Some ^{13}C and ^{15}N NMR Studies on 1,8-Bis (dimethylamino) Naphthalene and Two of Its Salts

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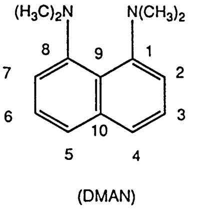
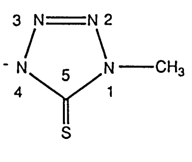
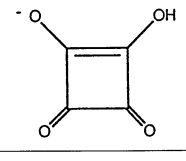
Synopsis. ^{13}C and ^{15}N NMR data are reported for 1,8-bis(dimethylamino)naphthalene (DMAN) and two of its salts in both the solid state and solutions in CD_3CN. Only the ^{15}N results are sufficiently sensitive to show the presence of the fully protonated form of DMAN in the solid state and of a partially protonated structure in solution.

We have previously reported some ^{13}C and ^{15}N NMR results taken on the solid, and in solution, for 1,8-bis(dimethylamino)naphthalene (DMAN) and its monoprotonated salt with tetrazole.[1] It was found that the ^{13}C chemical shifts were relatively insensitive to salt formation whereas the ^{15}N chemical shifts were very informative regarding differences in structures between the solution and solid states. The present report concerns a similar investigation of a further two salts of DMAN.

Results and Discussion

The results of some ^{13}C and ^{15}N NMR measurements on DMAN and two of its salts at room temperature are presented in Table 1 for both the solid state and for solutions in CD_3CN. The reported assignments of the observed NMR signals are straightforward and in the case of the salts with 1-methyl-1,4-dihydro-5*H*-tetrazole-5-thione (MDTT) the procedures given elsewhere[2] were employed. In general, the ^{13}C chemical shifts for a given compound in Table 1 are very similar for both the solid state and solution cases. Thus not all of the observed ^{13}C chemical shifts are reported in Table 1. In contrast the ^{15}N chemical shifts show some significant differences between the solid state and solution. An exception being the ^{15}N signals for the bis(dimethyl-

Table 1. Some ^{13}C and ^{15}N Solution and Solid State NMR Data for 1,8-Bis(dimethylamino)naphthalene [DMAN] and Two of Its Salts

		Chemical Shifts in a CD_3CN solution[a]	CP MAS chemical shifts[a]
	CH_3	44.7	42.1, 45.2[b]
	N	−338.1	−336.9
	C_1	151.3	150.1
	C_2	113.5	113.2
	C_3	126.0	125.2
	C_4	122.5	121.7
	C_9	121.4	120.9
(DMAN)	C_{10}	138.7	137.3
DMANH$^+$	CH_3	45.7	47.3
	N	−345.4	−345.9
	N_1-CH_3	32.4	32.0
	C_5	168.2	169.7
	N_1	−156.7	−153.6
	N_2	−17.1	−15.3
	N_3	3.4	5.5
	N_4	−136.6	−59.3
DMANH$^+$	CH_3	47.0	46.0
	N	−347.2	−346.0
	C-ring	198.0	193.7[c]

a) ^{13}C chemical shifts are given with respect to TMS and ^{15}N chemical shifts with respect to neat nitromethane. b) Two methyl ^{13}C signals are observed in the solid state spectrum. These probably are due to packing effects. c) Very broad ^{13}C signal indicating that averaging of the four ring carbon atom environments may not be complete in the solid state.

amino) groups of DMAN. This relative insensitivity of the ^{15}N resonance position to protonation of two dimethylamino groups has been discussed previously.[3]

As noted in the case of the DMAN salt with tetrazole,[1] the N_4 signal of the salt with MDTT shows a large difference between the solid and solution cases. As observed before[1] the solid state ^{15}N signal for N_4 is shielded with respect to that for the solution. In the present case this shielding amounts to about 80 ppm. Comparison of the present ^{15}N chemical shifts for the DMAN salt may be made with those for the free MDTT published previously.[2] For N_4, the position of the signal for the solution of the salt in CD_3CN solution of the salt in CD_3CN solution lies between that of the salt in the solid state and that of the free MDTT in DMSO solution. This suggests that in CD_3CN solution the salt exists in an equilibrium involving the half protonated form of the base as discussed previously.[1]

For the DMAN salt with squaric acid(3,4-dihydroxy-3-cyclobutene-1,2-dione) there are no nitrogen atoms in positions which are sensitive to differences between the solution and solid state cases. However, the averaged position of the ^{13}C signal from the four carbons of the squarate ring shows a small difference between the solution and solid state. Thus ^{13}C NMR is unable to provide information of the type noted above from ^{15}N measurements concerning a possible equilibrium for the salt in solution.

In addition we have some ^{1}H NMR results, for the compounds studied, taken on CD_3CN solutions. We observe that the $N-CH_3$ protons of DMAN are deshielded upon protonation from a chemical shift of 2.7 ppm for DMAN to 3.2 ppm for $DMANH^+Cl^-$, the other salts reported here lie between these values. In the case of $DMANH^+Cl^-$ we have observed $^{3}J(H-H)$, for the $N-CH_3$ protons and the proton transferred upon salt formation, this is found to be 2.6 Hz in CD_3CN solution. The chemical shift of the transferred proton is observed to be 18.5 ppm, and this proton has a value of 5.1 Hz for $^{2}J(C-H)$ for its coupling to the carbon atom of the $N-CH_3$ group of DMAN which has a chemical shift of 48.2 ppm in the hydrochloride salt.

The chemical shift of the nitrogen atom in the hydrochloride is −352 ppm which is the most highly shielded of the $N-CH_3$ nitrogens observed in solutions in the present work. Further supporting the conclusion of partial protonation for the other salts studied in solution.

We conclude that nitrogen NMR measurement have again been demonstrated to be the most satisfactory means of investigating the structures studied both in solution and the solid state. Rather less information becomes available for those compounds which do not contain nitrogen atoms in the deprotonated ring.

Experimental

The compounds studied were prepared by published procedures.[4] The solution NMR spectra were taken on a Bruker AM 500 spectrometer operating at 125 and 50.5 MHz for ^{13}C and ^{15}N nuclei, respectively. Solid state NMR measurements were performed on a JEOL GSX 270 instrument operating at 67.5 and 27.3 MHz for the ^{13}C and ^{15}N nuclei respectively. ^{15}N INEPT and inverse gated decoupling measurments were taken on the solutions of the samples.

References

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