

A ^1H , ^{13}C and ^{15}N NMR investigation of three substituted DMAN derivatives and their monoprotonated salts†

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ABSTRACT: We report a ^1H , ^{13}C and ^{15}N NMR investigation of one symmetrically substituted 2,7-dichloro and two unsymmetrically substituted 2-chloro and 4-bromo DMAN [1,8-bis(dimethylamino)naphthalene] proton sponges and their protonated salts. From a consideration of the NMR data reported we conclude, that the most sensitive parameters for investigating compounds of this kind are $^1J(^{15}\text{N}-^1\text{H})$ and ^{15}N and ^1H chemical shifts for the nuclei in the $[\text{N}8-\text{H}-\text{N}1]^+$ bridge. A further significant NMR parameter is $^3J(^1\text{H}-^1\text{H})$ for the bridging proton and the $\text{N}(\text{CH}_3)_2$ protons. An analysis of the values of $^1J(^{15}\text{N}-^1\text{H})$ for the studied compounds is consistent with the view that in the investigated system equilibrium between two tautomeric forms occurs. A study at temperatures between 27 and -40°C , and a change of solvent, show that the values of the ^{15}N chemical shifts and couplings $^1J(^{15}\text{N}-^1\text{H})$ and $^3J(^1\text{H}-^1\text{H})$ for the $[\text{N}8-\text{H}-\text{N}1]^+$ bridge are essentially unchanged. This shows that the bonding arrangements of the bridge atoms are stable under these experimental conditions. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: substituted DMAN; protonation; ^1H , ^{13}C and ^{15}N NMR spectroscopy; proton sponge; $[\text{N}-\text{H}-\text{N}]^+$ bridge; $^1J(^{15}\text{N}-^1\text{H})$

INTRODUCTION

Previously we have reported ^1H , ^{13}C and ^{15}N NMR data for the symmetrical proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) (Fig. 1) and the unsymmetrical derivatives 4-nitro and 4-picryl, both as free bases and in their monoprotonated forms.^{3–8} It is the purpose of the present publication to extend our systematic investigation of proton sponges based upon DMAN. To this end we now report ^1H , ^{13}C and ^{15}N NMR data on the symmetrical compound 2,7-dichloro-DMAN and the unsymmetrically substituted 2-chloro and 4-bromo-DMAN, together with their monoprotonated forms.

RESULTS AND DISCUSSION

The ^1H , ^{13}C and ^{15}N NMR data for the three bases

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†We dedicate this paper to Professor José Elguero, in connection with his 65th birthday, especially because he is always interested in proton sponges, in particular in DMAN.^{1,2}

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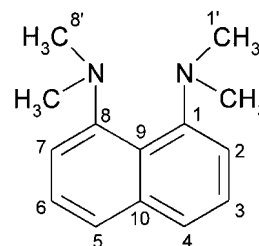


Figure 1. Formula of DMAN

studied, and their monoprotonated forms, are reported in Table 1. The ^1H , ^{13}C and ^{15}N NMR assignments given are based upon those published previously^{3–8} together with the observation of ^{13}C signal intensities, $^1\text{H}-^1\text{H}$ and $^{13}\text{C}-^1\text{H}$ couplings, correlation measurements taken between ^1H and ^{13}C signals, as well as between ^1H and ^{15}N , and INEPT experiments for ^{13}C and ^{15}N .

