Protonation of 1,8-Bis(dimethylamino)naphthalene by Various Acids in Acetonitrile

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FTIR studies on a number of systems composed of 1,8-bis(dimethylamino)naphthalene (DMAN) and various organic acids (phenols, benzoic acid derivatives and dicarboxylic acids) were carried out. The degree of protonation was estimated based on the intensity of the Bohlmann bands. In the ionic equilibria the homoconjugated anions play an essential role so that the degree of protonation depends on the excess of acid. The 1:1 complexes of phenols and benzoic acids in acetonitrile form a mixture of protonated DMAN, free DMAN, homoconjugated anions and more complicated species. The broad absorption extending over the whole IR region results from the combination of bands ascribed to $\nu(NHN^+)$ of protonated DMAN and $\nu(OHO^-)$ of homoconjugated anions.

Quite recently it was shown[1,2] that protonation of the proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) by phenols in polar solvents proceeds mainly with the participation of two phenol molecules forming homoconjugated anions. There is competition between DMAN molecules and phenolate anions as proton acceptors. The formation constant for 2:1 complexes is one order of magnitude higher than that for 1:1 complexes.[1] Even in the case of such a strong proton donor as pentachlorophenol both in acetonitrile and in 1,2-dichloroethane the protonation takes place only to a limited extent if no excess of phenol is used for binding the phenolate anion into a homoconjugated species. These results seemed to be unexpected, taking into account that DMAN is one of the strongest bases (pK_a 12.34,[3] proton affinity in the gas phase *PA* 242 kcal mol^{-1}).[4],† It was also shown that intensity of the Bohlmann bands ascribed to the C–H stretching vibrations of methyl groups in a *trans* position to the lone electron pair of the nitrogen atom can be used for the estimation of the degree of protonation.[5–7] The attachment of one proton to the DMAN molecule causes complete disappearance of these bands.

In the present report we give the results of the protonation of DMAN for a broader selection of organic acids including weak and strong phenols, benzoic acid derivatives and dicarboxylic acids.

Table 1 Percentage of protonation of DMAN

Acid	pK_a,[a]	1:1 Salt	2:1 Salt
Phenols			
Phenol	9.99	0.4	4.7
4-Bromophenol	9.37	1.3	13.8
4-Nitrophenol	7.16	36	72
3,4-Dinitrophenol	5.42	49	98
Pentachlorophenol	5.26	50	99
2,4-Dinitrophenol	4.07	100	100
2,4,6-Trinitrophenol	0.33	100	*b*
Benzoic acids			
4-Methoxybenzoic	4.52	26	52
4-Butylbenzoic	4.34	29	55
4-Fluorobenzoic	4.14	34	61
4-Bromobenzoic	3.96	35	65
Pentafluorobenzoic	1.75	*c*	100
Dicarboxylic acids[d]			
2,3-Dimethylsuccinic	3.77	82	*b*
Dimethylmalonic	3.16	92	*b*
Phthalic	2.76	100	*b*
Maleic	1.89	100	*b*

[a] Ref. 8. [b] The 2:1 complex is not formed. [c] Decarboxylation. [d] The pK_1-values.

Experimental

The complexes of DMAN with carboxylic acids and phenols were obtained from 0.5 mol dm^{-3} acetonitrile solutions of the base and 0.5 mol dm^{-3} acetonitrile solutions of the acids in the stoichiometry desired.

The IR spectra were recorded in acetonitrile solutions (0.1 mol dm^{-3}). The solvent was purified by standard procedures and was dried over a 3 Å molecular sieve. A cell with Si windows and a wedge-shaped layer to avoid interference (mean layer thickness 0.4 mm) was used. The spectra were taken with a Bruker FTIR spectrophotometer IFS 113v.

