

Theoretical study of the dimethylamino radical $(\text{CH}_3)_2\text{N}$ and its protonated cation $(\text{CH}_3)_2\text{NH}^+$

M.-B. Huang, H.U. Suter, B. Engels *

Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

Received 29 November 1993

Abstract

In the present work the dimethylamino radical $((\text{CH}_3)_2\text{N})$ and its protonated cation $((\text{CH}_3)_2\text{NH}^+)$ are investigated by means of ab initio methods. The geometries of various conformations of both compounds are obtained with UMP2/6-31G** calculations, while the hyperfine structure and its dependence on the geometry is studied using the MRD-CI/ B_K method. The two molecules are compared to study the influence of the protonation on geometry and hyperfine structure. The effects of the rotational barriers on the hyperfine structures of $(\text{CH}_3)_2\text{N}$, $(\text{CH}_3\text{CH}_2)_2\text{N}$ and $((\text{CH}_3)_2\text{CH})_2\text{N}$ will be discussed.

1. Introduction

ESR spectroscopy is a powerful tool that provides valuable information on the spin distribution in free radicals. It is based on the magnetic hyperfine interaction which describes the interaction between the electron spin (S) and the spins of the various nuclei (I_N). The magnetic hyperfine interaction consists of an isotropic part, A_{iso} , which is proportional to the spin density at the given nucleus, and an anisotropic part, which describes the dipole–dipole interaction between I_N and S and has the form of a second rank tensor [1]. Since the interaction occurs at each nucleus with a non-vanishing spin I_N , a map of the spin distribution over the whole molecule can be obtained from ESR spectra.

While the ab initio calculation of anisotropic hyperfine coupling constants (hfcc's) is simple, a reliable prediction of the isotropic hfcc's, A_{iso} , is still a very difficult task. The difficulties arise because the dominant contributions to A_{iso} are typically a mixture of

correlation and polarization effects, often summarized as “spin polarization effects” [2]. Moreover, a balanced description of the correlation of the inner and the valence shells is necessary because in many cases the two contributions are similar in magnitude but differ in sign. The RHF method is inappropriate because it neglects spin polarization effects completely. UHF calculations overestimate the magnitude of isotropic hfcc's by a factor of two or more [2]. The use of spin projected UHF calculations (UHFAA) normally yield in too small values.

In configuration interaction (CI) calculations, it is important to account for higher excitations [2–6]. In the multi-reference CI (MR-CI) approach, A_{iso} depends strongly on the number of reference configurations and, if configuration-selected MR-CI calculations are performed, the number of variationally handled configurations is also crucial for the description of A_{iso} . However, using a non-selecting MR-CI approach for the description of A_{iso} is a very expensive alternative to the configuration selected MR-CI method, since the number of electrons and the number of reference con-

* Corresponding author.

figurations are very large as compared to “standard problems”. Despite all these problems *ab initio* calculations of ESR parameters are desirable because the interpretation of ESR parameters is doubtful if simple orbital models are used, due to the spin polarization effects.

In recent studies [7–10] it has been shown that the configuration selected MR-CI approach can be used for reliable calculation of isotropic hfcc's if the indirect influence of the neglected configurations is taken into account perturbationally, using the modified B_K treatment [7,11].

The present study is devoted to the dimethylamino radical $(\text{CH}_3)_2\text{N}$ and its protonated cation $(\text{CH}_3)_2\text{NH}^+$. It is part of our systematic investigation on radicals containing one nitrogen atom, such as NH_2 [12], H_2CN [9], $(\text{CH}_2)_2\text{N}$, $(\text{CH}_2)_2\text{NH}^+$, and the cyclic compounds $\text{C}_3\text{H}_6\text{N}$ and $\text{C}_3\text{H}_6\text{NH}^+$ [10]. The first investigation on the neutral compound $(\text{CH}_3)_2\text{N}$ was carried out by Hadly and Volman [13] who concluded that the unpaired electron resides in a sp^3 hybrid orbital, based on the large isotropic hfcc's measured for the nitrogen center (32 G). Different results were reported by Danen and Kensler [14] who observed a far smaller isotropic hfcc (14.78 G) for the nitrogen center. In their interpretation the nitrogen center is sp^2 hybridized and the unpaired electron occupies the nitrogen p -orbital perpendicular to the C–N–C plane. To the best of our knowledge no *ab initio* studies for the hyperfine structure for the neutral radical exist.

