

# $^{15}\text{N}$ AND $^{13}\text{C}$ NMR STUDY OF TWO ADDUCTS CONTAINING $\text{NHN}^+$ AND $\text{NHN}^-$ HYDROGEN BONDS

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$^{13}\text{C}$  and  $^{15}\text{N}$  NMR data are reported for two substituted nitronaphthalenes 1,8-bis(4-toluenesulphonamido)-2,4,7-trinitronaphthalene and 1,8-bis(4-toluenesulphonamido)-2,4,5,7-tetranitronaphthalene and their salts with 1,8-dimethylaminonaphthalene. The salts are shown to contain  $\text{NHN}^+$  and  $\text{NHN}^-$  intramolecular hydrogen-bonded systems in  $\text{CD}_3\text{CN}$  solutions, in agreement with x-ray diffraction data on solid samples and  $^1\text{H}$  NMR studies on solutions. Examples are given of both a symmetrical and an unsymmetrical bonding system for the  $\text{NHN}$  atoms.  $^{15}\text{N}$  NMR is shown to be particularly helpful in these studies, both  $^{15}\text{N}$  shielding and  $^1J(^{15}\text{N}, ^1\text{H})$  couplings are of value. Additional assistance is obtained from  $^3J(^{13}\text{C}_9, \text{N}1\text{H})$  data.

## INTRODUCTION

$^1\text{H}$  NMR studies have been reported for the NH acids; 1,8-bis(4-toluenesulphonamido)-2,4,7-trinitronaphthalene (TSATrNN) and 1,8-bis(4-toluenesulphonamido)-2,4,5,7-tetranitronaphthalene (TSATeNN) and their salts with the proton sponge 1,8-dimethylaminonaphthalene (DMAN) (Figure 1).<sup>1</sup> An obvious extension of this work is to apply  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR measurements to these compounds. These techniques and, in particular,  $^{15}\text{N}$  NMR, are well known to be very suitable for the determination of the structures of compounds containing charge separation.<sup>2</sup> This paper deals with the application of  $^{15}\text{N}$  and  $^{13}\text{C}$  NMR to TSATrNN, TSATeNN and their salts with DMAN with a particular view to investigating the  $\text{NHN}^+$  and  $\text{NHN}^-$  hydrogen bonds and their influence on molecular structure.

## RESULTS AND DISCUSSION

The  $^{13}\text{C}$  NMR data obtained from TSATrNN, TSATeNN and their salts with DMAN are reported in

Table 1. The  $^{13}\text{C}$  signal assignments for TSATeNN are made as follows.

The relative intensities of the  $^{13}\text{C}$  signals provide a clear distinction between the protonated and the quaternary carbon nuclei. In the  $^1\text{H}$ -coupled  $^{13}\text{C}$  spectrum, carbon atoms 3, 6, 2', 2'', 3' and 3'' show a large doublet splitting which is removed upon  $^1\text{H}$  decoupling. The C-3 and C-6  $^{13}\text{C}$  signals are distinguished from those of the 2', 2'', 3' and 3'' carbons since the latter show additional coupling to protons on adjacent carbon atoms. The C-2' and C-2'' signals are separately identified with respect to those from C-3' and C-3'', since the latter show additional  $^3J(^{13}\text{C}, ^1\text{H})$  interactions with the protons of the 4' and 4'' methyl groups. The  $^{13}\text{C}$  signals of the methyl groups appear in a characteristic region of the spectrum.

