^1H and ^{13}C NMR and FT-IR studies of the interaction between 1,8-bis(dimethylamino)naphthalene and 3,5-dichlorophenol

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The ^1H and ^{13}C NMR spectra of the complex between 1,8-bis(dimethylamino)naphthalene and 3,5-dichlorophenol have been studied at temperatures between 30 °C and −70 °C in CD_2Cl_2 and at different acid to base concentration ratios. At a temperature of −60 °C a splitting of the ^1H and ^{13}C signals of DMAN and $DMANH^+$ is observed. The protonation degree deduced from the NMR data and the intensity of the Bohlmann bands are in very good agreement. At a temperature below 8 °C, a splitting (2.6 Hz) of the methyl protons caused by spin–spin coupling with the $(NHN)^+$ bridge protons is observed. Comparison with literature data and with the coupling constant determined in this work for protonated *N*,*N*-dimethylaniline suggest that the potential surface of the NHN^+ cation includes two symmetrically situated wells between which fast proton migration takes place.

The interaction between strong proton donor (AH) and proton acceptor (B) molecules in aprotic solvents is known to result in the formation of several kinds of complex, involving more or less ionic character.[1] Tautomeric complexes, $AH \cdots B \rightleftharpoons A^- \cdots H^+B$ with the proton migrating between the two wells on the potential surface, are generally present in solution. More complicated systems involving several hydrogen bonds ($AH \cdots AH \cdots B$, $AHA^- \cdots HB^+$, $BHB^+ \cdots A^-$) can also be formed in solution. 1,8-Bis(dimethylamino)naphthalene (DMAN) is one of the best recognized members of the family of proton sponges. The unusual behaviour of this strong base results from sterically favourable arrangement of two basic centres so that an attached proton is shared between the two nitrogen atoms, forming strong NHN^+ hydrogen bridges. In the solid state, this intramolecular bond can be symmetrical or slightly asymmetrical depending on the nature of the anion.[2–8] Protonation of DMAN in solvents such as 1,2-dichloroethane or acetonitrile proceeds mainly with the participation of two proton donor molecules forming homoconjugated cations. With OH and NH proton donors, OHO^- [9–11] or NHN^- [12–13] species are formed. A lot of ^1H and ^{13}C NMR data have been recorded on DMAN protonated by strong acids such as HCl, HBr, $HClO_4$, HNO_3 and tetrazole.[8,11,14–16] These data refer to room temperature studies. In this work the interaction between DMAN and 3,5-dichlorophenol is investigated by ^1H and ^{13}C NMR spectroscopy at temperatures ranging from 30 °C to −70 °C at different acid to base concentration ratios. The spectra were recorded for samples in CD_2Cl_2. The data allowed us to compute the degree of protonation and to compare it with that obtained from the intensity of the Bohlmann bands ascribed to the CH stretching vibrations of the methyl group in a *trans* position to the lone pair of the nitrogen atom.

Experimental

NMR spectra

The ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 250.13 MHz (^1H) and 62.4 MHz (^{13}C) and on a Bruker AMX 400 operating at 400.14 MHz (^1H) and 100.62 MHz (^{13}C). The number of scans varied from 8 to 16 for the protons and from 1000 to 2000 for the carbon atoms. The chemical shifts were measured relative to internal tetramethylsilane.

IR spectra

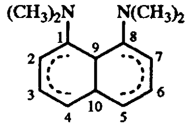
The IR spectra were recorded on a Bruker FTIR spectrometer IFS 88 at a resolution of 1 cm^{-1}.

Materials

DMAN from Janssen Chimica was crystallized from benzene–light petroleum. CD_2Cl_2 was purchased from Janssen Chimica. 3,5-Dichlorophenol from Aldrich was crystallized from carbon tetrachloride–light petroleum.

Results and discussion

The atoms in DMAN are labelled as shown.



(a) Degree of protonation

Tables 1 and 2 indicate the ^1H and ^{13}C NMR chemical shifts of DMAN complexed with 3,5-dichlorophenol at various proton donor (F_A) and proton acceptor (F_B) concentrations. The formal concentration of DMAN for all the spectra is equal to 0.2 mol dm^{-3}. All the NMR spectra have been recorded in CD_2Cl_2. The tables also list the chemical shifts for DMAN protonated by $HClO_4$ in acetonitrile.[8] Some ^1H and ^{13}C NMR spectra recorded at various temperatures are reproduced in Figs. 1 and 2.

