Two Ground State Conformers of the Proton Sponge 1,8-Bis(dimethylamino)naphthalene Revealed by Fluorescence Spectroscopy and ab Initio Calculations

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Abstract: The $S_1 \leftrightarrow S_0$ transitions of the “proton sponge” 1,8-bis(dimethylamino)naphthalene have been studied by experiment and ab initio calculations. Fluorescence excitation and single vibronic level emission spectroscopy on the sample seeded in a supersonic expansion lead to the conclusion that the molecule can adopt two conformations in the ground state. This conclusion is supported by ab initio calculations at the HF/6-31G* level. The most stable conformer is shown to carry the spectroscopic characteristics of the naphthalene chromophore, while torsional motions of the dimethylamino groups dominate the spectroscopy of the other conformer.

I. Introduction

Bi-center nitrogen bases which combine an exceptionally high basicity with a low nucleophilic character are called “proton sponges”.[1,2] The best-known representative is 1,8-bis(dimethylamino)naphthalene, henceforth called DMAN. Its basicity is exceptionally high ($pK_a = 12.1$)[3] and its gas-phase proton affinity (1030.1 kJ/mol)[4] is among the highest for aromatic bases. Among the diamino systems the proton sponges are characterized by the presence of two nearby nitrogens which can share a proton to form a strong intramolecular hydrogen bond. Apparently, the high basicity of the proton sponges depends on the proximity of these two nitrogens, and it has been discussed in terms of the changes on protonation of the repulsion between the nitrogen lone pairs, of the molecular strain, and of the energy of solvation.[5]

Several reviews have been published on the proton sponges and their monoprotonated cations.[1,2,8−11] The crystal and molecular structure of DMAN have been determined by X-ray diffraction.[12] It was shown that the molecule is strained with a large deviation of the naphthalene skeleton from planarity. The central C−C bond is twisted so that the $N(CH_3)_2$ groups are on different sides of the naphthalene plane, with their nitrogen atoms lying 0.4 Å above and below this plane. Via rotation about the $C_{aryl}{-}N$ bonds, the dimethylamino groups assume a conformation where one of the methyl carbons in each of the two groups is practically located in the plane of the ring and the nitrogen lone pairs avoid the destabilizing overlap as far as possible. Protonation causes the molecule to become more planar, and the insertion of the proton into DMAN brings about the formation of a six-membered ring where the N···N distance changes from 2.5 Å[6] to 2.71 Å. Relief of electron repulsion seems to be a driving force for protonation. Computed ab initio geometries of DMAN and its protonated form have recently been reported.[13] The isolated molecule was predicted to approximate C_2 symmetry with a distinctly nonplanar $N{-}(C_{10}H_6){-}N$ fragment, similar to that derived from the X-ray crystallographic data.[12]

In the past few years one of us (A.S.-H.) has been involved in extensive studies of the solution spectra of DMAN in a range of solvents of different polarity.[14] From the puzzling results it seemed that in certain solvents one is dealing with a mixture of two species, and the same appeared to be true when the low-temperature emission spectra of glassy solutions were investigated.[15] At first impurities were suspected, but this suspicion

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(1) Staab, H. A.; Saupe, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27,* 865.

(2) Alder, R. W. *Chem. Rev.* **1989**, *89*, 1215.

(3) Hibbert, F. J. *J. Chem. Soc., Perkin. Trans.* **1974**, *2,* 1862.

(4) Lou, Yan K.; Saluja, P. P. S.; Kebarle, P.; Alder, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7328.

(5) Perakyla, M. *J. Org. Chem.* **1996**, *61*, 7420.

(6) Pyzalska, D.; Pyzalski, R.; Borowiak, T. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 211.

(7) Brzezinski, B.; Glowiak, T.; Grech, E.; Malarski, Z.; Sawka-Dobrowolska, W.; Sobczyk, L. *J. Mol. Struct.* **1993**, *299*, 1.

(8) Alder, R. W. *Tetrahedron* **1990**, *46*, 683.

