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LETTERS

Carbon-13 NMR Relaxation Study of 1,8-Bis(dimethylamino)naphthalene in Isotropic Solution

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Carbon-13 nuclear spin relaxation in 1,8-bis(dimethylamino)naphthalene (DMAN) was investigated in a dimethylformamide-d_7 solution. In addition, the chemical shielding tensors were measured in the crystalline powder. Detailed analysis of ^{13}C longitudinal relaxation in this molecule yielded its rotational diffusion tensor. Comparison to the protonated form of DMAN, DMANH$^+$, leads to conclusions concerning interaction of the latter with its counterion.

1. Introduction

In a recent communication, we reported a ^{13}C NMR relaxation study on the protonated form of 1,8-bis(dimethylamino)naphthalene (DMAN) in solution.[1] For that compound, i.e. DMANH$^+$, we determined the components of its rotational diffusion tensor (RDT) with quite high accuracy, which was generally better than 10%. Using these results, we managed to assess the lower limit of the rate of stochastic dynamics of the proton within the N···H···N bridge, on the basis of ^{15}N NMR relaxation data for the nitrogens engaged in the bridge. Here, we report ^{13}C NMR relaxation measurements, for the unprotonated form of DMAN. We have used the same experimental conditions, i.e., the solvent, temperature range, concentration, etc., as in the previous study; thus a direct comparison of the results obtained for both the samples is possible. The main purpose of the present study is to provide comparative material enabling one to get some insight into details of interaction of DMANH$^+$ with its counterion.

Below we present experimental details of our current study, followed by new results and their discussion in the context of the data previously published for DMANH$^+$. The theoretical background of the data processing can be found in our previous paper, ref 1.

2. Experimental Details

N,*N*,*N*′,*N*′-Tetramethyl-1,8-naphthalenediamine was purchased from Fluka and purified by 2-fold recrystallization from pentane at 248 K. A 0.15 M solution in DMF-d_7 was sealed in a 5 mm NMR sample tube under an atmosphere of inert gas.

The ^{13}C relaxation rates were measured at temperatures of 303 (magnetic fields of 14.1, 11.7 and 9.4 T), 293 (9.4 T), 283 (14.1, 11.7 and 9.4 T), 273 (9.4 T), 263 (9.4 and 11.7 T), 243 (14.1 and 9.4 T), 228 (14.1 and 9.4 T) and 213 K (14.1 and 9.4 T), using a Varian Unity Inova 600 MHz, Bruker Avance 500 MHz, and Bruker Avance 400 MHz spectrometers. The direct proton-decoupled carbon-detected, fast inversion−recovery experiments[2] were performed. Typical parameters were as follows: 64 scans for each of the 16 incremented delays, spectral widths between 110 and 135 ppm, acquisition times between 1.5 and 2.5 s, and 90° pulses between 7 and 10 μs. The recycle delay was always longer than 2 times the longest T_1. All the experiments were repeated at least twice. We judge the overall accuracy of the measured spin−lattice relaxation rates to be 3−5%.

All the spectrometers were equipped with variable temperature units allowing for temperature control with an accuracy of 0.1 K. Temperature calibration was carefully performed using a methanol chemical shift thermometer.[3] Both the gas flow and decoupling power were carefully controlled,[4] to diminish temperature gradients in the sample. Spectrometers were stabilized for at least 2 h before the measurements were commenced.

Components of the RDT of DMAN in the whole temperature range of interest were obtained from a least-squares iterative analysis of the relaxation data, which was performed using a Fortran routine written in-house, based on the Newton−Raphson algorithm.

The components of the ^{13}C chemical shielding tensors needed for the interpretation of the relaxation data were obtained from solid-state experiments performed on solid DMAN at a field of 7.04 T on a Bruker Avance II 300 MHz spectrometer, using a 4 mm double-resonance VTN MAS probe. The ^{1}H decoupling field strength corresponded to the nutation frequency of 50 kHz.