The hfcc's in the radical cation $(\text{CH}_3)_2\text{NH}^+$ were also measured by Danen and Richard [14] and the results were confirmed by Fessenden and Neta [15]. In both studies $A_{\text{iso}}(^{14}\text{N})$ is about 20 G, while the values of approximately 22 and 34 G are found for the α hydrogen and the β hydrogens, respectively. For the radical cation the hfcc were also interpreted by assuming the sp^2 hybridization of the nitrogen center [14,16]. In their second paper Danen et al. compared the radical $(\text{CH}_3)_2\text{N}$ to its protonated cation $(\text{CH}_3)_2\text{NH}^+$. While the higher isotropic hfcc's of the β protons (27.36 versus 34.27 G) were attributed to hyperconjugation effects, the reason for the trend seen for $A_{\text{iso}}(^{14}\text{N})$ (14.78 to 19.28 G) was unclear.

For the radical cation Bonazzola et al. [17] calculated the hyperfine structure using UHF and UHFAA methods. The geometry was optimized with an UHF/4-31G calculation. Their calculations confirmed the

experimental finding as to the electronic structure but, as they already stated in their own study, the calculated isotropic hfcc's turned out to be too inaccurate.

In the present work the equilibrium geometries of various conformations, their electronic structures and hyperfine structures, and the dependence of the hyperfine structure on the geometry are investigated for $(\text{CH}_3)_2\text{N}$ and $(\text{CH}_3)_2\text{NH}^+$. The influence of the protonation on geometry and hyperfine structure is studied. The influence of the rotational barriers on the hyperfine structures of $(\text{CH}_3)_2\text{N}$, $(\text{CH}_3\text{CH}_2)_2\text{N}$ and $((\text{CH}_3)_2\text{CH})_2\text{N}$ will be addressed.

2. Methods of calculation

For the present investigation the AO basis sets were constructed based on Chipman's studies [2,18]. They consist of Huzinaga's (9s5p) and (4s) basis sets for the heavy atoms and the hydrogens, respectively, and were contracted to [4s2p] and [2s] [19]. For a reliable description of the spin polarization effects each AO basis was augmented by diffuse functions (one s and one p functions for the heavy atoms, and one s function for hydrogen). Bauschlicher et al. [20] have shown that the inclusion of one diffuse function saturates the (sp) space. Additionally one s function with a very high exponent was added at each center. The corresponding exponents are as follows: N: 0.0667, 0.0517, 40030.9; C: 0.0479, 0.0358, 28191.9; and H: 0.0483, 88.675 [18]. In addition, one d function each was placed at the heavy centers (N: 0.8; C: 0.7). The total number of the basis functions is thus 91 for $(\text{CH}_3)_2\text{NH}^+$ and 87 for $(\text{CH}_3)_2\text{N}$.

The calculations for the hyperfine structures, using the configuration selected MR-CI approach and a modified B_K correction [7,11], were performed with a modified version of the MRD-CI program package of Peyerimhoff and Buenker [21] using the Table CI algorithm [22]. The reference configurations in the calculations were selected according to two criteria. First, the squared coefficients of the reference configurations should be larger than 0.001 in the final wavefunctions, and secondly, their importance in the spin density matrix was analyzed.

The reference spaces of the final calculations included 14–16 configurations. The sizes of the total MR-CI spaces varied between 9 and 13 million config-

Table 1
UMP2/6-31G** optimized geometries and energies for the conformations A, B and C of the dimethylaminium radical^a and dimethylamino radical^a

Conformation	(CH ₃) ₂ NH ⁺			(CH ₃) ₂ N		
	A	B	C	A	B	C
R(N–C1)	1.439	1.441	1.439	1.442	1.443	1.446
			1.439			1.441
R(C–H1)	1.082	1.082	1.083	1.093	1.086	1.094
			1.082			1.086
R(C–H3)	1.092	1.091	1.091	1.092	1.095	1.091
			1.091			1.095
R(N–H7)	1.020	1.019	1.019			
∠C1NC2	125.9	122.7	123.6	114.6	110.6	111.6
∠NC1H1	110.1	110.1	110.2	115.0	110.2	115.1
			109.9			110.5
∠NC1H3	108.3	108.3	108.4	108.7	110.9	108.6
			108.2			110.8
∠H1C1H3	111.1	110.9	111.1	108.8	108.9	108.8
			111.1			109.0
⟨S ² ⟩	0.765	0.765	0.765	0.762	0.761	0.761
E + 134.0	−0.44198	−0.44152	−0.44214	−0.07808	−0.08090	−0.07976

^a See Figs. 1a and 1b for notation. Conformation C (C_s) is obtained by rotation of one CH₃ group in A by 60°. Distances in Å, angles in degrees and energies in hartree, 1 hartree = 627.51 kcal/mol.

urations. The number of selected configurations treated in the configuration selected MR-CI calculations was around 25 000–30 000. To obtain faster convergence of the CI expansion all calculations were performed using natural orbitals (NOs) as the one-particle basis set. The NOs were obtained from a preceding MR-CI calculations.