We now turn to consideration of the signals of the quaternary carbon atoms. From the previously reported  $^1\text{H}$  spectra,<sup>1</sup> selective INEPT measurements permit the assignments of carbons 1', 1'' and 4', 4'' by means of  $^3J(^{13}\text{C}, ^1\text{H})$  interactions with the protons on the 3', 3'' and 2', 2'' carbons, respectively. The  $^{13}\text{C}$  signal of C-10 is similarly identified by means of  $^3J(^{13}\text{C}, ^1\text{H})$  with the protons on C-6 and C-3. These protons are also coupled to C-1, C-8 and C-10. However the C-1, C-8 signal has

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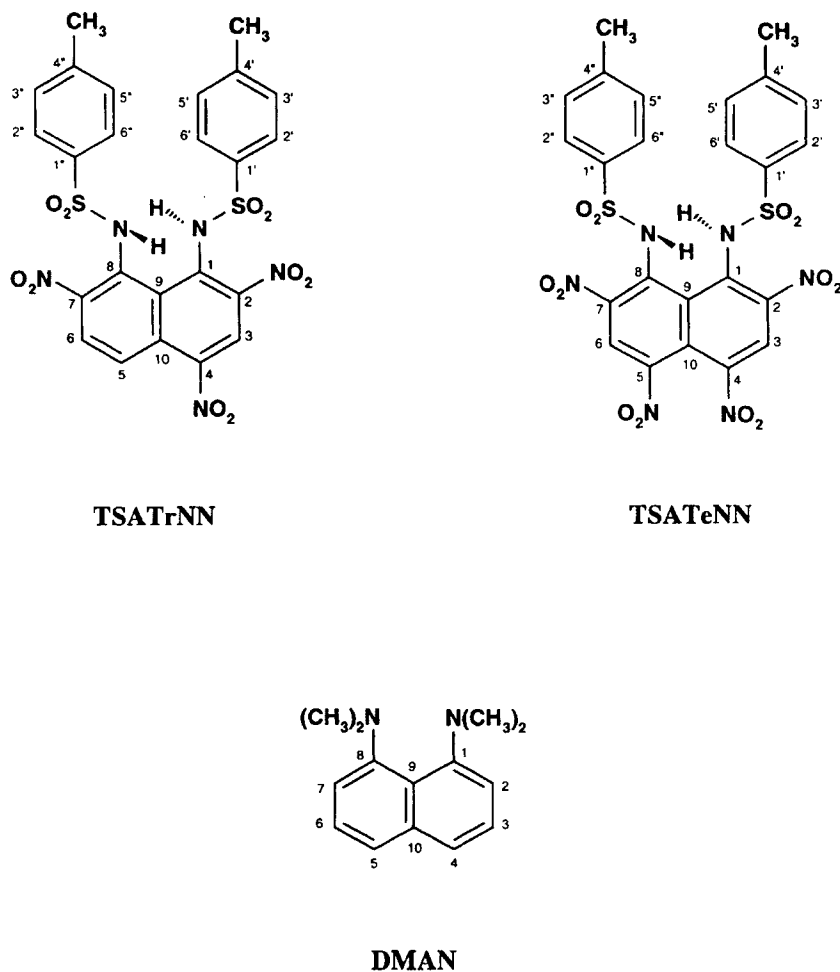


Figure 1. Structures of the compounds studied

only one  $^3J(^{13}\text{C}, ^1\text{H})$  interaction, whereas that for C-10 has two, hence the C-1, C-8 and C-10 signals are separately identified. Consideration of the C- $\text{NO}_2$  carbon atoms, 2,7 and 4,5, shows that they all experience  $^2J(^{13}\text{C}, ^1\text{H})$  coupling with the protons on C-3 and C-6. However, the 2,7 and 4,5  $^{13}\text{C}$  signals are distinguished by means of the  $^3J(^{13}\text{C}, ^1\text{H})$  interaction with the NH proton which occurs for the signal of the 2,7 carbons but not for the 4,5 carbons. The remaining  $^{13}\text{C}$  signal at 131.7 ppm is attributed to C-9.