The chemical shifts for free DMAN (δ^{free}) are very similar to those reported in the literature for measurement at 30 °C. For the complex between DMAN and 3,5-dichlorophenol, only one average shift for the DMAN and $DMANH^+$ species is observed at room temperature. As can be seen from Fig. 1, at a temperature of 15 °C, a broadening of the ^1H signals is observed and at a temperature of −60 °C, a splitting of the signals of DMAN and $DMANH^+$ is clearly seen. This splitting is also observed for the ^{13}C signals and can be explained by the slow exchange rate of the acid protons between DMAN and $DMANH^+$

Inspection of the results of Tables 1 and 2 clearly shows that the chemical shifts are concentration dependent and this dependence is illustrated in Fig. 3 for the ^{13}C signals. From an

Table 1 ^1H NMR chemical shifts (ppm) of free DMAN and DMAN complexed with 3,5-dichlorophenol at various temperatures and F_A/F_B ratios in CD_2Cl_2, F_B = 0.2 mol dm^{-3}

F_A/F_B	T/°C	$N(CH_3)_2$	H2/7	H3/6	H4/5	$(NHN)^+$
Free base	30	2.77	6.92	7.26	7.32	
	−65	2.76	6.93	7.31	7.32	
0.5	30	2.81	7.02	7.32	7.41	No[a]
	−65	2.76	6.93	7.31	7.32	
		2.95	7.58	7.58	7.97	19.6
2.8	30	2.96	7.47	7.55	7.82	No[a]
4.2	30	3.01	7.60	7.60	7.96	19.2
	−15	3[b]	7.61	7.61	7.96	19.5
$HClO_4$ (1:1 adduct)[b]	25	3.11	8.03	7.69	7.89	18.7

[a] Not observed. [b] $J(CH_3, NHN)$ = 2.6 Hz.

Table 2 ^{13}C NMR chemical shifts (ppm) of free DMAN and DMAN complexed with 3,5-dichlorophenol at various temperatures and F_A/F_B ratios in CD_2Cl_2, F_B = 0.2 mol dm^{-3}

F_A/F_B	T/°C	$N(CH_3)_2$	C1/8	C2/7	C3/6	C4/5	C9	C10
Free base	30	44.57	151.27	113.13	125.84	121.89	121.07	138.30
	−65	43.98	150.31	112.22	125.18	120.91	119.48	137.17
0.5	30	44.86	150.13	114.33	126.10	123.10	120.66	137.94
	−45	44.12	150.52	112.42	125.35	121.10	119.78	137.37
	−65	43.96[b]	150.31	112.21	125.19	120.89	119.45	137.13
		45.80[b]	142.40	120.88	126.88	129.51	No[a]	No[a]
2.8	30	46.20	144.93	119.69	127.27	128.63	119.12	136.40
4.2	30	46.59	143.20	121.31	127.62	130.42	118.59	135.88
8	30	46.63	143.10	121.32	127.66	130.52	118.54	135.90
$HClO_4$ (1:1 adduct)	25	46.73	145.12	122.36	127.86	130.04	120.02	136.19

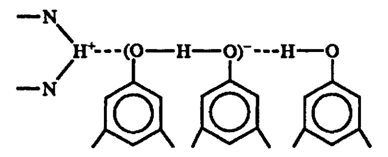
[a] Not observed. [b] The ratio of the areas of the low field/high field signals is 4.

Table 3 %PT for the complex between DMAN and 3,5-dichlorophenol computed from several ^1H and ^{13}C NMR signals; T = 30 °C, solvent = CD_2Cl_2

		F_A/F_B		
		0.5	2.8	4.2
^1H	$N(CH_3)_2$	17	79	100
	H2/7	15	81	100
	H3/6	18	85	100
	H4/5	14	78	100
^{13}C	$N(CH_3)_2$	15	80	100
	C1/8	15	78	99
	C2/7	15	80	100
	C3/6	16	79	97
	C4/5	14	78	99
	C9	13	79	100
	C10	17	79	100
Mean value		15	80	99

F_A/F_B value of 5, the chemical shifts remain practically constant and do not differ greatly from those observed in DMAN protonated by strong acids such as $HClO_4$. The small differences observed between the 3,5-dichlorophenol and the $HClO_4$ adducts can be accounted for by the existence of a specific bifurcate interaction between the $(NHN)^+$ bridge and the counteranion. This interaction has been proved by IR measurements. The $\nu_s(NHN)^+$ protonic vibration is indeed observed at low frequencies and shifts to higher frequency with increasing proton-acceptor properties of the anion.[17] This vibration is observed at 488 cm^{-1} in the $HClO_4$ complex[17] and at 600 cm^{-1} in the 3,5-dichlorophenol complex.[9] It is also notable that in an excess of phenol, the $(OHO)^-$ anion must be solvated by one or several phenol molecules and the species shown below are present in solution.[18]