In recent studies [6,9] it was shown that to obtain reliable hfcc's using configuration selected MR-CI calculations it is necessary to include the influence of the discarded configurations onto the coefficients of the single excitations with respect to the main configuration. Therefore it is necessary to include all single excitations into the B_K treatment. The relaxation of the coefficients of higher excitations is of less importance so that an inclusion of those configurations into the B_K treatment having coefficients larger than 0.035 were found to be sufficient [10]. Therefore in addition to the single excitations all configurations having a coefficient larger than 0.035 were also included in the B_K correction. This treatment incorporates the important part of the spin polarization effects. Further improvements, e.g. increasing the number of selected configurations and/or the number of the configurations

corrected within the B_K treatment, lead to only small changes in A_{100} . A detailed description of the various effects is given elsewhere [6–9].

2.1. Geometry optimization

All geometry optimizations were performed using the Gaussian90 program [23]. The optimized geometrical parameters from UMP2/6-31G** calculations and the total energies for the conformations A, B and C of (CH₃)₂NH⁺ and (CH₃)₂N are given in Table 1. The eclipsed conformations A and B are sketched in Figs. 1a and 1b. The staggered conformation C, which is the energetically lowest rotamer ($\Delta E \leq 1$ kcal/mol), is obtained from A by rotating one methyl group by 60°. As expected the differences in energy are quite small, so the CH₃ groups in both molecules can rotate almost freely. Comparing the optimized geometrical parameters of both compounds, only the C–N–C angles differ considerably ($\approx 10^\circ$). The larger N–C₁–H₁ angle found in conformation A of (CH₃)₂N is a consequence of the smaller ∠CNC value. It results from the repulsion between the two hydrogen centers H₁ and H₂.

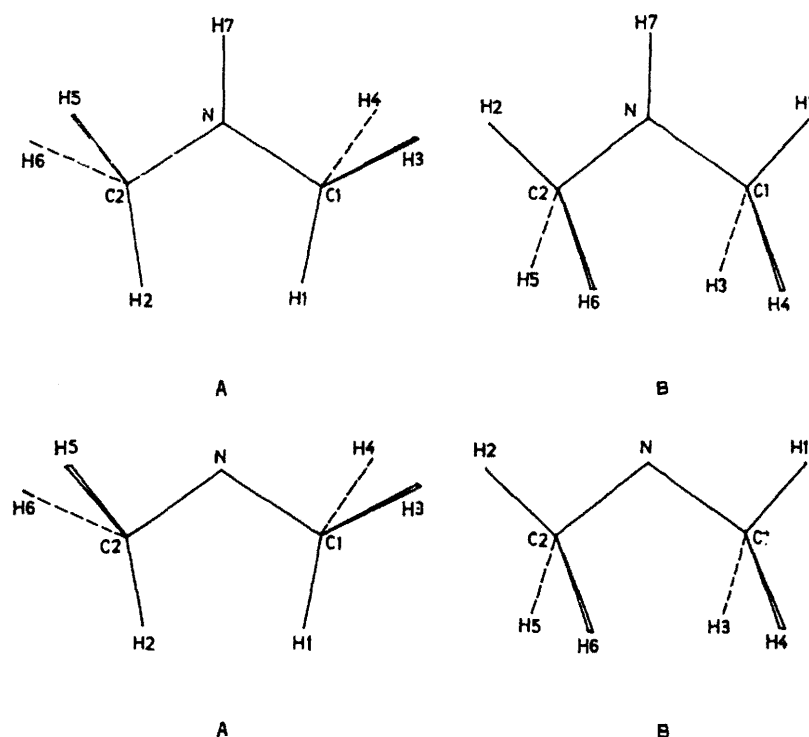


Fig. 1. Conformations A and B (C_{2v} symmetry) for $(CH_3)_2NH^+$ and $(CH_3)_2N$.