(9) Llamaz-Saiz, A. L.; Foces-Foces, C.; Elguero, J. *J. Mol. Struct.* **1992**, *273*, 183.

(10) Bakshi, P. K.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1996**, *74*, 201.

(11) Brzezinski, B.; Glowiak, T.; Grech, E.; Malarski, Z.; Sobczyk, L. *Croat. Chem. Acta* **1992**, *65*, 101.

(12) Einspar, H.; Robert, J. B.; Marsh, R. E.; Roberts, J. D. *Acta Crystallogr.* **1973**, *B29*, 1611.

(13) Platts, J. A.; Howard, S. T.; Wozniak, K. *J. Org Chem.* **1995**, *59*, 4647.

(14) Szemik-Hojniak, A.; Rettig, W.; Herbich, J.; van der Waals, J. H.; Allonas, X. To be submitted for publication.

(15) Unpublished results.

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was all but eliminated by renewed experiments with thoroughly dried samples and solvents of various origin. Hence we turned to an investigation of the molecule under isolated conditions by fluorescence excitation spectroscopy on samples seeded in a supersonic expansion.

Here we present the results of the latter experiments performed at the University of Amsterdam, which demonstrate that in the beam two species are present. On the basis of the observed temperature dependence of the fluorescence excitation spectrum these two species are attributed to two conformations the DMAN molecule can adopt in the electronic ground state. To get insight into the possible nature of these conformers ab initio calculations were performed at the HF/6-31G* level. The results of these calculations support the idea of the existence of two conformations differing little in energy (*i.e.*, probably $<kT$ at room temperature) but substantially in structure. The optimized geometries of the two conformers are compared to the crystallographic data[12] and the previously calculated[13] structure. The conformational changes on excitation of DMAN are discussed on the basis of the vibronic structure in the fluorescence excitation spectrum and single vibronic level emission spectra assigned to each of the ground state conformers.

II. Experimental Details

The experimental setup for performing fluorescence excitation and dispersed emission spectroscopy on samples seeded in a continuous supersonic jet expansion has been described in detail elsewhere.[16,17] Briefly, excitation light was obtained from a XeCl excimer laser (Lambda Physik EMG103MSC) working at a repetition rate of 40 Hz, which pumped a dye laser (Lumonics HyperDye-300) operating on PTP or DCM. In the case of DCM the output of the dye laser was frequency-doubled by using an angle-tuned BBO crystal in an Inrad Autotracker II unit. The intensity of the excitation light was monitored by measuring the intensity of a reflection with an EG&G radiometer model 580, which was read out by a computer controlling the experiment.

This excitation beam was steered into the vacuum chamber, where it crossed at right angles a continuous free jet made by expanding 4 bar of He seeded with the vapor of the DMAN sample heated to 120−180 °C through a nozzle with a diameter of 100 μm. Excitation of the jet occurred at a distance of 10 nozzle diameters, *i.e.*, 1 mm, from the nozzle. Fluorescence was collected at right angles with respect to the excitation light and the molecular beam by a spherical quartz condenser (Melles Griot 01MCP119, diameter 50 mm, focal length 50 mm) and imaged onto the slit of a Zeiss M20 grating monochromator equipped with an EMI 9558 QA (S20) photomultiplier.

In the fluorescence excitation experiments the monochromator was used in first order with a slit width of 3 mm (spectral resolution 15 nm) and set at a wavelength of 365 nm. The output of the photomultiplier was integrated by using a boxcar integrator (SR250), whose output was read out and averaged by the computer. In a typical experiment excitation spectra were obtained by scanning the dye laser in steps of 0.25 cm^{-1}, averaging over 60 laser pulses, and dividing the fluorescence signal by the laser intensity as measured by the radiometer. For some of the relevant bands observed in the excitation spectra single vibronic level emission spectra have been recorded. In these experiments the photomultiplier was cooled down to −78 °C with a mixture of ethanol and dry ice in order to reduce the dark current. Emission spectra were obtained by scanning the monochromator with a slit width of 0.1 mm, resulting in a resolution of about 45 cm^{-1}, and averaging the signal over 1200 laser pulses.