Results and Discussion

The list of investigated salts is presented in Table 1. The first group consists of phenols with pK_a-values in the range 9.99 (for phenol) to 0.33 (for picric acid). The last one is such a strong acid that the salt of composition 1:1 is present in acetonitrile in the form of fully protonated DMAN and simple picrate anions. The steric hindrance makes the formation of homoconjugated anions impossible, so that the salt of 2:1 ratio is not formed at all. Weaker proton donors, such as 2,4-dinitrophenol, form, apart from the 1:1 complex, the 2:1 one. In both cases full dissociation and formation of protonated DMAN take place. The presence of one nitro group in the *ortho* position is not a sufficient obstacle for the formation of the homoconjugated anion. In the spectrum of DMAN itself [curve (i) in Fig. 1], which serves as a reference, there are seen intense Bohlmann bands below 2850 cm^{-1}. As a reference the spectrum of tetrabutylammonium bis-3,4-dinitrophenolate was also used [curve (ii)]. As can be seen the homoconjugated bisphenolate anion is characterized in the fingerprint region by an intense, broad absorption which is extended to higher wavenumber (up to 3000 cm^{-1}). Phenol itself in acetonitrile behaves typically, *i.e.*

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† 1 cal = 4.184 J.

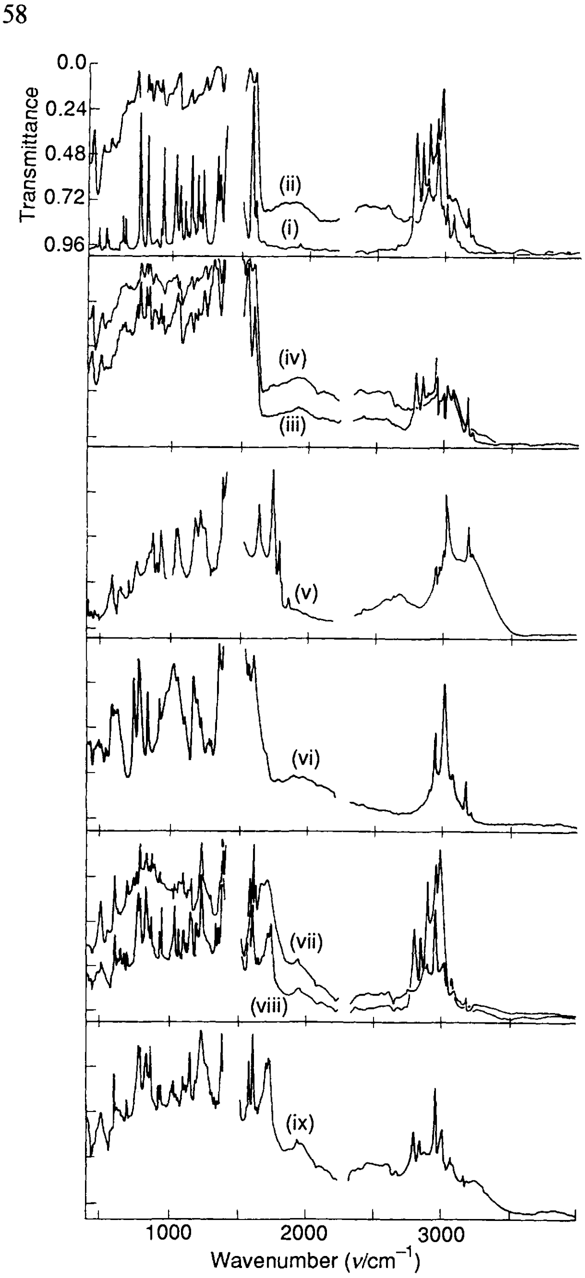


Fig. 1 FTIR spectra of DMAN–acid systems in acetonitrile: (i) DMAN, (ii) tetrabutylammonium bis-3,4-dinitrophenolate, (iii) 3,4-dinitrophenol–DMAN (1:1), (iv) 3,4-dinitrophenol–DMAN (2:1), (v) maleic acid, (vi) phthalic acid–DMAN (1:1), (vii) tetrabutylammonium bis-4-fluorobenzoate, (viii) 4-fluorobenzoic acid–DMAN (1:1), (ix) 4-fluorobenzoic acid–DMAN (2:1)

binding of the OH group *via* hydrogen bonds with C≡N groups of the solvent takes place. The broad, intense band of the ν(OH) stretching vibration is localized at ~3250 cm^{-1}.

