carbon atom signal was detected in the ^{13}C NMR spectrum of a 1:1 mixture of DMAN and PFBCOOH. PFBCOOH displays the carbonyl carbon atom signal at 160.13 ppm, whereas an acidic salt of PFBCOOH shows this signal at 161.13 ppm. The above data clearly suggest that PFBCOOH undergoes a decarboxylation in the 1:1 mixture with DMAN giving pentafluorobenzene (PFB). As can be seen from Table 3, the ^{19}F chemical shifts of pentafluorobenzene (PFB) are closely related to those obtained for the 1:1 mixture of DMAN and PFBCOOH.

In order to confirm the decarboxylation process of PFBCOOH in the 1:1 mixture of DMAN and PFBCOOH the acetonitrile solution of this mixture was evaporated under reduced pressure (0.1 mm Hg; 298 K) and the residue was again dissolved in [$^2H_3$] acetonitrile. The ^1H and ^{13}C NMR spectra of this sample were exactly the same as those of pure DMAN and no fluorine atoms were detected by ^{19}F NMR.

More information about the interactions of DMAN with PFBCOOH has been obtained from FTIR studies. Fig. 1(*a*) shows the spectra of PFBCOOH and its mixtures with DMAN in [$^2H_3$]acetonitrile solution. For comparison the spectra of 2,3,5,6-tetrafluorobenzoic acid (TFBCOOH) and its mixtures with DMAN in [$^2H_3$]acetonitrile solution are given in Fig. 1(*b*). The spectrum of [$^2H_3$]acetonitrile solution of free DMAN (Fig. 1, •–•–•–) displays three intense bands at 2780, 2831 and 2869 cm^{-1} (so called Bohlmann bands) indicating a lone electron pair on the nitrogen atom.[14,15] In the 1:1 mixture of DMAN and TFBCOOH [Fig. 1(*b*), ——] the intensity of these bands diminishes, demonstrating the protonation of the nitrogen atom of DMAN. However, in this mixture DMAN is only partially protonated. In the case of the 1:2 mixture the protonation of DMAN is complete. In the spectra of 1:1 and 1:2 mixtures of DMAN and TFBCOOH neither ν_{OH} nor $\nu_{C=O}$ stretching vibrations are found; those bands are observed for free acid at 3150 and 1745 cm^{-1}, respectively [Fig. 1(*b*), – – –]. Instead of this ν_{OH} band an intense continuum below 2500 cm^{-1} appears. Superimposed upon this continuum in the absorption of two species, *i.e.* $(NHN)^+$ and $(OHO)^-$, discussed earlier.[7,16,17] Furthermore, the shift of the $\nu_{C=O}$ band from 1745 cm^{-1} for free acid to 1690 cm^{-1} in both 1:1 and 1:2 mixtures demonstrates the formation of homoconjugated $(COOH\cdots OOC)^-$ anions. The above results suggest the following equilibria occurring in acetonitrile for 1:1 mixture [eqn. (1)] and for the 1:2 mixture [eqn. (2)].

$$2\text{DMAN} + 2\text{TFBCOOH} \rightleftharpoons \text{DMAN} + \text{DMANH}^+ + (\text{TFBCOOH}\cdots\text{OOCTFB})^- \quad (1)$$

$$\text{DMAN} + 2\text{TFBCOOH} \rightleftharpoons \text{DMANH}^+ + (\text{TFBCOOH}\cdots\text{OOCTFB})^- \quad (2)$$

The FTIR spectrum of a 1:2 mixture of DMAN and PFBCOOH [Fig. 1(*a*), •–•–•–] is essentially similar to that of DMAN–TFBCOOH (1:2) [Fig. 1(*b*), •–•–•–]. Hence, the interactions between DMAN and PFBCOOH in this mixture can be described by eqn. (2). In contrast with the spectrum of the 1:2 mixture of DMAN and PFBCOOH, the spectrum of the 1:1 mixture [Fig. 1(*a*), ——] is completely different from that with TFBCOOH [Fig. 1(*b*), ——]. The intensity of the Bohlmann bands in the spectrum of 1:1 mixture of DMAN and PFBCOOH is only slightly weaker in comparison with the spectrum of free DMAN indicating a very limited degree of protonation. This spectrum displays neither ν_{OH} nor $\nu_{C=O}$ stretching vibration bands. The continuous absorption below 2800 cm^{-1} is also not observed. However, a very characteristic band at 2338 cm^{-1} which is attributed to asymmetric stretching vibrations of carbon dioxide appears in the spectrum. The same band is observed in the FTIR spectrum of acetonitrile saturated with CO_2.[8] The above data suggest that the interactions between DMAN and PFBCOOH in a 1:1 mixture in acetonitrile can be described by Scheme 1. It is well known that proton transfer reactions are very fast.[18] Hence, one can think that proton transfer from PFBCOOH to DMAN occurs in the first step almost quantitatively to give the protonated $DMANH^+$ and free pentafluorobenzoate anion ($PFBCOO^-$). This free anion, as a weaker proton acceptor than tetra-

$$\begin{array}{l} \text{DMAN} + \text{PFBCOOH} \longrightarrow \text{DMANH}^+ + \text{PFBCOO}^- \longrightarrow \\ \qquad\qquad\qquad\qquad\qquad \text{DMANH}^+ + \text{PFB}^- + \text{CO}_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad \text{DMAN} + \text{PFB} + \text{CO}_2 \end{array}$$