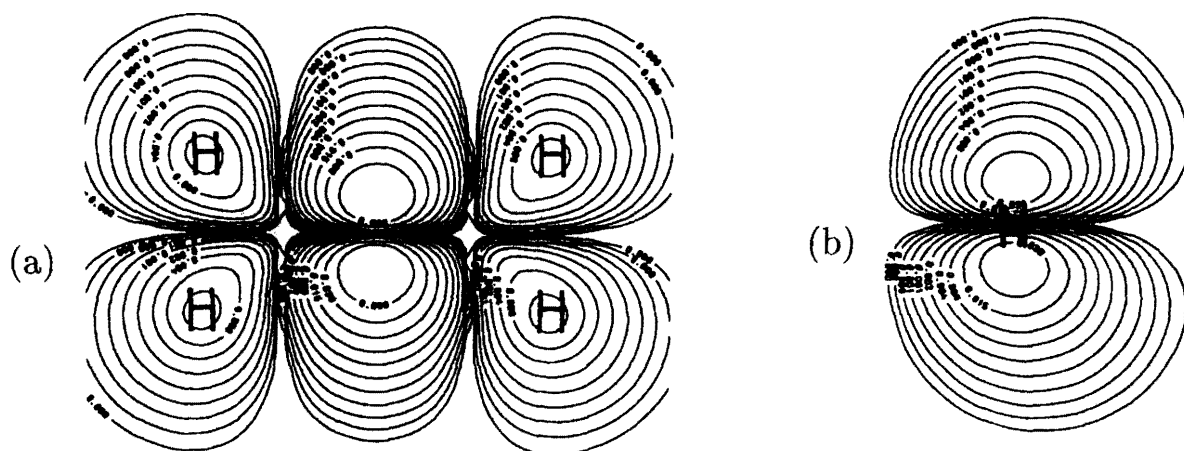


Fig. 2. Charge density contours of the singly occupied orbital (SOMO) $2b_1$ of $(CH_3)_2NH^+$ (X^2B_1 ground state): (a) Cut through the plane spanned by the four hydrogens. (b) Cut through the xz plane (for the definition of the molecular coordinate system see text).

The main configurations of both compounds are equivalent. Rotamers A and B have both C_{2v} symmetry. Assuming the z axis along the N–H bond and the CNC plane to coincide with the yz plane, the electronic ground state of both rotamers is X^2B_1 . The main configuration is $[\dots]6a_1^2 4b_2^2 1a_2^2 2b_1^1$. Rotamer C has a sim-

ilar electronic structure, but in C_s rather than in C_{2v} symmetry. The singly occupied orbital (SOMO) of the radical cation and the neutral radical is the slightly distorted p orbital of the nitrogen center perpendicular to the N–C–N plane. This was assumed by Danen et al. [14,16] and for the radical cation already mentioned

Table 2

Calculated isotropic hyperfine coupling constants (in G) for the dimethylaminium radical cation in the rotamers A^a and B^a

Conformation center	A		B		Exp. ^b	Exp. ^c
	MRD-CI	MRD-CI/ B_K	MRD-CI	MRD-CI/ B_K		
N	12.7	21.5	13.1	21.0	19.28	19.23
C	-10.0	-11.6	-10.0	-10.8		
H _α (H7)	-19.3	-24.0	-20.1	-24.8	22.73	21.96
H1	-0.3	0.0	-0.1	0.1		
H3	36.0	41.1	34.1	39.0		
$\langle H_\beta \rangle^d$	23.9	27.4	22.7	26.0	34.27	33.61

^a See Fig. 1a for notation.^b Danen et al. [16]; only absolute values given.^c Fessenden et al. [15].^d Averaged value assuming free rotation of the methyl groups.

by Bonazzola et al. [17]. The shape of the SOMO is depicted in Fig. 2. Fig. 2a shows a cut through the four hydrogens H3–H6 (see Fig. 1 for the labels of the various atoms) and Fig. 2b contains a charge density plot in the xz plane (perpendicular to the CNC plane, see above). The shapes of the SOMOs of the two molecules are very similar, so that only the SOMO of the radical cation $(\text{CH}_3)_2\text{NH}^+$ is shown. As expected the SOMO of the cation is found to be more compact in size.

2.2. Calculation of the hyperfine coupling constants

The isotropic hfcc's obtained in the present study along with measured hfcc's reported by Danen et al. [14,16] and by Fessenden [15] are given in Tables 2 ($(\text{CH}_3)_2\text{NH}^+$) and 3 ($(\text{CH}_3)_2\text{N}$). We have only calculated the hyperfine structures for conformations A

and B, since as will be discussed below, no further insight is to be gained from the calculation of conformer C. In the present work no effects arising from the nuclear motion are taken into account. These effects can be important [24–26] but for the present molecule will only affect the hfcc's of the β hydrogens to some extent as can be seen from experimental [27] and theoretical [10] results about the $\text{C}_3\text{H}_6\text{N}/\text{C}_3\text{H}_7\text{N}^+$ system.