The  $^{13}\text{C}$  signal assignments for the TSATeNN salt with DMAN are obtained by means of similar arguments. In the case of the salt the C-9 signal is split into a doublet of 3.8 Hz owing to coupling with the NH proton. This coupling is not found in the  $^{13}\text{C}$  spectrum of the free acid, which indicates rapid proton exchange. Probably this occurs between one proton bonded to the

amine nitrogen atoms and the second one engaged in hydrogen bonding with the nitro groups in positions 2 and 7. The  $^{13}\text{C}$  signal assignments of DMAN on  $\text{CD}_3\text{CN}$  have been published previously<sup>3</sup> and use of them is made in the assignments given here.

We now turn to a consideration of the assignment of the  $^{13}\text{C}$  NMR signals of TSATrNN and of its salt with DMAN. The non-symmetrical disposition of the nitro groups in TSATrNN results in more  $^{13}\text{C}$  signals than are found in the spectrum of TSATeNN. The  $^{13}\text{C}$  signals of the quaternary carbon atoms of TSATrNN are readily identified by means of their intensities, with respect to those of the carbon atoms bonded to protons.

The  $^{13}\text{C}$  signals of the two phenyl rings in TSATrNN are similar to each other and to those found for the equivalent pair of phenyl rings in TSATeNN. Hence it is not difficult to distinguish these  $^{13}\text{C}$  signals from those

Table 1. <sup>13</sup>C NMR data for TSATeNN, TSATrNN and their 1:1 complexes with DMAN in acetonitrile

Carbon	<sup>13</sup> C NMR chemical shifts (ppm) with $J_{CH}$ coupling constants (Hz) in parentheses					
	TSATeNN	TSATrNN-DMAN		TSATrNN	TSATeNN-DMAN	
		Anion	Cation		Anion	Cation
C-1	136.0 (5.8) <sup>c</sup>	143.6 (6.4) <sup>c</sup>	145.3 (5.6) <sup>c</sup>	144.8	149.6 (5.6) <sup>c</sup>	145.2
C-2	144.2 (4.7) <sup>b</sup>	137.5	122.5 (8.3) <sup>c</sup>	135.2 (5.3) <sup>b</sup>	134.4 (4.4) <sup>b</sup>	122.5 (8.8) <sup>c</sup>
C-3	126.2 (179.1) <sup>a</sup>	126.3 (173.2) <sup>a</sup>	128.1 (163.9) <sup>a</sup>	123.7 (177.2) <sup>a</sup>	126.9 (169.5) <sup>a</sup>	128.0 (164.2) <sup>a</sup>
C-4	143.8	136.6 (5.4) <sup>b</sup>	130.3 (6.6) <sup>c</sup>	130.9 (9.7) <sup>c</sup>	131.6 (9.4) <sup>c</sup>	130.2
C-5	143.8	136.6 (5.4) <sup>b</sup>	130.3 (6.6) <sup>c</sup>	127.2 (174.9) <sup>a</sup>	126.7 (170.8) <sup>a</sup>	130.2
C-6	126.2 (179.1) <sup>a</sup>	126.3 (173.2) <sup>a</sup>	128.1 (163.9) <sup>a</sup>	125.7 (174.6) <sup>a</sup>	121.5 (172.0) <sup>a</sup>	128.0 (164.2) <sup>a</sup>
C-7	144.2 (4.7) <sup>b</sup>	137.5	122.5 (8.3) <sup>c</sup>	129.9 (5.9) <sup>c</sup>	133.0 (4.4) <sup>c</sup>	122.5 (8.8) <sup>c</sup>
C-8	136.0 (5.8) <sup>c</sup>	143.6 (6.4) <sup>c</sup>	145.3 (5.6) <sup>c</sup>	147.6 (9.7) <sup>c</sup>	144.5 (10.7) <sup>c</sup>	145.2
C-9	131.7	127.7 (3.8) <sup>c</sup>	120.2 (6.2) <sup>c</sup>	145.7	132.7 (6.4) <sup>c</sup>	120.1 (6.7) <sup>c</sup>
C-10	122.9(6.6) <sup>c</sup>	124.3 (7.1) <sup>c</sup>	136.4	130.2 (7.9) <sup>c</sup>	126.0 (7.7) <sup>c</sup>	136.3 (8.5) <sup>c</sup>
C-1'	134.8 (8.4) <sup>c</sup>	140.0 (8.6) <sup>c</sup>		133.7 (8.2) <sup>c</sup>	143.7 (8.3) <sup>c</sup>	
C-2'	127.9 (5.5) <sup>c</sup>	127.1 (5.8) <sup>c</sup>		128.2 (5.2) <sup>c</sup>	126.4 (5.6) <sup>c</sup>	
C-3'	131.3 (5.0) <sup>c</sup>	130.5 (5.7) <sup>c</sup>		131.2 (6.0) <sup>c</sup>	130.2	
C-4'	147.2 (7.4) <sup>c</sup>	144.5 (7.3) <sup>c</sup>		147.1 (7.1) <sup>c</sup>	143.0	
C-1''	134.8 (8.4) <sup>c</sup>	140.0 (8.6) <sup>c</sup>		134.5 (9.2) <sup>c</sup>	136.1 (8.7) <sup>c</sup>	
C-2''	127.9 (5.5) <sup>c</sup>	127.1 (5.8) <sup>c</sup>		127.8 (5.5) <sup>c</sup>	127.7 (5.5) <sup>c</sup>	
C-3''	131.3 (5.0) <sup>c</sup>	130.5 (5.7) <sup>c</sup>		131.2 (6.8) <sup>c</sup>	130.2	
C-4''	147.2 (7.4) <sup>c</sup>	144.5 (7.3) <sup>c</sup>		146.8 (7.4) <sup>c</sup>	144.9	
CH <sub>3</sub> -4'	21.6 (127.6) <sup>a</sup>	21.5 (127.0) <sup>a</sup>		21.5 (127.5) <sup>a</sup>	21.4 (127.1) <sup>a</sup>	
CH <sub>3</sub> -4''	21.6 (127.6) <sup>a</sup>	21.5 (127.0) <sup>a</sup>		21.4 (127.6) <sup>a</sup>	21.3 (127.0) <sup>a</sup>	
CH <sub>3</sub> -1,8			46.8 (140.2) <sup>a</sup>			46.7 (140.9) <sup>a</sup>