For a given F_A/F_B value, the degree of protonation can be estimated from the experimental shifts (δ^{exp}) by eqn. (1) where



$$\frac{\delta^{exp} - \delta^{free}}{\delta^{prot} - \delta^{free}} \times 100 = \%PT \qquad (1)$$

δ^{prot} is the shift observed at an F_A/F_B ratio higher than 5. From this ratio, the chemical shifts of the proton and the carbon atoms remain constant. The values computed at 30 °C from different ^1H and ^{13}C signals are reported in Table 3 and are in very good agreement. It is also noteworthy that at −65 °C and for an F_A/F_B ratio of 0.5, the protonation degree calculated from the area of the split ^{13}C signals is 20%. This value is, as expected, higher than at 30 °C.

The percentage of protonation can also be estimated from the decrease intensity from the Bohlmann bands lying at 2836 and 2776 cm^{-1}. The results are indicated in Table 4 for different F_A/F_B ratios, F_B being the same as in the NMR experiments (0.2 mol dm^{-3}). The solvent is 1,2-dichloroethane, the polarity of which does not greatly differ from that of dichloromethane.

Fig. 4, in which the degree of protonation is plotted against the F_A/F_B values, illustrates the good agreement between the NMR and IR results. The percentage of protonation for DMAN complex with a series of phenols having pK_a between 10 and 0.33 has been determined by infrared spectrometry in acetonitrile for F_A/F_B ratios of 1 and 2.[13] The experimental results show that there is a rough correlation between the degree of protonation and the pK_a of the proton donors. The pK_a of 3,5-dichlorophenol is 8.18 and from the data of ref. 13, protonation degrees of about 15 and 40% can be predicted for respective values of F_A/F_B equal to 1 and 2. As shown by the

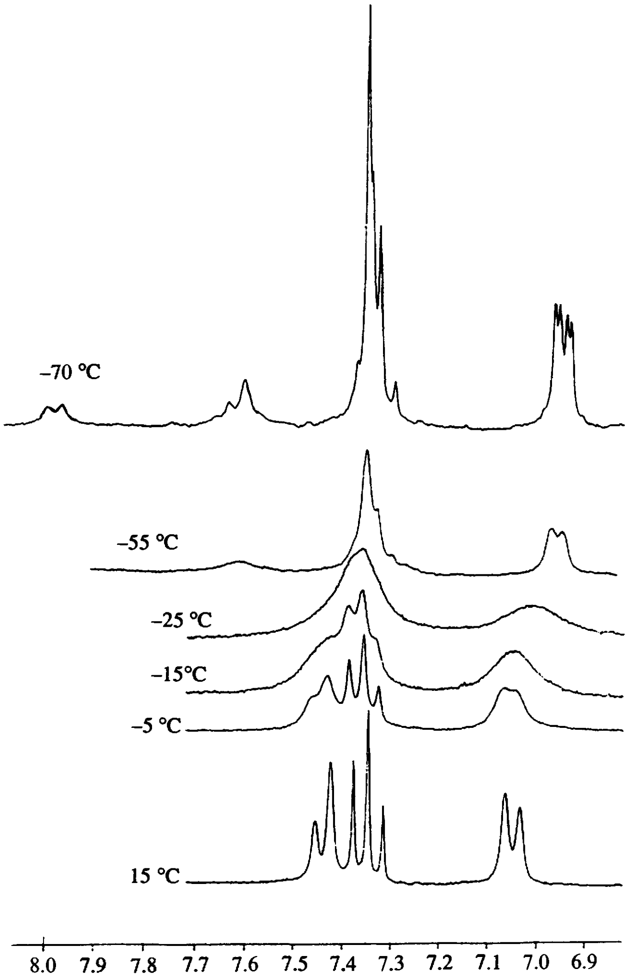


Fig. 1 ^{1}H NMR spectra (ring protons) of a solution of DMAN (F_B = 0.2 mol dm^{-3}) and 3,5-dichlorophenol (F_A = 0.1 mol dm^{-3}) at different temperatures, solvent = CD_2Cl_2

