Some Multinuclear NMR Solution and Solid State Studies on 1,8-Bis(dimethylamino)naphthalene and Its Complex with Tetrazole

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Synopsis. ^{13}C and ^{15}N NMR spectra are measured for 1,8-bis(dimethylamino)naphthalene and its complex with tetrazole in both solution and the solid state. On the basis of the solution and solid state ^{15}N results, an equilibrium involving the half protonated form of the base in the solution of the complex salt was identified. On the other hand, it is found that the ^{13}C results for the solutions are closely similar to those found for the solid state, and are rather insensitive to salt formation.

Previously vibrational spectra,[1,2] X-ray[3] diffraction data and ^1H NMR results[4,5] have been reported for 1,8-bis(dimethylamino)naphthalene and some of its salts formed by protonation. These earlier results show that proton migration results in a symmetrical structure for the cation. Most recently, one of us has been involved in an X-ray diffraction study of 1, 8-bis(dimethylamino)naphthalene and its monohydrated salt with terazole which reveal that the base cation has a symmetrical hydrogen bond in the salt.

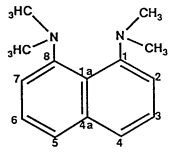
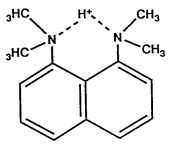
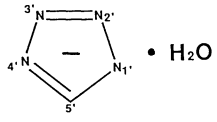
The present report is concerned with the results of ^{13}C and ^{15}N NMR studies on 1,8-bis(dimethylamino)-naphthalene and its monohydrated salt with terazole, in order to know further information about their structures in both solution and the solid state.

Results and Discussion

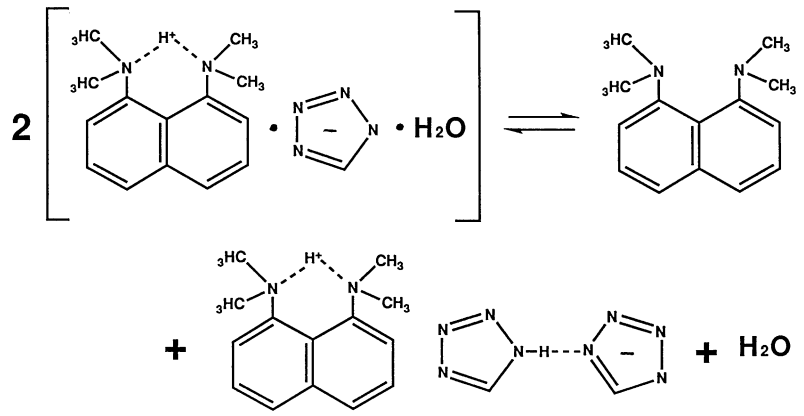
The results obtained from the ^{13}C and ^{15}N NMR studies of 1,8-bis(dimethylamino)naphthalene and its monohydrated salt with terazole are presented in Table 1. The ^{13}C signal assignments are made with the assistance of a comparison between the proton coupled and uncoupled ^{13}C spectra and by comparison with the known ^{13}C data for aniline. The ^{15}N assignments given are based upon our earlier results.[7]

The ^{13}C signal of C_5' for the tetrazole anion is similar to that of tetrazole (δ=143.7 ppm and ^1J(^{13}C–^1H)=217.8 Hz) in the same solvent. Comparison of the ^{13}C data, for any chosen carbon, in either of the

Table 1. ^{13}C and ^{15}N Solution and Solid State NMR Data for 1,8-Bis(dimethylamino) Naphthalene and Its Monohydrated Salt with Tetrazole

		Chemical shifts[a] for a solution in CD_3CN	CP MAS Chemical shifts[a]
	$N-CH_3$	44.7 (134.4)[b]	42.0
			45.4
	C_2	113.8 (156.9)[b]	113.4
	C_{1a}	121.3	122.1
	C_4	122.5	122.1
	C_3	126.5 (159.1)[b]	125.3
	C_{4a}	138.8 (160.8)[b]	138.2
	C_1	151.7	150.6
	N	−338.1	−329.7
	$N-CH_3$	46.0 (138.4)[b]	44.7
	C_2	119.3 (161.7)[b]	117.8
	C_{1a}	120.5	124.3
	C_4	127.3 (162.5)[b]	128.7
	C_3	127.5 (162.7)[b]	131.2
	C_{4a}	137.2	136.2
	C_1	147.6	151.0
	N	−343.7	−340.0
	C_5'	147.7 (204.0)[b]	145.2
	N_1'	−78.8	−56.4
	N_2'	−1.6	+11.4

a) ^{13}C chemical shifts are given with respect to TMS and ^{15}N chemical shifts with respect to external neat nitromethane.
b) ^1J coupling data are given in parenthesis.



Scheme 1.

compounds studied whether in solution or the solid state shows that ^{13}C chemical shifts are rather insensitive to salt formulation and to a change from solid to solution in CD_3CN.

The ^{15}N signal for the $N(CH_3)_2$ group, in the solid state spectra shows shows an increase in shielding, in passing from the free base to the salt, of about 10 ppm. The corresponding signals for the solution spectra show a shielding increase of about 6 ppm. This suggests that in solution the extent of protonation of $N(CH_3)_2$ group is reduced. However, possible solvent effects on the nitrogen chemical shifts should also be considered.

The N_1' chemical shifts of tetrazole are −98.3, −78.8, −67.0, and −56.4 ppm for the tetrazole,[7] our solution of the salt in salt in CD_3CN, a basic solution with NaOH[7] and our solid state measurement. The corresponding ^{15}N chemical shift shifts for N_2' being −5.8, −1.6, 3.0, and 11.4 ppm respectively, which shows that in solution the salt exists essentially in the half protonated form as implied in the above equilibrium. From the above results we are able to deduce that in solution an equilibrium of the following type exists. This supports the results of vibrational spectra.[1,2]

We have extended our study to include ^1H NMR data. However, the results obtained were not particularly informative in the context of the present investigation.

Finally we conclude that the ^{15}N NMR data provide the most suitable mean of investigating the structure of the compounds studied both in solution and the solid state.

Experimental

The compounds studied were prepared according to published procedures.[8] The solution NMR spectra were on a Bruker AM500 instrument operating at 125 and 50.5 MHz for ^{13}C and ^{15}N nuclei, respectively solid state measurements were made on a JEOL GSX-270 spectrometer operating at 67.5 and 27.3 MHz for ^{13}C and ^{15}N nuclei, respectively. ^{15}N INEPT and inverse gated decouple measurements were taken on the solutions of the samples.

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