<sup>a</sup>  $^1J(^{13}C, ^1H)$ .<sup>b</sup>  $^2J(^{13}C, ^1H)$ .<sup>c</sup>  $^3J(^{13}C, ^1H)$ .

of the remaining carbon atoms in TSATrNN. The individual signals from analogous carbon atoms, e.g. C-1' and C-1'', in the two non-equivalent phenyl rings of TSATrNN are identified by means of proton decoupling experiments based on assignments made for the <sup>1</sup>H spectrum of TSATrNN.<sup>1</sup>

The signals for the carbon atoms 1–4 are assigned in the same way as those for the analogous atoms in TSATeNN. The C-5 and C-6 signals are directly bonded to protons whose chemical shifts are known, thus INEPT measurements reveal the relative shieldings of the C-5 and C-6. The <sup>13</sup>C signals from the remaining quaternary carbon atoms 7–10, are all relatively weak. The positions of the signals for C-7, C-8 and C-10 are identified and assigned by means of COSY measurements correlation spectroscopy and  $^3J(^{13}C, ^1H)$  interactions with H-5, H-6 and H-6, respectively. The presence of the directly bonded nitrogen atom results in the signal for C-8 being deshielded with respect to that from C-10. Hence C-8 and C-10 are separately identified. The remaining <sup>13</sup>C signal of 145.7 ppm is assigned to C-9. Similar considerations apply to the <sup>13</sup>C signal assignments of the salt formed by TSATrNN with DMAN. The <sup>15</sup>N NMR data for the two NH acids studied, and their salts with DMAN, are reported in Table 2.