Let us first focus on the radical cation (Table 2). Due to the shape of the SOMO (Fig. 2), $A_{\text{iso}}(^{14}\text{N})$ is solely determined by spin polarization effects. As for $\text{C}_3\text{H}_6\text{NH}^+$ [10] $A_{\text{iso}}(^{14}\text{N})$ increases by nearly 100% when the indirect effect of the neglected configurations is taken into account via the B_K correction. The MRD-CI/ B_K calculations slightly overestimate the isotropic hfcc of the nitrogen center. This is due to the basis set

Table 3

Calculated isotropic hyperfine coupling constants (in G) for the dimethylamino radical in the rotamers A^a and B^a

Conformation center	A		B		Exp. ^b	Exp. ^c
	MRD-CI	MRD-CI/ B_K	MRD-CI	MRD-CI/ B_K		
N	8.3	13.3	7.6	13.0	14.78	15.65
C	-11.7	-14.0	-11.3	-13.4		
H1	-0.2	-0.1	-0.3	0.0		
H3	29.0	32.6	26.9	30.4		
$\langle H_\beta \rangle^d$	19.3	21.7	17.9	20.2	27.36	28.48

^a See Fig. 1b for notation.^b Danen et al. [14]; only absolute values given.^c Fessenden et al. [15].^d Averaged value assuming free rotation of the methyl groups.

deficiencies, as discussed in ref. [10] $A_{\text{iso}}(^{14}\text{N})$ is found to depend little on the geometry (conformation A and B). This was also seen earlier for the ring compounds $\text{C}_3\text{H}_6\text{NH}^+$ and $\text{C}_3\text{H}_6\text{N}$. Like $A_{\text{iso}}(^{14}\text{N})$, $A_{\text{iso}}(^{13}\text{C})$ and $A_{\text{iso}}(^1\text{H}_\alpha)$ are a result of spin polarization effects. $A_{\text{iso}}(^1\text{H}_\alpha)$ is also somewhat overestimated, as was found for $A_{\text{iso}}(^{14}\text{N})$.

According to the empirical $\cos^2\theta$ rule [28] two different kinds of β hydrogens can be distinguished. If the molecule is considered to be in a single conformation A, B or C, those β hydrogen atoms lying in the C–N–C plane have very small isotropic hfcc's while the isotropic hfcc's of all other β hydrogens are very large. This difference arises from the fact that the isotropic hfcc's of the β hydrogens in the C–N–C plane are only influenced by spin polarization effects (which are nearly zero for $(\text{CH}_3)_2\text{NH}^+$), while the SOMO makes large contributions for the remaining β protons (see below). However, as found for other molecules the corresponding isotropic hfcc's of conformations A and B are similar, which indicates that the $\cos^2\theta$ expression provides a suitable description for $(\text{CH}_3)_2\text{NH}^+$. Since in conformation C the relative positions of the β protons with respect to the SOMO are similar to those in conformations A and B, the isotropic hfcc's in conformation C will be almost equal to those in conformations A and B.

Since in practice the rotation of the methyl group cannot be frozen, our theoretical values have to be averaged for the comparison with the experimental data. In Table 2 the averaged values are listed as $\langle H_\beta \rangle$. The deviation from the experimental value is about 6 G. While experimental uncertainties arise from solvent effects [15], theoretical errors due to inaccuracies in the equilibrium geometries or the neglect of higher excitations, as discussed in detail for the H_2CN molecule [9] and the ring structures $\text{C}_3\text{H}_6\text{NH}^+$ and $\text{C}_3\text{H}_6\text{N}$ [10], are the reason for the remaining discrepancies. Furthermore, averaging over other nuclear motions than the rotation of the CH_3 groups may have to be considered.

Similar trends are found for the neutral dimethylamino radical $(\text{CH}_3)_2\text{N}$ (Table 3). Again, the B_K correction improves the isotropic hfcc values considerably. In contrast to the radical cation the theoretical $A_{\text{iso}}(^{14}\text{N})$ values are somewhat lower than the experimental values. However, solvent effects are found to be stronger for the neutral radical than for the

cation [15]. The averaged isotropic hfcc's of the β protons are about 5–6 G lower than the experimental results, as was also the case for the radical cation. The isotropic hfcc's of the radical cation are found to be significantly larger than those of the neutral species.