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The recycle delay and $^1H-^{13}C$ cross-polarization (CP) contact time were 30 s and 2 ms, respectively. The mass of the powder sample for the solid-state NMR experiments was approximately 50 mg. The principal components of the ^{13}C chemical shielding tensors were determined from simultaneous numerical analysis of spinning sidebands patterns in a set of 5 1D-CP/MAS spectra acquired under sample rotation frequencies of 10.0, 4.5, 3.0, 2.5 and 2.0 kHz, respectively. An in-house written Newton–Raphson Fortran routine for the least-squares minimization was used in this case as well. A set of the fitted parameters comprises baseline positions and spinning frequencies in consecutive spectra, intensities of individual resonances, Lorenzian and Gaussian line broadenings, isotropic chemical shieldings, anisotropic shieldings and asymmetries of CSA tensors. The details of this procedure will be described in a forthcoming article.

Directions of the principal axes of the ^{13}C CSA tensors cannot be determined using simple MAS experiments performed on powder samples. The tensor orientations can be detemined, for example, by using the rotational resonance R2 method,[5] but the task is experimentally challenging and time-consuming. Therefore, the angles relevant for the relaxation data analysis were obtained from relatively facile quantum-mechanical calculations on a DFT level.[6] The molecular geometry for the calculations was taken from neutron diffraction;[7] the basis sets for carbon and hydrogen atoms were IGLO-II,[8] and the IGLO-III basis was used for the nitrogen atoms. The exchange-correlation potential was PW91.[9,10] Some of the angles were imposed by the average C_{2v} symmetry of the molecule.

3. Results and Discussion

The starting point for the analysis of relaxation data is a knowledge of the strengths of the relaxation interactions. In the case of spin-$^1/_2$ nuclei such as ^{13}C, the relevant interactions are dipolar spin–spin couplings and anisotropic parts of chemical shielding tensors. The former are functions of internuclear distances and can be estimated if the geometry of the molecule is known. However, if a higher accuracy is needed, a determination of the dipolar couplings becomes a nontrivial task, because the effective internuclear distances which should be used for calculations are influenced by vibrational motions.[11–14] In the course of our former investigations on DMANH$^+$, we succeeded in determining these vibrational corrections at low temperatures, where the spin system of interest was outside the extreme narrowing regime. The relaxation rates are given as products of the interaction strengths and reduced spectral densities[15] and the individual factors can only be evaluated under such conditions. The dynamic behavior of the unprotonated DMAN molecules, investigated presently, falls within or close to the extreme narrowing regime in the whole temperature range. Hence, a determination of the vibrational corrections could not be possible in this case. This difficulty was circumvented by exploiting the effective dipolar couplings determined for DMANH$^+$,[1] rescaled by the ratios of third powers of the respective $^{13}C-^1H$ distances for DMAN and DMANH$^+$, measured in crystals.[7,16] Because the proton-carbon bond lengths in both the molecules are not very different, such a procedure appears to be well justified. Specifically, as the relevant dipolar coupling values for carbons 2, 3 and 4 (see Figure 1), we take 20.9, 20.7 and 20.7 kHz, respectively. For the sake of accuracy we took also into account the long-range dipolar couplings whose magnitudes were calculated directly from the solid-state geometry without vibrational corrections (which are practically irrelevant for long-rang interactions).

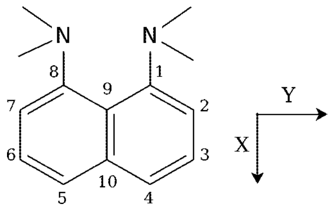

Figure 1. Directions of principal axes of the RDT in the DMAN molecule.

As already mentioned in the Experimental Details, the ^{13}C CSA tensors, which in the case of aromatic systems can substantially contribute to the relaxation rates, were determined in crystalline powder of DMAN, by iterative fits to a set of ^{13}C CP/MAS spectra. The principal components of all of the determined CSA tensors, and the corresponding principal directions relevant for further numerical analysis are shown in Table 1. For the sake of completeness, we also list the isotropic shieldings with respect to TMS (note that these quantities have the opposite sign with respect to the "delta" scale chemical shifts), but the latter parameters are not relevant for analysis of relaxation data. Our isotropic shifts agree well with the results of Woźniak,[17] who presented a detailed discussion on these quantities and their changes upon protonation. Although similar analysis of individual tensor components is beyond the scope of the present paper, we note briefly their very high sensivity to protonation. An extreme example is carbon-9, whose signal moves upfield by about 3 ppm only, and changes in its individual CSA components approach 50 ppm. Components of other tensors respond milder, but changes by 15–20 ppm (carbons 1, 8, 2, 7, 4 and 5) are usual.