The <sup>15</sup>N signals found for TSATeNN are readily identified from their relative positions as belonging to the NH and NO<sub>2</sub> groups.<sup>4</sup> The assignment of the signal at –32.5 ppm to the 2,7-NO<sub>2</sub> groups and that at –15.5 ppm to the 4,5-NO<sub>2</sub> groups is in accord with observation that hydrogen bonding to nitro groups results in an increase in their nitrogen shielding.<sup>5</sup> Consequently, the 2,7-nitro groups in TSATeNN appear to be strongly hydrogen bonded to the NH proton. The value of  $^1J(^{15}N, ^1H)$  of 86.0 Hz for the NH <sup>15</sup>N signal of TSATeNN is in the normal range for such interactions. The <sup>15</sup>N NMR signals for the TSATeNN salt with DMAN are in typical positions for the environments of the nitrogen atoms concerned.<sup>4</sup> The two signals at –11.6 and –12.1 ppm are assigned to the two pairs of nitro groups 2,7 and 4,5, but it is not possible to distinguish between them at the present. All nitrogen signals received for TSATeNN at lower temperature (233 K) are in almost the same positions as in the spectrum taken in 300 K.

In the case of TSATrNN the positions of the <sup>15</sup>N NMR signals are typical of the groups involved, with the exception of that at –31.0 ppm. This is assigned to the NO<sub>2</sub> group in position 2 (or 7), which has a higher shielding than normal owing to hydrogen bonding with the NH group. <sup>15</sup>N NMR measurements on the salt of

Table 2.  $^{15}\text{N}$  NMR data for TSATeNN, TSATrNN and their 1 : 1 complexes with DMAN in acetonitrile

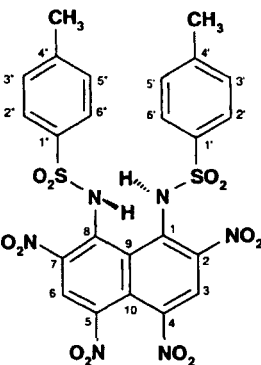
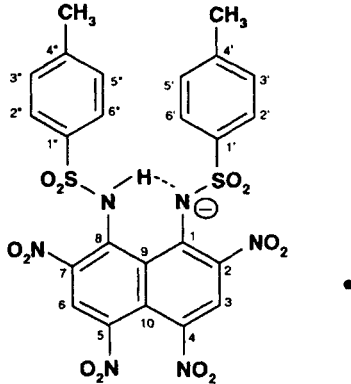
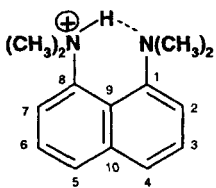
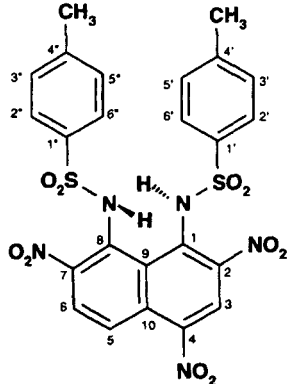
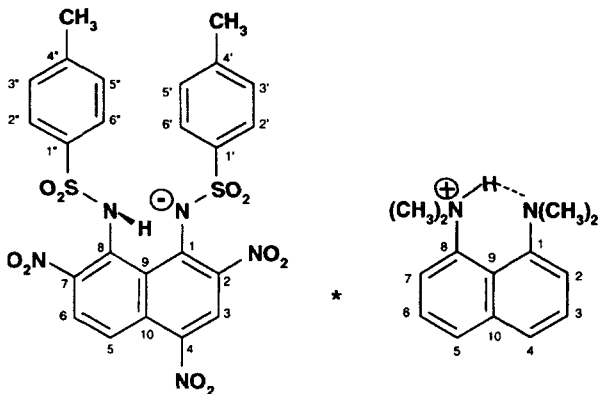
Compound	Temperature (K)	Nitrogen chemical shifts referred to neat nitromethane (ppm)	$^nJ(^{15}\text{N}, ^1\text{H})(\text{Hz})$
	300	-261.0(1,8-NH) -32.5 (2,7-NO <sub>2</sub> ) -15.5 (4,5-NO <sub>2</sub> )	$^1J_{\text{NH}} = 86.0$
	300	-346.2 (1,8-NMe <sub>2</sub> ) -218.3 (1,8-NH) -12.1 (4,5-NO <sub>2</sub> ) <sup>a</sup> -11.6 (2,7-NO <sub>2</sub> ) <sup>a</sup>	$^1J_{\text{NH}} = 30.7$ $^1J_{\text{NH}} = 34.9$
	233	-346.1 (1,8-NMe <sub>2</sub> ) -219.3 (1,8-NH) -11.9 (4,5-NO <sub>2</sub> ) <sup>a</sup> -11.6 (2,7-NO <sub>2</sub> ) <sup>a</sup>	$^1J_{\text{NH}} = 32.6$ $^1J_{\text{NH}} = 35.0$
	300	-261.7 (1-NH) -265.8 (8-NH) -31.0 (2-NO <sub>2</sub> ) -14.9 (7-NO <sub>2</sub> ) <sup>a</sup> -14.4; (4-NO <sub>2</sub> ) <sup>a</sup>	$^1J_{\text{NH}} = 82.1$ $^1J_{\text{NH}} = 84.0$