DMAN was purchased from Aldrich. Experiments have been performed on samples as received, but also from samples which had been sublimed under vacuum prior to use. In all cases the same experimental results have been obtained.

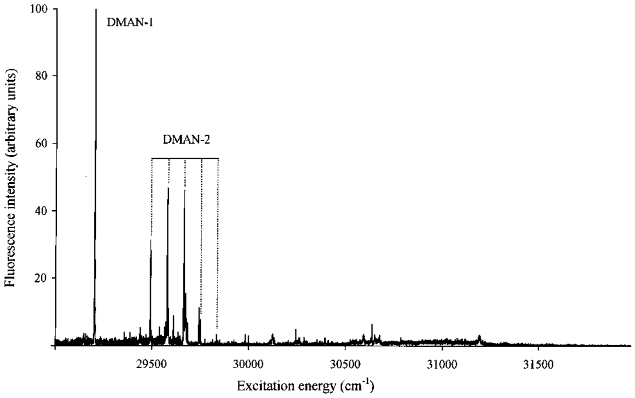

Figure 1. Fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ transition of 1,8-bis(dimethylamino)naphthalene. The spectrum shows evidence for the presence of two conformations of the molecule in the electronic ground state. The first conformer, designated as DMAN-1, has an excitation spectrum whose 0_0^0 transition is found at 29 203 cm^{-1}, while the excitation spectrum of the second conformer, designated as DMAN-2, displays the indicated progression built upon a 0_0^0 transition at 29 492 cm^{-1}.

III. Results and Discussion

A. Fluorescence Excitation Spectroscopy. It is well-known from studies in solution that the quantum yield for emission from the first excited singlet state of DMAN is rather low (of the order of 10^{-3}).[14] In our studies the sample, consequently, had to be heated to relatively high temperatures to obtain excitation spectra with an acceptable signal-to-noise ratio. In Figure 1 the fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ transition of DMAN heated to 165 °C and seeded in a supersonic expansion is depicted. This spectrum has been constructed by linking two consecutive scans over the wavelength ranges accessible by the PTP and DCM dyes and linearly scaling the intensities from one scan with respect to the other, using bands present in both scans. The spectrum might seem deceivingly simple, since it is dominated by an apparent 0_0^0 transition at 29203 cm^{-1} with a large number of bands of lower intensity at higher excitation energies. Closer inspection of the spectrum, however, reveals the presence of a progression with an average spacing of 86 cm^{-1} starting at 289 cm^{-1} above the 0_0^0 transition and formed by the medium intense bands at 29 493, 29 580, 29 667, and 29 752 cm^{-1} and the weak band at 29 835 cm^{-1}. The transition energies of these bands and their intensity distribution—in particular the higher intensity of the 29 580 cm^{-1} band with respect to the 29 493 cm^{-1} band—are at odds with an assignment that relates them to the electronic transition whose vibrationless transition occurs at 29 203 cm^{-1}, but might be rationalized if one assumes that they derive from the transition to the first excited singlet state of another “species” with a 0_0^0 transition at 29 493 cm^{-1}. The intensity distribution would then suggest that for this species excitation to the first excited singlet state is accompanied by relatively large geometry changes along the relevant vibrational coordinate. It is of interest to notice that the $S_1 \leftarrow S_0$ excitation spectra of dimethylaniline (DMA) and 3- or 4-cyano- or trifluoromethyl-substituted dimethylanilines exhibit a similar progression in the dimethylamino torsional vibration,[18] albeit with a slightly lower frequency and considerably more anharmonic. For these molecules displacements of 30−40° along the dimethylamino twist coordinate were calculated on the basis of Franck−Condon

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(16) Wegewijs, B. R, Ph.D. Thesis, University of Amsterdam, 1994.

(17) Zwier, J. M.; Wiering, P. G.; Brouwer, A. M.; Bebelaar, D.; Buma, W. J. *J. Am. Chem. Soc.* **1997**, *119*, 11523.

(18) Grassian, V. H.; Warren, J. A.; Bernstein, E. R.; Secor, H. V. *J. Chem. Phys.* **1989**, *90*, 3994.