Scheme 1

Table 1 ^1H NMR Chemical shifts (ppm) of 1,8-bis(dimethylamino)naphthalene (DMAN) and its mixtures with acids in [$^2H_3$]acetonitrile

Compound	2,7-H	3,6-H	4,5-H	CH_3	$(NHN)^+$
DMAN[a]	6.93	7.25	7.32	2.75	—
DMAN•HCl[a]	8.04	7.70	7.90	3.12, 3.13	18.68
DMAN + PFBCOOH (1:1)	6.95	7.26	7.33	2.75	—
DMAN + PFBCOOH (1:2)	8.03	7.71	7.90	3.12, 3.13	18.56

[a] Ref. 6.

Table 3 ^{19}F Chemical shifts (ppm) of pentafluorobenzene (PFB), pentafluorobenzoic acid (PFBCOOH) and its mixtures with 1,8-bis(dimethylamino)naphthalene in [$^2H_3$]acetonitrile

Compound	F-2,6	F-3,5	F-4
PFB[a]	138.7	162.6	154.3
PFBCOOH[a]	139.2	161.9	150.9
DMAN + PFBCOOH (1:1)	139.4	162.9	155.0
DMAN + PFBCOOH (1:2)	142.0	162.6	155.5

[a] In benzene; ref. 19.

Table 2 ^{13}C Chemical shifts (ppm) of 1,8-bis(dimethylamino)naphthalene (DMAN) and its mixtures with acids in [$^2H_3$]acetonitrile

Compound	C-1	C-2	C-3	C-4	C-9	C-10	CH_3
DMAN[a]	151.3	113.5	126.0	122.5	121.4	138.7	44.6
DMAN•HCl[a]	145.3	122.5	130.2	128.0	120.2	136.4	46.7
DMAN + PFBCOOH (1:1)	151.7	113.7	126.5	122.4	121.3	138.8	44.7
DMAN + PFBCOOH (1:2)	144.5	121.8	129.9	128.2	119.9	136.2	46.8