The distinctive features of the ^1H , ^{13}C and ^{15}N NMR data given in Table 1 permit a clear differentiation between the free bases and their monoprotonated forms. From a consideration of our previously reported results and those given in Table 1 we conclude that the most sensitive NMR chemical shifts for distinguishing between a given free DMAN type base and its monoprotonated form are the ^1H signal of the $[\text{N}8-\text{H}-\text{N}1]^+$

Table 1. ^1H , ^{13}C and ^{15}N NMR data of the DMAN derivatives studied (H = bridging proton)

Compound	Solvent	δ (^1H) (ppm)	δ (^{13}C) (ppm)	δ (^{15}N) (ppm)	J (Hz)
2,7-dichloro DMAN	DMF	H3 7.45, H4 7.72, H 1' 2.96	C1 146.2, C2 135.4, C3 129.1, C4 128.0, C9 135.6, C10 134.4, C1' 43.6	N -361.0	
2,7-dichloro DMAN *HBr	CD_3CN	H3 7.69, H4 8.04, H1' 3.36, H 20.1	C1 138.6, C2 132.9, C3 131.5, C4 132.2, C9 124.5, C10 134.0, C1' 43.1	N -349.4	1J (N-H) 33.0, 3J (H1'-H) 2.6
4-bromo DMAN	CDCl_3	H2 6.71, H3 7.53, H5 7.73, H6 7.36, H7 6.94, H1' 2.74, H8' 2.76	C1 150.4, C2 112.3, C3 129.3, C4 113.9, C5 119.9, C6 126.6, C7 112.9, C8 150.7, C9 120.9, C10 135.1, C1' 43.8, C8' 43.9	N1 -335.1, N8 -335.4	
4-bromo DMAN *HClO ₄	CD_3CN	H2 7.80, H3 8.05, H5 8.39, H6 7.84, H7 8.01, H1' 3.09, H8' 3.12, H 18.8	C1 145.7, C2 123.5, C3 132.3, C4 123.8, C5 129.5, C6 129.7, C7 123.7, C8 145.6, C9 121.7, C10 134.3, C1' 46.7, C8' 46.8	N1 -346.2, N8 -345.9	1J (N1-H) 29.4, 1J (N8-H) 34.6, 3J (H1'-H) 2.4, 3J (H8'-H) 2.7
2-chloro DMAN	DMF	H3 7.39, H4 7.55, H5 7.49, H6 7.36, H7 7.15, H1' 2.99, H8' 2.76	C1 145.1, C2 129.6, C3 128.0, C4 125.1, C5 122.7, C6 126.0, C7 115.4, C8 151.6, C9 125.8, C10 136.7, C1' 43.4, C8' 45.2	N1 -354.0, N8 -338.1	
2-chloro DMAN *HBr	DMF	H3 7.76, H4 8.21, H5 8.25, H6 7.83, H7 8.45, H1' 3.34, H8' 3.60, H 18.4	C1 141.1, C2 132.5, C3 130.6, C4 131.0, C5 130.8, C6 127.9, C7 123.5, C8 143.1, C9 122.4, C10 134.8, C1' 41.9, C8' 47.0	N1 -353.5, N8 -343.8	1J (N1-H) 9.1, 1J (N8-H) 53.7, 3J (H1'-H) 1.2, 3J (H8'-H) 4.0