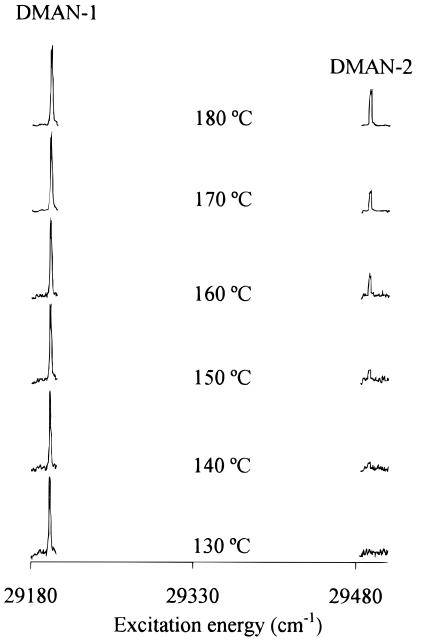

Figure 2. Temperature dependence of the relative intensities of the 0_0^0 transitions of DMAN-1 at 29 203 cm^{-1} and DMAN-2 at 29 492 cm^{-1}.

analyses. The observation that in the present case the maximum intensity occurs earlier in the progression suggests smaller geometry changes upon excitation than in (substituted) DMA. The assignment of the previously discussed bands to a second species implies that the vibronic bands built upon the 29 203 cm^{-1} transition are of minor intensity (less than 10% of the 0_0^0 transition) and, concurrently, that the molecular geometry of the first species is considerably less affected by excitation.

We thus conclude that the excitation spectrum shown in Figure 1 contains contributions from two separate excitation spectra, one with a 0_0^0 transition at 29 203 cm^{-1} (henceforth referred to as DMAN-1) and one with a 0_0^0 transition at 29 493 cm^{-1} (DMAN-2). These two excitation spectra might in principle be associated with different conformations of the molecule in the ground state or with excitation from one common conformation in the ground state to two different conformations in the excited state. The observed temperature dependence of the fluorescence excitation spectrum provides evidence for the presence of two different conformations in the *ground state* of the molecule. Figure 2 displays the temperature dependence of the transition intensities of the two 0_0^0 bands at 29 203 and 29 493 cm^{-1} when the sample is heated stepwise from 130 to 180 °C. The spectra show that at a temperature of 130 °C the intensity of the 29 493 cm^{-1} band can hardly be measured, while at 180 °C the intensities of the two bands are in the ratio of 2:1. This observation argues against the presence of two conformations in the excited state reached from a common ground state since then the intensities of the two bands should be more or less independent of the temperature. The fit of the ratio of the transition intensities of the two 0_0^0 bands to the expression $\exp(-\Delta E/RT)$ leads to a value of 0.1−0.2 kcal/mol for the parameter ΔE. One might be tempted to identify this parameter with a ground state energy difference between the two conformations or with an activation energy for the interconversion of the two species, but the non-equilibrium conditions under which the supersonic expansion of the sample occurs make such an identification questionable.