Table 2. (continued)

Compound	Temperature (K)	Nitrogen chemical shifts referred to neat nitromethane (ppm)	$^a J(^{15}\text{N}, ^1\text{H})$ (Hz)
	300	-346.1 (1,8-NMe <sub>2</sub> ) ? (1-N <sup>-</sup> ) -262.4 (8-NH) -10.7 (7-NO <sub>2</sub> ) <sup>a</sup> -9.1 (4-NO <sub>2</sub> ) <sup>a</sup> -8.3 (2-NO <sub>2</sub> ) <sup>a</sup>	$^1 J_{\text{NH}} = 31.3$ $^1 J_{\text{NH}} = 70.1$
	233	-346.1 (1,8-NMe <sub>2</sub> ) -182.7 (1-N <sup>-</sup> ) -264.3 (8-NH) -11.2 (7-NO <sub>2</sub> ) <sup>a</sup> -9.1 (4-NO <sub>2</sub> ) <sup>a</sup> -7.8 (2-NO <sub>2</sub> ) <sup>a</sup>	$^1 J_{\text{NH}} = 30.4$ $^4 J_{\text{NH}} = 1.8^b$ $^1 J_{\text{NH}} = 71.3$

<sup>a</sup> Or reversed.<sup>b</sup> Triplet (N<sup>-</sup> coupled with the 2' and 6' protons).

TSATrNN with DMAN were taken both at room temperature (300 K) and at 233 K. As shown in Table 2, the  $^{15}\text{N}$  data for this salt taken at 300 K do not reveal separate signals for the two nitrogen atoms (NH and N<sup>-</sup>). The value of 70.1 Hz for  $^1 J(^{15}\text{N}, ^1\text{H})$  of this salt at 300 K shows that the proton is localized on one of these two nitrogen atoms. At 233 K, two signals are observed in the ranges typical of NH and N<sup>-</sup> nuclei.<sup>4</sup> At both temperatures  $^{15}\text{N}$  signals due to DMAN and the three nitro groups are observed and are readily assigned.

From the  $^{13}\text{C}$  NMR data reported in Table 1 we note the value for  $^3 J(\text{C9}, \text{NH})$  of 3.8 Hz for the DMAN salts of TSATeNN. The corresponding values of  $^1 J(^{15}\text{N}, ^1\text{H})$  for the NH groups are 30.7 and 71.3 Hz in the two salts. Taken together, these spin-spin coupling data support the structures given in Table 2 for these two salts, namely, for the TSATeNN salt we find N1—H—N8<sup>-</sup> bonding and for the TSATrNN salt the corresponding situation is —N8—H and N1<sup>-</sup>. Thus we have a symmetrical hydrogen bonded structure in the first case and an unsymmetrical N8,N1 environment in the latter indicating that the potential hydrogen bond is weaker.