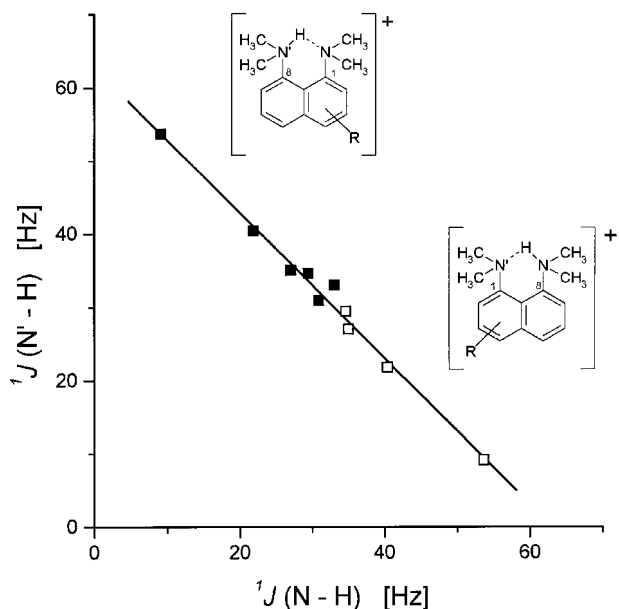


Figure 2. Experimental values of the one-bond coupling constant $^1J(\text{N}-\text{H})$ vs the second one-bond coupling constant $^1J(\text{N}'-\text{H})$ for protonated DMAN and its protonated derivatives studied at present and previously.^{7,8} (■) $^1J(\text{N8}-\text{H})$ vs $^1J(\text{N1}-\text{H})$; (□) $^1J(\text{N1}-\text{H})$ vs $^1J(\text{N8}-\text{H})$. Parameters of the fitted line: $y = Ax + B$, $A = -0.99 \pm 0.04$, $B = 62.8 \pm 1.3$ Hz, $R = -0.994$

bridging proton 18–20 ppm and the ^{15}N amino NMR signals which are changed by about 10 ppm upon protonation. More sensitive probes to protonation are provided by the $^1J(^{15}\text{N}-^1\text{H})$ and $^3J(^1\text{H}-^1\text{H})$ couplings of the bridging proton to its bonded nitrogen atoms and the $\text{N}(\text{CH}_3)_2$ protons respectively.

In the case of the 2,7-dichloro-DMAN we observe one value for each of the couplings $^1J(^{15}\text{N}-^1\text{H})$ and $^3J(^1\text{H}-^1\text{H})$: 33.0 Hz and 2.6 Hz, respectively. This is consistent with the view that the hydrogen atom in the $[\text{N8}-\text{H}-\text{N1}]^+$ bridge is equally bonded to the two nitrogen atoms.

The two protonated unsymmetrically substituted DMAN compounds both show two values for $^1J(^{15}\text{N}-^1\text{H})$ and two for $^3J(^1\text{H}-^1\text{H})$. In the case of the protonated 4-bromo-DMAN the two values of $^1J(^{15}\text{N}-^1\text{H})$ are very similar to each other, as are the two values of $^3J(^1\text{H}-^1\text{H})$. This is consistent with the view that the 4-bromo substituent is not a strong electron donating or withdrawing group. From the pairs of values for $^1J(^{15}\text{N}-^1\text{H})$ and for $^3J(^1\text{H}-^1\text{H})$ for this compound given in Table 1, it is apparent that the proton in the $[\text{N8}-\text{H}-\text{N1}]^+$ bridge is slightly more strongly bonded to N8 than it is to N1. This observation suggests that the overall influence of the 4-bromo substituent is a small electron withdrawing effect from DMAN.⁹

The data given in Table 1 for the protonated form of 2-chloro-DMAN reveal that the proton in the $[\text{N8}-\text{H}-\text{N1}]^+$ bridge is very unequally bonded to N1 and N8. The

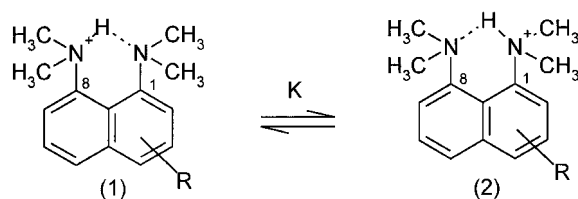


Figure 3. Equilibrium between two tautomeric forms of protonated DMAN and its protonated derivatives

values obtained for $^1J(^{15}\text{N}-^1\text{H})$ and $^3J(^1\text{H}-^1\text{H})$ indicate a much stronger N8–H bond than that for N1–H. This situation probably arises from the steric interaction between the 2-chloro substituent and the $\text{N1}-(\text{CH}_3)_2$ methyl groups, and in some part from I-inductive effect of the *ortho*-chlorine atom. Such an interaction could result in the N1 lone pair electrons becoming rotated into an unfavourable position for the formation of a bond with the $[\text{N8}-\text{H}-\text{N1}]^+$ bridging proton. A further consideration of the $^1J(^{15}\text{N}-^1\text{H})$ data given in Table 1 reveals that the sum of $^1J(^{15}\text{N8}-^1\text{H})$ and $^1J(^{15}\text{N1}-^1\text{H})$ for both the 4-bromo and 2-chloro unsymmetrically substituted protonated DMAN derivatives is approximately the same as twice the value observed for $^1J(^{15}\text{N}-^1\text{H})$ in the symmetrically substituted 2,7-dichloro compound, namely about 63 Hz. Similar comments apply to the relevant values of $^3J(^1\text{H}-^1\text{H})$ for these compounds. This shows a consistency between the three compounds studied in the total bond arrangement in the bridging $[\text{N8}-\text{H}-\text{N1}]^+$ group and to previous investigation by some of us.⁹