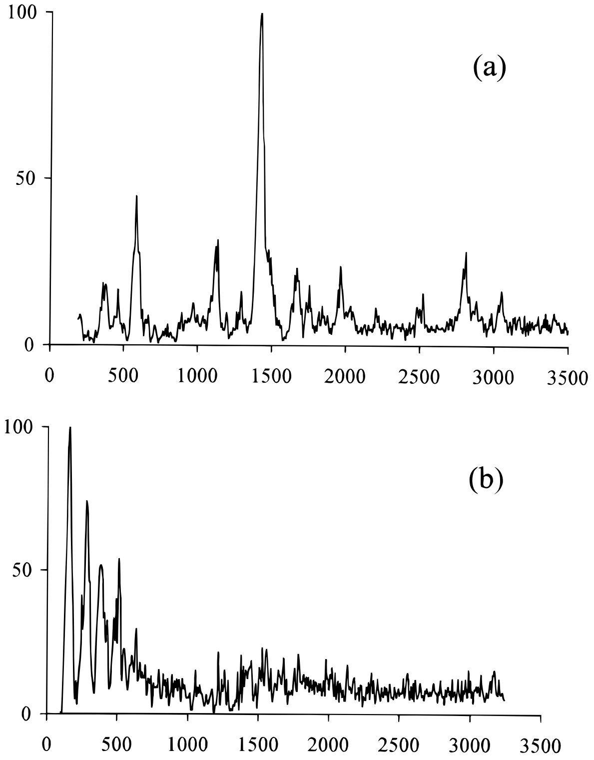

Figure 3. Emission spectra obtained by excitation of (a) DMAN-1 at 29 203 cm^{-1} and (b) DMAN-2 at 29 492 cm^{-1}. Emission wavelengths are given as shifts (cm^{-1}) from the excitation wavelength.

Previously we concluded that on excitation the species giving rise to the 0_0^0 transition at 29 493 cm^{-1} (DMAN-2) suffers a relatively large geometry change, while the geometry of DMAN-1 by comparison is significantly less affected. Emission spectra obtained on excitation of either of the vibrationless levels in the first excited singlet state of the two species corroborate this conclusion and give further information on the nature of the two transitions. Figure 3a displays the emission spectrum obtained by excitation at 29 203 cm^{-1}. Because of the low quantum yield for emission, the vibrationless transition was buried in the stray light and could not be recorded; the remainder of the spectrum carries all the characteristics of the emission spectrum of a substituted naphthalene molecule whose photophysical properties are primarily determined by the naphthalene chromophore (see, for example, ref 19). The dominant band at 1417 cm^{-1} and the bands of lesser intensity at 373, 584, and 1125 cm^{-1} all correspond to deformation vibrations of the naphthalene ring, coupled in some cases with torsional τ(CCH) and τ(DMA) modes having frequencies that agree well with those observed in IR and Raman spectra.[20] The emission spectrum obtained on excitation at 29 493 cm^{-1}, by contrast, is dominated by transitions to low-frequency vibronic levels with hardly any intensity in the 1400 cm^{-1} region. This, indeed, is what would be expected on the basis of the excitation spectrum, where such an activity was also observed for the low-frequency vibration of 85 cm^{-1}. Both the excitation and emission spectra thus indicate that the spectroscopic properties of DMAN-1 are similar to those of substituted naphthalenes, while those of DMAN-2 are dominated by geometry changes along torsional coordinates.

B. Ab Initio Calculations. The experimental studies described above provided evidence that DMAN can adopt two different conformations in its electronic ground state. In

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(19) Johnson, J. R.; Jordan, K. D.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1990**, *93*, 2258.

(20) Szemik-Hojniak, A.; Hanuza, J.; Bursi, R.; Buma, W. J.; van der Waals, J. H. To be submitted for publication.