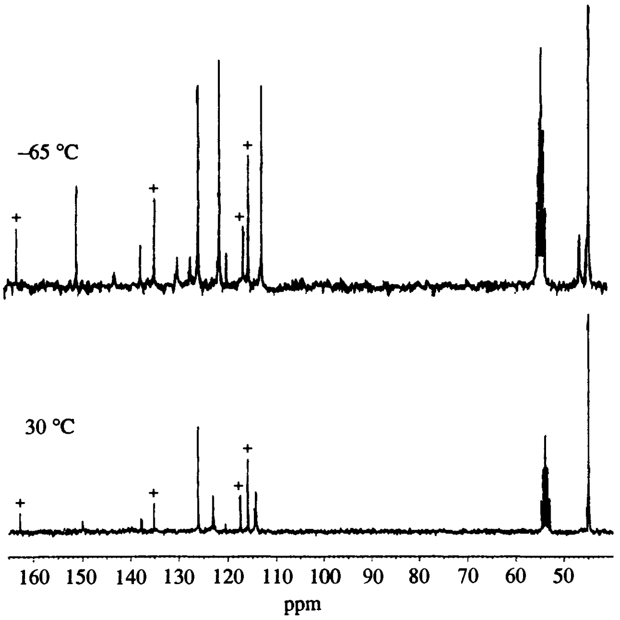


Fig. 2 ^{13}C NMR spectra of a solution of DMAN (F_B = 0.2 mol dm^{-3}) and 3,5-dichlorophenol (F_A = 0.1 mol dm^{-3}) at 30 °C and −65 °C, solvent = CD_2Cl_2. The ^{13}C signals of 3,5-dichlorophenol are indicated by a cross.

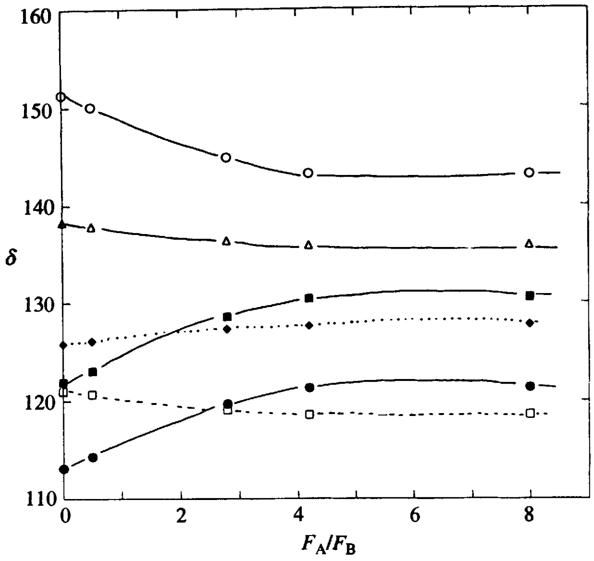


Fig. 3 ^{13}C chemical shifts (ppm) at different F_A/F_B ratios: ○, C1/8; ●, C2/7; ◆, C3/6; ■, C4/5; □, C9; △, C10

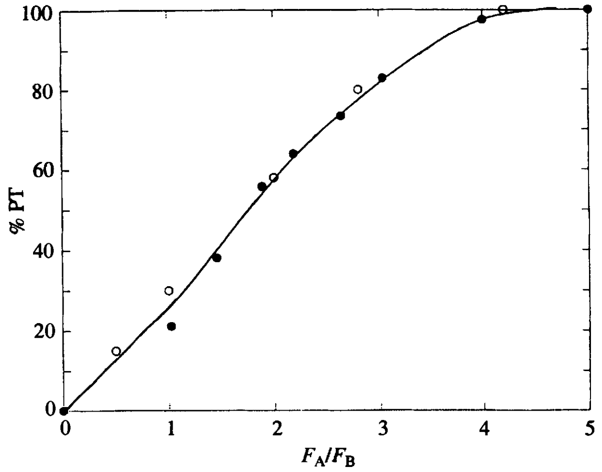


Fig. 4 %PT as a function of F_A/F_B: ●, IR data; ○, NMR data

Table 4 %PT determined from the decrease in intensity of the Bohlmann bands; T = 30 °C, solvent = 1,2-dichloroethane, F_B = 0.2 mol dm^{-3}

F_A/F_B	%PT
1.02	21.1
1.45	38.1
1.89	55.8
2.19	63.9
2.63	73.4
3.03	82.8
4.00	97.5
5.040	100

results of Tables 3 and 4, the values deduced in this work in the less polar solvents dichloromethane or 1,2-dichloroethane are 5 and 20% higher. This can be accounted for, at least qualitatively by specific interactions between the CN bond of acetonitrile and OH groups. The formation of OH···NC hydrogen bonds is clearly evidenced by the fact that the ν_{OH} stretching vibration is observed at 3200 cm^{-1} for samples in acetonitrile, about 350 cm^{-1} lower than in 1,2-dichloroethane.