To evaluate the relaxation contributions of the chemical shielding anisotropy, one commonly assumes that the CSA tensors are not seriously affected by the dissolution/solvation processes. However, in the course of analysis of the relaxation data we noticed that this assumption was not valid for carbon-9 which links both the aromatic rings of the naphthalene moiety. This feature is probably a consequence of repulsion of the electronic pairs of nitrogen atoms, which in a crystal causes significant distortion of the "natural" planarity of the naphthalene fragment. The effect does not of course occur in solution, where the local dynamics of the NMe_2 fragments imposes the average C_{2v} symmetry on the whole molecule. For this reason we excluded relaxation rates of carbon-9 in the course of further numerical analysis. The other naphthalene carbons whose relaxation rates were not taken into account, were carbon-1 and carbon-8. We rejected the corresponding data for two reasons: (i) the carbon nucleus suffers considerable dipolar coupling to its direct neighbor, the ^{14}N nucleus, which aggravates evaluation of its CSA tensor; (ii) its relaxation behavior can be seriously affected by the complex local dynamics of the methyl groups.

Having settled the issue of interactions strength, we turn now to the carbon-13 relaxation data (the full set of experimentally determined spin–lattice relaxation rates is available in the Supporting Information) and their analysis in terms of molecular dynamics. We use the same dynamic model as in the DMANH$^+$ paper;[1] i.e., we treat the molecule as a rigid anisotropic rotational diffusor.[15,18,19] In the calculations of the CSA contributions, the nonaxially symmetric tensors were decomposed into pairs of axially symmetric tensors.[19–21] The numerical results of the analysis are shown in Table 2, and in Figure 2 they are visualized in the form of Arrhenius plots. First, we see that, at each temperature, the components of the RDT come with relative standard errors generally not exceeding 10%. Second, we see in Figure 2 that the results are consistent in the whole temperature range.

TABLE 1: Experimental ^{13}C Chemical Shielding Tensors[a]

atom no.	σ_{iso} (ppm)	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	θ_{33}, φ_{33}[b] (deg)	θ_{11}, φ_{11} (deg)
1,8[c]	−149.0	21.6 ± 0.3	74.4 ± 0.3	−96.0 ± 0.5	−, −	−, −
2,7[d]	−111.1	17.0 ± 0.6	81.9 ± 0.5	−98.9 ± 0.4	0, −	90, 38
	−112.2	15.3 ± 0.3	83.4 ± 0.3	−98.6 ± 0.2	0, −	90, 38
3,6	−123.6	6.6 ± 0.2	99.6 ± 0.1	−106.3 ± 0.2	0, −	90, 143
4,5	−121.3	−2.6 ± 0.4	−85.5 ± 0.3	88.1 ± 0.3	90, 101	0, −
9[c]	−120.0	11.8 ± 0.2	84.4 ± 0.2	−96.2 ± 0.2	−, −	−, −
10	−136.3	62.0 ± 4.3	67.4 ± 4.3	−129.4 ± 0.3	0, −	−, −
CH_3[c,e]	−40.3	17.1 ± 5.3	19.6 ± 5.3	−36.8 ± 0.2	−, −	−, −
	−43.7	15.7 ± 1.4	23.1 ± 1.4	−38.8 ± 0.2	−, −	−, −

[a] The principal components were extracted from solid-state MAS measurements of DMAN powder. The polar coordinates used in the course of relaxation data analysis are shown. Polar angles are imposed by the average C_{2v} symmetry of the molecule; azimuthal angles are calculated at the DFT level. Standard errors are given for σ_{11}, σ_{22} and σ_{33}, while accuracy of σ_{iso} is limited by spectral resolution which was about 25 Hz/pt. [b] θ denotes the polar angle with respect to the Z axis of RDT, and φ denotes the azimuthal angle with respect to the X axis of this tensor. [c] Relaxation rates of these nuclei were neglected in the course of RDT estimation. [d] There are two resonances from nonequivalent carbons 2 and 7 of a single molecule in the solid state. [e] There are two resonances from nonequivalent methyl carbons of a single molecule in the solid state.