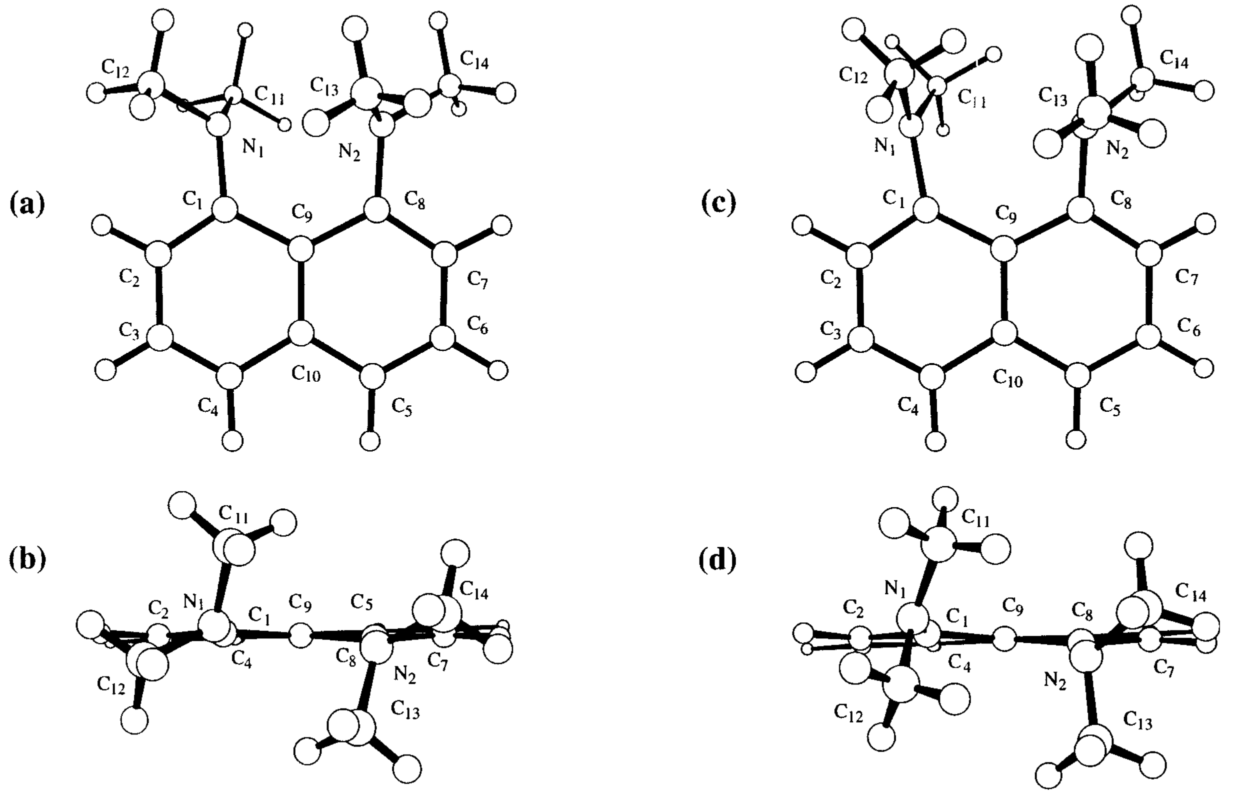

Figure 4. Structures associated with the two stable minima found on the potential energy surface of the electronic ground state of 1,8-bis-(dimethylamino)naphthalene. The structure depicted in (a) (top view) and (b) (side view) is assigned to DMAN-1, while the structure depicted in (c) (top view) and (d) (side view) is assigned to DMAN-2.

previous X-ray[12] and ab initio studies at the HF/6-31G level,[13] however, only one conformer has been identified. To substantiate our experimental findings, we performed ab initio calculations at the Hartree–Fock level employing the Gaussian 94 program[21] to probe the possible conformations of DMAN. Instead of using the 6-31G basis set, we have employed the 6-31G* basis set since previous calculations on amino substituted compounds have demonstrated that polarization functions are essential for a correct description of the wave functions of these species.[22,23]

The present calculations indeed yield two minima on the potential energy surface of the ground state. These minima correspond to the structures depicted in Figure 4. The relevant geometrical parameters of the two structures are reported in Table 1 and compared with the parameters obtained in the crystallographic studies and previous calculations. The two extrema could be shown to be stable minima by force field calculations, and differ in energy (corrected for the zero-point vibrational energies) by 4.7 kcal/mol ($\sim$1650 cm^{-1}).

The conformer of lowest energy closely resembles the structure found in the X-ray and ab initio studies at the HF/6-31G level. Though it is known that at the Hartree–Fock level it is rather difficult to calculate the energy difference between conformers accurately, it is generally observed that the predicted ordering is correct. We assign this conformer therefore to DMAN-1, the conformer of lowest energy of the previous section. Figure 4 and Table 1 show that it possesses an approximate C_2 symmetry with differences in the bond lengths and valence angles between the two halves of the naphthalene ring not exceeding 0.001 Å and 0.1°, respectively. The other conformer resulting from the calculation which should then be assigned to DMAN-2, has no symmetry and exhibits significantly larger differences within the naphthalene system. For instance the C_1-C_9 bond length is 1.448 Å, while the corresponding bond length C_9-C_8 in the other half of the naphthalene system is 1.442 Å. Similarly $C_9C_1C_2$ and $C_9C_8C_7$ angles of 118.9° and 119.9°, respectively, are found. It is interesting to note that in Einspar's work[12] a conformation resembling that assigned here to DMAN-2 was put forward as one of the possibilities to achieve a compromise between steric restrictions and resonance interactions between the dimethylamino groups and the naphthalene ring.