2.3. Discussion

Both experiment and theory find the isotropic hfcc's of the protonated species to be 5–6 G larger than those of the neutral radical. In order to explain the differences spin polarization effects were analyzed in detail. An estimate of the influence of a doubly occupied shell on the isotropic hfcc's can be obtained, by comparing the result of a core calculation in which the orbital under consideration is frozen (no excitations are allowed out of the given orbital) to the isotropic hfcc's from an all-electron calculation. The results are given in Table 4. The first line shows the hfcc's calculated with an all-electron CISD calculation, while the other hfcc's are obtained by freezing the given orbitals. The procedure can only give trends since the interaction between doubly occupied shells is not properly accounted for. Let us first focus on the nitrogen center. $A_{\text{iso}}(^{14}\text{N})$ is determined by spin polarization effects (RHF value is zero) as mentioned above. The largest difference in $A_{\text{iso}}(^{14}\text{N})$ between the radical cation and the neutral radical is found when the $5a_1$ (Fig. 4) or the $6a_1$ (Fig. 3) is frozen. For example $A_{\text{iso}}(^{14}\text{N})$ of the radical cation drops by 4 G if no excitation are allowed out of the $6a_1$. The same procedure causes an increase of about 2 G for the neutral radical. Allowing no excitation out of the $5a_1$ $A_{\text{iso}}(^{14}\text{N})$ decreases by about 12 G in the neutral species but only 4 G in the protonated compound. The different behaviour of $A_{\text{iso}}(^{14}\text{N})$ reflects the different nature of these orbitals in each molecule. The influence of all other orbitals on $A_{\text{iso}}(^{14}\text{N})$ are almost the same in both compounds. It is worth noting that also the $1a_1$ which is the 1s orbital of the nitrogen center also contributes strongly to $A_{\text{iso}}(^{14}\text{N})$.

For the β hydrogens the isotropic hfcc's of the radical cation and those of the neutral radical differ by about 7–9 G. At the RHF level a difference of about 5 G is found, i.e. most of the effect results from the more compact form of the SOMO of the radical cation. Spin polarization effects contributes by about 30% to 40% for $A_{\text{iso}}(^1\text{H}_1)$, however large differences in the contributions of the various shells cannot be seen.

Table 4
Summary of the core calculations performed to study spin polarization effects (all values are in gauss)

MO ^a	C ₂ H ₆ NH ⁺				C ₂ H ₆ N		
	N	C	H _β	H _α	N	C	H _β
– ^b	11.7	–10.0	35.9	–18.7	8.0	–11.5	28.8
	correlation of the valence shell						
6a ₁	9.4	–10.2	36.6	–14.7	9.7	–10.8	29.4
5a ₁	7.3	–11.0	35.3	–15.8	–4.3	–14.1	28.8
4a ₁	–3.6	–13.3	36.8	–6.4	–2.9	–13.2	29.2
3a ₁	6.0	–1.2	35.4	–17.6	3.4	–2.9	28.4
1b ₁	13.4	–10.2	29.6	–20.3	9.3	–11.7	23.6
4b ₂	13.3	–9.4	35.7	–20.4	9.6	–9.5	28.8
3b ₂	13.4	–10.7	36.0	–19.0	9.4	–12.5	28.9
2b ₂	13.0	–5.5	34.8	–19.6	9.1	–7.2	28.0
1a ₂	13.4	–10.2	31.9	–20.1	9.3	–11.9	25.7
	correlation of the 1s shell						
2a ₁ /1b ₂ ^c	12.1	–9.9	36.0	–18.8	8.3	–11.7	28.9
1a ₁ ^d	31.8	–10.0	36.0	–18.8	27.1	–11.5	28.9
	no correlation (RHF)						
	0.0	0.0	23.4	0.0	0.0	0.0	18.8

^a No excitations out of the given MO were allowed (see text).

^b Reference: SD-CI, all electrons correlated.

^c 1s shell of the carbon centers.

^d 1s shell of the nitrogen center.

A very important feature for further applications can be seen through the analysis of the contributions to the isotropic hfcc's of the carbon centers. In neither compound do we find contributions out of the 1s shell of the carbon centers. This indicates that at least for the present molecules only the innershell electrons of the nitrogen centers i.e. the center at which the SOMO is located have to be correlated, for the description of the isotropic hfcc's.

Other interesting features are the variations in the isotropic hfcc's of the β protons in the series of

(CH₃)₂N, (CH₃CH₂)₂N, and ((CH₃)₂CH)₂N. As measured by Danen and Kensler [14] A_{iso}(H_β) increases from 27.3 G in (CH₃)₂N to 36.8 G in (CH₃CH₂)₂N, and then decreases to 14.3 G if further hydrogens are substituted by methyl groups in ((CH₃)₂CH)₂N. As shown in the present calculation the trend is mainly determined by the shape of the potential of the rotation around the C–N bonds. Due to the steric interaction of the methyl groups in (CH₃CH₂)₂N, the B conformer in which H1 and H2 are replaced by the CH₃ groups (Fig. 1b) is most stable.