TABLE 2: RDT Components D_X, D_Y, and D_Z Delivered by the Newton−Raphson Fitting Routine

T (K)	10^{-9} D_X (s^{-1})	10^{-9} D_Y (s^{-1})	10^{-9} D_Z (s^{-1})
303	8.69 ± 0.43	6.29 ± 0.39	11.78 ± 0.59
293	7.03 ± 0.28	4.92 ± 0.25	11.26 ± 0.47
283	6.22 ± 0.33	4.51 ± 0.30	8.34 ± 0.45
273	5.03 ± 0.16	3.60 ± 0.14	7.57 ± 0.24
263	4.08 ± 0.27	2.89 ± 0.24	5.82 ± 0.39
243	2.49 ± 0.29	1.76 ± 0.26	3.41 ± 0.38
228	1.48 ± 0.16	1.01 ± 0.15	2.12 ± 0.21
213	0.86 ± 0.04	0.59 ± 0.04	1.03 ± 0.05

The DMAN molecule generally tumbles faster than its protonated form. Comparing the RDT elements for $DMANH^+$ and DMAN, we obtain at 303 K the ratios of 1.6, 2.5 and 3.2, respectively, for the X, Y and Z components of RDTs. At 213 K, the corresponding ratios are 1.7, 4.5 and 6.4. The obtained activation energies, $E_X^a = 13.7 \pm 0.3$, $E_Y^a = 13.9 \pm 0.4$, $E_Z^a = 14.6 \pm 0.6$, can be compared to the respective values of 14.5 ± 0.2, 17.4 ± 0.8 and 18.3 ± 0.5 kJ/mol for $DMANH^+$. We see that although E_X^a remains practically unaffected by protonation, the remaining activation energies increase by 3.5 and 3.7 kJ/mol, respectively. This comparison suggests strongly that a mere protonation of the molecule, despite of introducing a charge to it, does not cause dramatic modifications of its solvation sphere. Actually, the observed modification of the reorientational behavior can be rationalized if the interaction of $DMANH^+$ with the counterion, NO_3^-, is considered. The latter is presumably located near the place where the positive charge is cummulated, i.e., near the proton bridge, or, in other words, on the X-axis. This may be the reason why diffusion around that axis remains practically the same for both species, DMAN and $DMANH^+$. Reorientations about the two remaining axes will be affected by the interaction within the ion pair, if it exists on the time scale of the molecular tumbling i.e. longer than 10^{-10} s.

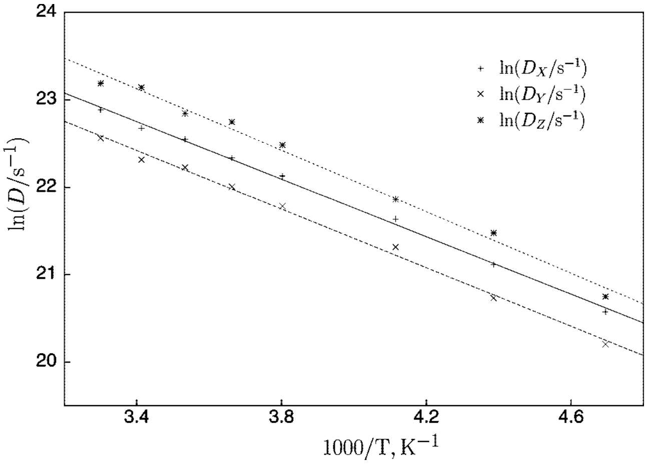

Figure 2. Arrhenius plot for components of the RDT of DMAN. The activation energies extracted from the slopes of these lines are 13.7 ± 0.3, 13.9 ± 0.4 and 14.6 ± 0.6 kJ/mol for tumbling about X, Y and Z axes, respectively.

The considerations of this paper should be looked at from a wider perspective. By and large, NMR relaxation studies on the RDTs in solutions have the potential of revealing details of some subtle solvent−solute interactions that are difficult or even impossible to be elucidated by other methods. In this context, it is worth quoting a recent paper by Kotsyubynskyy and Gryff-Keller,[22] where a comparison of the diffusion tensors for two structurally similar objects led the authors to quite unexpected conclusions regarding such interactions.

4. Conclusions

Analysis of longitudinal relaxation rates measured at several magnetic fields in a wide temperature range on a solution of 1,8-bis(dimethylamino)naphthalene yielded detailed information about the RDT of the molecule. Comparison to similar, already published data on its protonated form led us to observe that changes in reorientation of the DMAN molecule under protonation are caused by formation of ion pairs rather than by charge-amplified interaction with solvent.

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Supporting Information Available: Experimental and calculated ^{13}C relaxation rates. This material is available free of charge via the Internet at http://pubs.acs.org/.

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