The final geometry of the molecule should to a large extent be determined by the overlap between the lone-pair orbitals of the two nitrogen atoms and the steric repulsion between the two dimethylamino groups.[12] In DMAN-1 the positions of the methyl groups are described by two almost equal dihedral angles $C_9C_1N_1C_{\mathrm{methyl}}$ and $C_9C_8N_2C_{\mathrm{methyl}}$ of $-74.6°$ and $-74.7°$, leading to a situation in which the N_1-C_{12} and N_2-C_{14} bonds are almost in the plane of the naphthalene system, while the other two $N-C_{\mathrm{methyl}}$ bonds are almost perpendicular to this plane. From the $C_{\mathrm{methyl}}NC_{\mathrm{methyl}}$ and the $C_{\mathrm{methyl}}NC_{\mathrm{aryl}}$ angles we conclude that in this conformation the two nitrogen atoms have a hybridization between sp^3 and sp^2, which is different from the sp^2 hybridization suggested on the basis of both the X-ray and the 6-31G structure. In DMAN-2 the orientation of the methyl groups

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(21) Gaussian 94, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Reprogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A., Gaussian Inc.: Pittsburgh, PA, 1995.

(22) Boggs, J. E.; Niu, Z. *J. Comp. Chem.* **1985**, *6*, 46.

(23) Bock, C. W.; George, P.; Trachtman, M. *Theor. Chim. Acta* **1986**, *69*, 235.

Table 1. Selected Geometrical Parameters of DMAN-1 and DMAN-2 (Å and deg)

	DMAN[a,c]	DMAN[b]	DMAN-1[c]	DMAN-2[c]	naphthalene[b]
C_1-C_2	1.383, 1.373	1.372	1.366, 1.367	1.367, 1.365	1.363
C_2-C_3	1.387, 1.410	1.407	1.410, 1.409	1.410, 1.410	1.415
C_3-C_4	1.337, 1.333	1.356	1.352, 1.351	1.352, 1.352	1.363
C_4-C_{10}	1.419, 1.408	1.419	1.420, 1.420	1.419, 1.420	1420
C_9-C_{10}	1.425	1.424	1.419	1.422	1.413
C_1-C_9	1.429, 1.449	1.447	1.450, 1.450	1.448, 1.442	1.420
C_1-N_1	1.395, 1.399	1.416	1.418, 1.417	1.420, 1.430	
N_1-C_{11}	1.458, 1.458	1.451	1.451, 1.450	1.440, 1.454	
N_1-C_{12}	1.467, 1.465	1.456	1.445, 1.445	1.439, 1.451	
$C_9-C_1-C_2$	119.4, 118.6	119.4	119.4, 119.3	118.9, 119.9	120.8
$C_1-C_2-C_3$	121.4, 121.4	122.3	122.4, 122.4	123.0, 122.4	120.2
$C_2-C_3-C_4$	120.7, 121.0	119.7	119.6, 119.6	119.1, 119.1	120.2
$C_3-C_4-C_{10}$	120.5, 120.3	120.5	120.4, 120.4	120.6, 120.8	120.8
$C_4-C_{10}-C_9$	120.0, 120.5	120.7	120.9, 120.9	120.9, 120.7	119.0
$C_{10}-C_9-C_1$	117.0, 117.2	117.1	117.0, 117.1	117.0, 116.7	119.0
$C_1-C_9-C_8$	125.8	125.9	125.9	126.3	122.0
$C_4-C_{10}-C_5$	119.5	118.6	118.2	118.4	122.0
$C_9-C_1-N_1$	120.8, 120.1	121.6	120.9, 120.9	126.3, 120.6	
$C_1-N_1-C_{11}$	118.5, 118.0	119.1	114.3, 114.4	119.5, 111.6	
$C_1-N_1-C_{12}$	117.1, 117.2	117.5	117.4, 117.4	120.9, 111.5	
$C_1-C_2-C_3-C_4$	3.0, 3.0	2.7	2.3, 2.2	3.4, 3.0	0.0
$C_3-C_4-C_{10}-C_9$	−1.1, −2.4	−1.5	−1.1, −1.2	1.6, −1.6	0.0
$C_4-C_{10}-C_9-C_1$	8.9, 10.5	6.2	4.9, 4.9	6.6, 6.3	0.0
$C_{10}-C_9-C_1-C_2$	−10.9, −11.8	−6.5	5.0, −5.1	−6.6, −6.5	0.0
$C_{10}-C_9-C_1-N_1$	168.5, 167.9	172.2	174.1, 174.5	169.0, 168.8	
$C_9-C_1-N_1-C_{11}$	162.7, 160.9	148.8	151.3, 151.2	94.9, 137.6	
$C_9-C_1-N_1-C_{12}$	−59.4, −60.6	−67.1	−74.6, −74.7	−61.8, −93.5	