The present study using CD<sub>3</sub>CN as solvent produced results showing the presence of a symmetrical hydrogen bonded system N—H—N<sup>-</sup> and an unsymmetrical N—H—N<sup>-</sup> system on the NMR time-scale for salts of TSATeNN and TSATrNN, respectively, with DMAN. We have previously shown that a CD<sub>3</sub>CN solution of DMAN contains the symmetrical hydrogen bonded

structure<sup>3</sup> N—H—N<sup>+</sup>. These NMR results are in very good agreement with those of x-ray diffraction measurements taken on solid samples of the compounds studied here.<sup>6</sup>  $^1\text{H}$  NMR measurements also support the view of strong and weak hydrogen bonded systems for these molecules.<sup>1</sup>

## CONCLUSIONS

This work contains the first example of a  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR study of an internal hydrogen bonded system of the type N—H...N<sup>-</sup> ⇌ N<sup>-</sup>...H—N for the complex of TSATeNN with DMAN. Of particular importance in the study of such systems is the  $^{15}\text{N}$  NMR measurements of shielding and  $^{15}\text{N}$ — $^1\text{H}$  spin-spin couplings. Since the systems studied are examples of intramolecular hydrogen bonding, the value of  $^1 J(^{15}\text{N}, ^1\text{H})$  is reduced to about half its normal value on formation of the NHN<sup>-</sup> bonding system. Interactions  $^3 J(^{13}\text{C9}, \text{N1H})$  are also constructive in the study of these systems. Concerning to the complex of TSATrNN with DMAN, a different type of system (NH and N<sup>-</sup>) was observed which has a typical value of a one-bond  $^1 J(^{15}\text{N}, ^1\text{H})$  coupling constant for the NH group and high-frequency shift of the nitrogen signal N<sup>-</sup>. This very large deshielding effect after deprotonation is well known in the literature.<sup>7,8</sup>

## EXPERIMENTAL

The compounds studied were prepared by previously published procedures.<sup>1,9,10</sup> All of the NMR measure-

ments were recorded on a Bruker AM 500 machine. The dedicated  $^{15}\text{N}$  Bruker probe (10 mm tube) was employed for  $^{15}\text{N}$  NMR experiments and 5 mm  $^1\text{H}/^{13}\text{C}$  dual probe for  $^{13}\text{C}$  NMR measurements. The solution concentration used were *ca* 0.1–0.2 M. Either the deuterium signal of the solvent ( $\text{CD}_3\text{CN}$ ) or the signal of an external reference ( $\text{CD}_3\text{NO}_2$ ) were used as a lock.

*$^{15}\text{N}$  NMR measurements.* The  $^{15}\text{N}$  NMR spectra were recorded at a frequency of 50.698 MHz with a flip angle of *ca*  $45^\circ$ , a relaxation delay of 10 s, an acquisition time of *ca* 1.5 s and *ca* 5000 scans for INVGATE experiments, but the INEPT measurements were optimized for 90 Hz and separately 2.5 Hz coupling constants with a relaxation delay of 2 s and 500–2000 scans. Nitromethane was used as an external standard.

*$^{13}\text{C}$  NMR measurements.* The spectra were recorded at 125.76 MHz with a relaxation delay of 2 s and an acquisition time of 1.2 s. A flip angle of *ca*  $45^\circ$  was applied. The solvent peak (1.3 ppm) was used as a reference. About 2000 scans were acquired in order to obtain good quality spectra.

*$^1\text{H}$  NMR measurements.* The 500 MHz  $^1\text{H}$  NMR spectra were recorded from point the of view of the purity of the investigated compounds only. Water present in the acetonitrile solvent, dried over 3A molecular sieves, was checked by proton NMR measurements.

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