In the case of the 1:1 3,4-dinitrophenol–DMAN salt we find that the degree of protonation equals ~50% of that deduced from the intensity of the Bohlmann bands [see curve (iii)]. In addition, we did not observe free OH groups. On the other hand a broad absorption characteristic of homoconjugated OHO$^-$ anions appeared. The intensity of the broad absorption is about a half that for tetrabutylammonium bisphenolate. We can thus conclude that the following equilibria [eqns. (1) and (2)] occur.

$$\mathrm{DMAN} + \varphi\mathrm{OH} \rightleftharpoons \mathrm{DMAN{\cdot}H^+} + \varphi\mathrm{O^-} \quad (1)$$

$$2(\mathrm{DMAN{\cdot}H^+}\ \varphi\mathrm{O^-}) \rightleftharpoons \mathrm{DMAN} + \mathrm{DMAN{\cdot}H^+} + [\varphi\mathrm{O}\cdots\mathrm{H}\cdots\mathrm{O}\varphi]^- \quad (2)$$

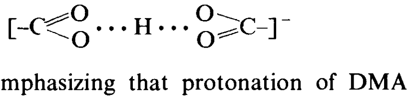
In the case of the 2:1 salt of 3,4-dinitrophenol with DMAN the Bohlmann bands almost completely vanish [curve (iv)] and the intensity of the broad protonic absorption increases by >100%. One should remember that following from studies of protonated DMAN in acetonitrile,[2] DMAN·H$^+$ contributes considerably to the broad absorption. We have confirmed such a contribution in this study by means of differential spectra of the 2:1 salt with DMAN and the corresponding tetrabutylammonium salt.

The situation is simpler in the case of protonation of DMAN by means of the dicarboxylic acids listed in Table 1. The detachment of one proton leads to the formation of stable intramolecular OHO$^-$ hydrogen bonds so that, in acetonitrile, dicarboxylic acids form only 1:1 salts with DMAN. Maleic acid is a very strong acid so that it partly dissociates in acetonitrile, as evidenced by a broad absorption [curve (v)] in the fingerprint region characteristic of intramolecular OHO$^-$ bridges. This absorption coincides with that of tetrabutylammonium maleate. In addition, however, there appears an absorption at >1800 cm^{-1} typical of homoconjugated cations. Presumably the dissociation is accompanied by the formation of self-solvated species **I**.

$$[\mathrm{MeC{\equiv}N\cdots H\cdots N{\equiv}CMe}]^+ \qquad \mathbf{I}$$

The protonation of DMAN by means of dicarboxylic acids is illustrated by taking phthalic acid as an example [curve (vi)]. The DMAN salt is completely dissociated to DMAN·H$^+$ cation and phthalate anion. The broad absorption (continuum) is formed by addition of the absorptions of two such species. It is visible both in the low wavenumber (<700 cm^{-1}) and high wavenumber (>1700 cm^{-1}) regions. The behaviour of phthalic acid is almost identical with that of maleic acid, although the first acid is a weaker proton donor. It is worthy of note that phthalic acid itself does not show any ionic dissociation in acetonitrile. The OH$^-$ stretching vibration band is located at higher wavenumber and is narrower and less intense than that of maleic acid. In the case of dimethylmalonic and dimethylsuccinic acids the protonation of DMAN is not complete.

For systems composed of benzoic acid derivatives (except pentafluorobenzoic acid) the protonation is considerably reduced, both for 1:1 and 2:1 adducts. Comparison of spectra of the 1:1 [curve (viii)] and 2:1 [curve (ix)] salts of 4-fluorobenzoic acid with the reference spectrum [curve (vii)] for tetrabutylammonium bis-4-fluorobenzoate shows clearly that the protonation proceeds *via* formation of homoconjugated anions[9] such as **II**.



$$\left[-\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O}}\cdots\mathrm{H}\cdots\genfrac{}{}{0pt}{}{\mathrm{O}\searrow}{\mathrm{O}\nearrow}\mathrm{C}-\right]^-$$

II

It is worth emphasizing that protonation of DMAN by carboxylic acids in acetonitrile is much harder than that by phenols of the same pK_a-values. It is also interesting to note that both for the 1:1 and 2:1 systems with carboxylic acids no free OH band is observed at 3250 cm^{-1}. Presumably this band is caused by the formation of carboxylate anions containing more than two molecules of the acid.

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