[a] Reference 12. [b] Reference 13. [c] In case of double entries the first entry gives the value of the distance or angle denoted in the first column, while the second entry gives the corresponding value in the other half of the naphthalene system.

around N_2 is similar to that in DMAN-1 ($C_9C_8N_2C_{13}$ and $C_9C_8N_2C_{14}$ angles of −93.5° and 137.6°) but around N_1 the methyl groups are oriented differently (here the $C_9C_1N_1C_{11}$ and $C_9C_1N_1C_{12}$ angles are 94.9° and −61.8°). As a result the hybridization of N_2 now tends to be approximately sp^3, but N_1 is to a good approximation of sp^2 hybridization. From the point of view of repulsion, the relative orientation of the two lone-pair orbitals is more favorable in DMAN-2 than in DMAN-1, but in DMAN-2 the methyl groups attached to N_1 interfere more with N_2 than in DMAN-1, leading to a larger $N_1 \cdots N_2$ distance in DMAN-2 (2.96 Å) than in DMAN-1 (2.79 Å).

The ab initio calculations thus corroborate our experimental results. The conformer of lowest energy has an approximate C_2 symmetry and gives rise to an $S_1 \leftarrow S_0$ excitation spectrum resembling that of substituted naphthalenes, while excitation of the nonsymmetric conformer induces significant changes in the orientation of the dimethylamino groups with respect to the naphthalene ring. Presently, these remarkable differences are investigated in more detail along two paths. On the one hand, IR and Raman spectra are being assigned on the basis of force field calculations.[20] This study should also allow us to obtain a more detailed assignment of the vibronic bands observed in the fluorescence excitation spectrum. On the other hand, we are engaged in a further investigation of the spectroscopic properties of the two conformers by ab initio calculations on the electronic character, the equilibrium geometry, and the force field of the first excited singlet state.

IV. Conclusions

Fluorescence excitation spectroscopy on supersonic beam expansions has been used to investigate the photophysical properties of DMAN. From the vibronic intensities in the excitation spectrum and the temperature dependence of this spectrum it was concluded that DMAN adopts at least two conformations in its electronic ground state. Both the excitation spectra of these two conformations and the single vibronic level emission spectra demonstrate that the most stable conformation gives rise to spectra which resemble those of substituted naphthalene derivatives, while torsional motions involving the dimethylamino groups dominate the $S_1 \leftarrow S_0$ and $S_1 \rightarrow S_0$ transitions of the conformation of higher energy. Ab initio calculations have confirmed the experimental observations: two stable minima have been found on the potential energy surface of the electronic ground state. The conformer of lowest energy has a geometry with approximately C_2 symmetry and is in good agreement with the structure found in X-ray and previous ab initio calculations. The other conformer does not have any symmetry and is characterized by a difference in hybridization of the two nitrogen atoms.

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