(b) $J(CH_3, NHN)$ coupling

At temperatures below 8 °C, a splitting of the CH_3 proton signals is observed for fully protonated DMAN. This coupling equals 2.6 Hz and a decoupling procedure proved that the $(NHN)^+$ bridge proton is responsible for the splitting. Such a splitting has been observed at room temperature for DMAN protonated by strong acids in acetonitrile[16] and for the same base protonated by maleic acid.[8] In this case the splitting takes values between 1.2 and 2.4 Hz, depending on the solvent. This spin–spin coupling has been discussed for intramolecular $(NHN)^+$ bonds in protonated *N,N'*-tetramethylalkanes[19] and *N,N'*-tetraalkyl-*o*-xylyldiamines.[20] From these studies it follows that the splitting of the proton signals of the methyl or methylene groups takes place when the proton is located on one nitrogen atom. In bridges with a delocalized proton, one should observe singlets. These last bridges are characterized by a 'continuum' of the IR absorption.[20] As discussed by Sobczyk *et al.*,[16] the observation of doublets in protonated DMAN can be interpreted in two different ways and no definitive conclusion can be drawn on the shape of the potential curve for the proton motion which can be characterized by a single minimum or by a symmetrical double minimum where the proton linked to one nitrogen atom can jump to the second one.

The localization of the protons inside hydrogen bonded complexes has been thoroughly discussed by Denisov *et al.*[21] who have shown that the spin–spin coupling (Δ) allows one to distinguish between complexes with fast proton migration between two wells on the potential surface and those with proton localized on one well particularly the central one.

The NMR data have been analysed for homoconjugated $(BHB)^+$ cations and suggest that where $\Delta \approx \frac{1}{2}J_{BH^+}$ (J_{BH^+} being the spin–spin coupling constant within the ionic form), the potential surface of the $(BHB)^+$ cation includes two symmetrically situated wells between which fast proton migration takes place. In the $(FHF)^-$ ion where the hydrogen bond is definitely of the central type, $\Delta = \frac{1}{5}J_{HF}$ and, generally, a considerable stretching of the proton donor bond brings about a strong decrease of the Δ value.[22]

The Δ value for protonated *N,N*-dimethylaniline determined in this work in CD_2Cl_2 is 5.2 Hz. This value is twice the Δ value determined for protonated DMAN. This strongly suggests that the potential surface of the $(NHN)^+$ is characterized by a double minimum symmetrical potential surface with fast proton transfer migration between the two wells. The conclusions of this work are in agreement with ^1H NMR studies on ^{15}N labelled porphyrin derivatives.[23] At −80 °C, the ^1H spectrum consists of a doublet with a separation of 97 Hz. At room temperature, the spectrum shows a quintet with an observed coupling constant of 24.2 Hz (=97/4 Hz) arising from the random spin orientation of four ^{15}N nuclei. In the porphyrins, the NH $\cdots$ N intramolecular hydrogen bond, is characterized by a double minimum potential. This has been thoroughly investigated by Limbach *et al.*[24,25]

Interestingly, recent *ab initio* studies suggest that in protonated DMAN, asymmetrical protonation at one nitrogen atom is energetically preferred to the symmetrical $N–H^+–N$ bridged form.[26]

(c) ^{13}C Chemical shifts of 3,5-dichlorophenol

The ^{13}C signals of the C2 and C3 atoms of the phenol moiety remain practically constant. They are observed at 115.9 and 135.23 ppm for an F_A/F_B ratio equal to 0.5 and at 115.55 and 135.48 ppm for an F_A/F_B ratio equal to 8. The C1 atom becomes increasingly more shielded and the experimental shift varies from 162.61 to 159.19 ppm. The C4 atom is deshielded and the ^{13}C signal varies from 117.62 to 119.98 ppm when the F_A/F_B value varies from 0.5 to 8. These changes are related to the formation of $(OHO)^-$ homoconjugated bonds and to the insertion of phenol molecules into this anion. As a consequence the data of this work cannot be quantitatively compared with the ^{13}C NMR data reported in the literature for associated phenols[27] and for phenols complexed with strong bases.[28]

Acknowledgements

The authors thank the National Fund of Research of Belgium for financial support.

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Paper 4/04945D
Received 11*th August* 1994
Accepted 23*rd December* 1994