Table 5
Calculated anisotropic coupling constants (in G) of ¹⁴N and ¹H_α

Conformation	(CH ₃) ₂ NH ⁺				(CH ₃) ₂ N			
	A		B		A		B	
	A _{zz}	A _{xx}	A _{zz}	A _{xx}	A _{zz}	A _{xx}	A _{zz}	A _{xx}
N	29.2	–14.6	29.3	–14.6	28.6	–14.1	28.5	–14.5
H _α	–5.2	22.8	–5.0	23.0				

See Figs. 1a and 1b for notation.

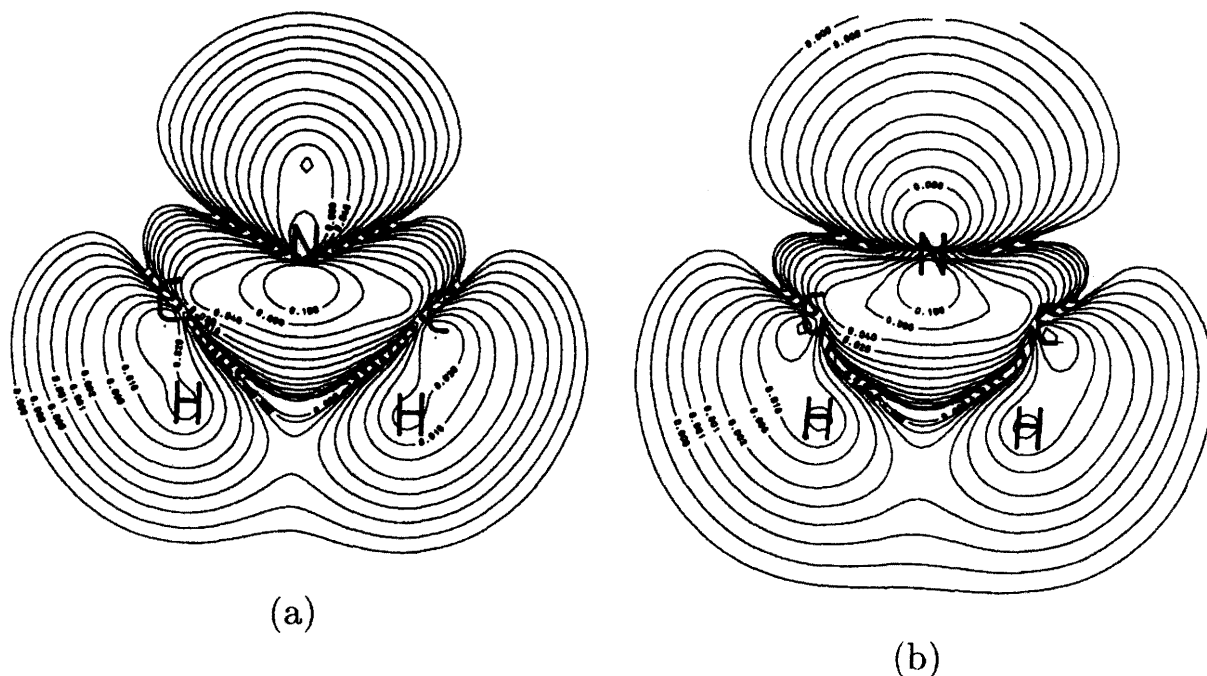


Fig. 3. Charge density plots for the $6a_1$ orbital of (a) $(\text{CH}_3)_2\text{NH}^+$ and (b) $(\text{CH}_3)_2\text{N}$. Cut through the CNC plane.

AM1 [29] calculations show that the barrier for the rotation of one (CH_3CH_2) group is greater than 3 kcal/mol. Due to the hindered free rotation in $(\text{CH}_3\text{CH}_2)_2\text{N}$ the averaged values of $A_{\text{iso}}(\text{H}_\beta)$ increase because the remaining hydrogens librate around those positions

having large isotropic hfcc's (see Table 3). By further substituting, conformation A (replacing H3–H6 by the CH_3 groups) becomes the most stable. Because in that conformation the hydrogens move around the position where $A_{\text{iso}}(\text{H})$ is very small (see Table 3) the averaged