In Fig. 2 we have plotted values of the one-bond coupling constant $^1J(^{15}\text{N}-^1\text{H})$ as a function of the second one-bond coupling constant $^1J(^{15}\text{N}-^1\text{H})$ for protonated DMAN and its protonated derivatives investigated at present and previously.^{7,8}

We observe a linear relation, which satisfies the equation:

$$^1J(^{15}\text{N}'-\text{H}) = -^1J(^{15}\text{N}-\text{H}) + J_0, J_0 \approx 63 \text{ Hz} \quad (1)$$

This equation is a special case of the other one presented previously by Golubev *et al.*¹⁰ for these of a proton transfer equilibrium of the type $\text{A}-\text{H} \dots \text{B} \rightleftharpoons \text{A}^- \dots \text{H}-\text{B}^+$. The finding of the validity of Eqn. (1) is consistent with the view of a tautomeric equilibrium between two forms of proton sponges, i.e. one with a fully protonated N1 atom and the other with a fully protonated N8 atom, as illustrated in Fig. 3.

We have decided to further investigate the bonding in this group as a function of temperature and solvent. In Table 2 we report the results of $^1J(^{15}\text{N1}-^1\text{H})$ and $^1J(^{15}\text{N8}-^1\text{H})$ measurements for the protonated 4-bromo-DMAN in CD_3CN at temperatures ranging from 27 to -40°C , and in DMSO as solvent at 27°C .

The values observed for these two coupling interac-

Table 2. ^{15}N NMR data for protonated 4-bromo DMAN at different temperatures and with different solvents

Solvent	Temperature	δ (N1) (ppm)	δ (N8) (ppm)	1J (N1–H) (Hz)	1J (N8–H) (Hz)
CD_3CN	27°C	–346.2	–345.9	29.4	34.6
	–20°C	–346.2	–345.9	30.2	35.0
	–40°C	–346.2	–345.9	30.3	34.9
DMSO	27°C	–345.4	–345.2	29.9	34.5

tions are essentially unchanged both as a function of temperature and a change of solvent. This suggests that the bonding arrangement in the $[\text{N8–H–N1}]^+$ group is fairly stable under the studied conditions. This view is supported by the almost constant values reported in Table 2 for the N1 and N8 chemical shifts.

In conclusion we note the power of ^{15}N NMR measurements in the study of $[\text{N–H–N}]^+$ bridges. This is particularly the case for the 1J ($^{15}\text{N–}^1\text{H}$) data as shown both in the present investigation and in our previous reports.^{5,7,8}

EXPERIMENTAL

The compounds studied were prepared by previously published procedures (4-bromo,¹¹ 2,7-dichloro and 2-chloro¹² substituents). The ^1H , ^{13}C and ^{15}N NMR measurements were taken on a Bruker DRX spectrometer operating at 500 MHz for ^1H , 125 MHz for ^{13}C and 50 MHz for ^{15}N . Standard operating conditions were employed to obtain the reported NMR data. The ^1H and ^{13}C NMR chemical shifts are reported with respect to TMS and the ^{15}N chemical shifts are given with respect to external neat nitromethane. The solvents used were dried over molecular sieves. The protonated form of the DMAN derivatives studied was prepared by the addition of 1 mol of acid to 1 mol of the DMAN base.

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