[a] Ref. 6

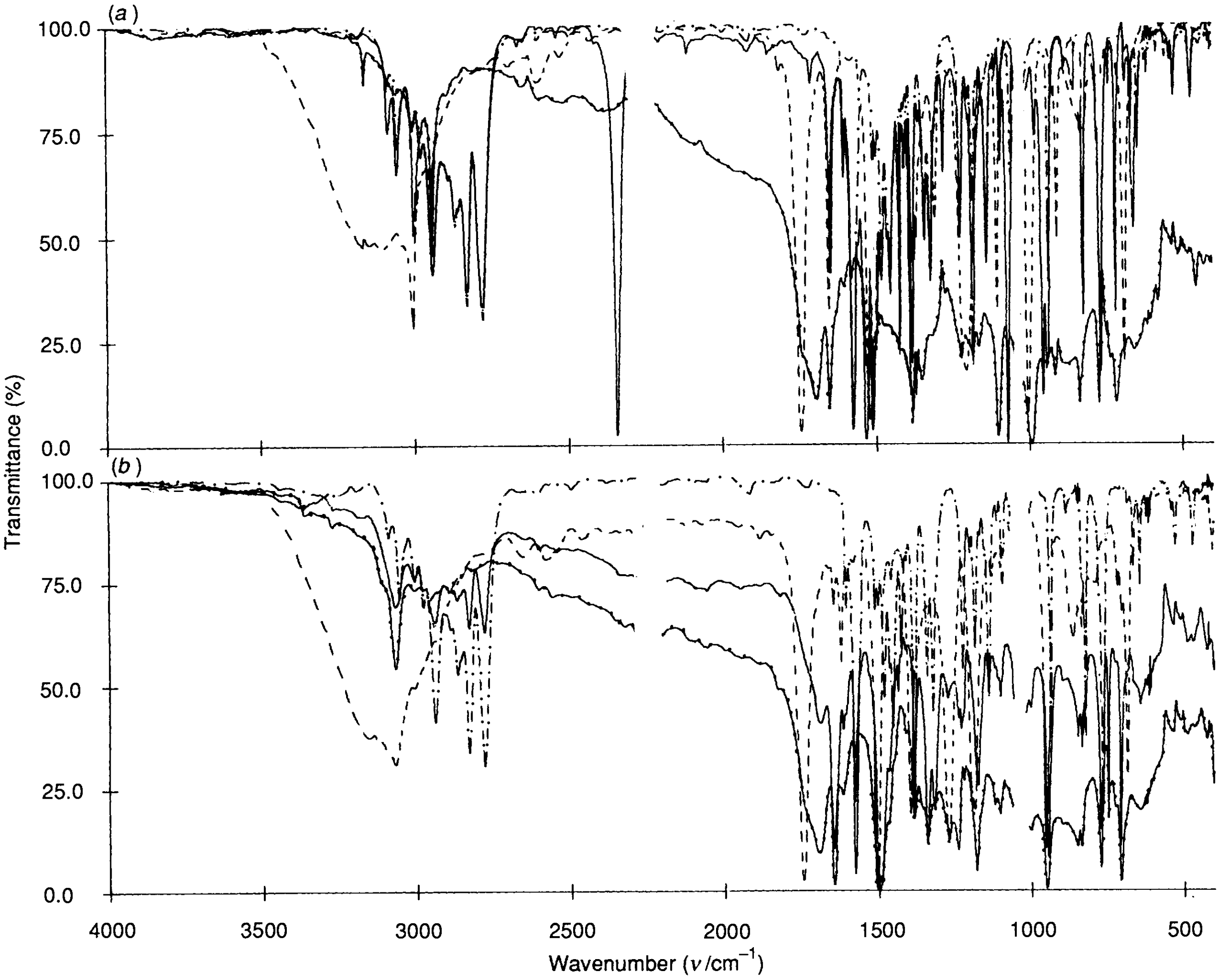

Fig. 1 IR spectra of: DMAN (-•-•-•); DMAN and acid (1:1) (——); DMAN and acid (1:2) (•-•-•-) and acid (- - - -); (*a*) pentafluorobenzoic acid (PFBCOOH), (*b*) tetrafluorobenzoic acid (TFBCOOH).

fluorobenzoate anion, cannot form homoconjugated anions because of the absence of an excess of free acid in a 1:1 mixture of DMAN and PFBCOOH and thus it undergoes decarboxylation. The same effects were observed for 1:1 mixtures of DMAN and PFBCOOH in [^{2}H] chloroform and [$^2H_6$]-DMSO.[8] In the case of a 1:2 mixture of DMAN and PFBCOOH the formed anion (PFBCOO$^-$) is immediately stabilized by excess of free acid to yield the stable homoconjugated anion (PFBCOO••• HOOCPFB)$^-$.

All the results taken together suggest that the pentafluorobenzoate anion cannot exist as a free anion in aprotic solvents.

References

1 D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution*, Butterworth, London, 1965; R. L. Benoit, D. Lefevre and M. Frequette, *Can. J. Chem.*, 1987, **65**, 996.
2 Z. Malarski, L. Sobczyk and E. Grech, *J. Mol. Struct.*, 1988, **177**, 339.
3 D. Pyżalska, R. Pyżalski and T. Borowiak, *J. Cryst. Spectrosc. Res.*, 1983, **13**, 211.
4 Z. Pawełka and Th. Zeegers-Huyskens, *J. Mol. Struct.*, 1989, **200**, 565.
5 B. Brzezinski, E. Grech, Z. Malarski and L. Sobczyk, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1777.
6 B. Brycki, B. Brzezinski, E. Grech, Z. Malarski and L. Sobczyk, *Magn. Reson. Chem.*, in press.
7 B. Brzezinski, E. Grech, Z. Malarski and L. Sobczyk, *J. Chem. Soc., Perkin Trans. 2*, in press, paper 1/00943E.
8 B. Brzezinski, B. Brycki and J. Olejnik, unpublished results.
9 G. Kortüm, W. Vogel and K. Andrussov, *Dissociation Constants of Organic Acids in Aqueous Solution*, Butterworth, London, 1961; E. P. Searjeant and B. Dempsey, *Ionisation Constants of Organic Acids in Aqueous Solution*, Pergamon Press, Oxford, 1979.
10 J. Burdon, W. B. Hollyhead and J. L. Tatlow, *J. Chem. Soc.*, 1965, 6336.
11 A. K. Pietrov, B. V. Makarov and G. G. Jakobson, *Dokl. Akad. Nauk SSSR*, 1968, **179**, 356.
12 A. Cairncross, J. R. Roland, R. M. Henderson and W. A. Sheppard, *J. Am. Chem. Soc.*, 1970, **92**, 3187.
13 G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 1973, **38**, 2682.
14 F. Bohlmann, *Chem. Ber.*, 1958, **91**, 2157.
15 J. Skolik, P. J. Kraeger and M. Wiewiórowski, *Tetrahedron*, 1968, **24**, 5439.
16 D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.
17 Z. Novak, *Structure and Bonding*, 1974, **18**, 180.
18 R. B. Martin, *J. Am. Chem. Soc.*, 1962, **84**, 4130.
19 A. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.*, 1969, **91**, 283.

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