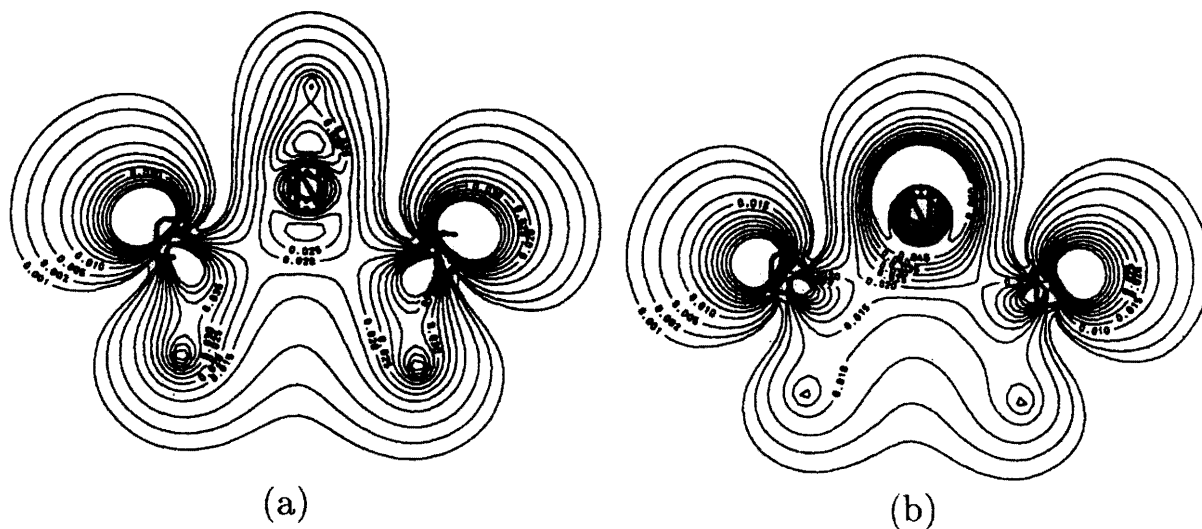


Fig. 4. Charge density plots for the $5a_1$ orbital of (a) $(\text{CH}_3)_2\text{NH}^+$ and (b) $(\text{CH}_3)_2\text{N}$. Cut through the CNC plane.

valued for the β protons drops drastically for $((\text{CH}_3)_2\text{CH})_2\text{N}$. The calculations support the interpretation of the ESR values given by Danen et al. [14,16].

The anisotropic hfcc's of the nitrogen center and the α proton in the radical cation and the neutral radical are given in Table 4. For symmetry reasons, the anisotropic tensors for both centers are diagonal. No experimental values are available, but our results agree with those of Bonazzola et al. [17], i.e. $A_{zz}(^{14}\text{N})$: 29.9 versus 30 G; $A_{zz}(\text{H}_\alpha)$: -5.36 versus -5.0 G.

3. Summary

The geometry and the hyperfine coupling constants of the dimethylamino radical $(\text{CH}_3)_2\text{N}$ and its protonated cation $(\text{CH}_3)_2\text{NH}^+$ have been studied with ab initio methods. While the geometries were optimized with UMP2/6-31G** calculations, the hyperfine structure was calculated with the MRD-CI/ B_K method. For the nitrogen center a value of about 21 G was obtained for the radical cation while a value of about 13 G was calculated for the neutral radical. This is in good agreement with the corresponding experimental values of about 19–20 and 15–16 G. For the β protons the calculated values deviate more from the experimental values (≈ 6 G) uncertainties in the experimental data (e.g. solvent effects [15]) and in the theoretical treatment (e.g. inaccuracies in the equilibrium geometry, etc.) have to be considered.

Reasons why the isotropic hfcc's of the radical cation are larger than those of the neutral radical were also investigated. In the case of the nitrogen center, spin polarization effects of the doubly occupied shells describing the N–H σ bond were found to be responsible. For the β hydrogens, spin polarization effects are less important (30%–40%). The main difference in $A_{\text{iso}}(\text{H}_\beta)$ between the two compounds is already obtained with ROHF calculations, i.e. it results from the more compact form of the SOMO of the radical cation.

The model proposed by Danen et al. [14,16] for explaining the variations of the isotropic hfcc's of the β protons in the series of $(\text{CH}_3)_2\text{N}$, $((\text{CH}_3)\text{CH})_2\text{N}$ is supported by the present study. The anisotropic hfcc's of both molecules were presented.

Acknowledgement

The authors thank Professor S.D. Peyerimhoff for her interest and for fruitful discussions during the progress of this work. Part of this work was financially supported by the Deutsche Forschungsgemeinschaft (DFG) in the framework of project EN 197/2–3 and the Leibniz prize awarded to Professor S.D. Peyerimhoff. A generous grant of computer time was provided by the computing center of the RWTH Aachen. We thank M. Carnell for carefully reading the manuscript.

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