Ab Initio Molecular Orbital Studies on the Structure of the Nitrenium Ion and Its Implication[1]

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Abstract: *Ab initio* SCF–CI calculations have been carried out for the lower singlet and triplet states of the nitrenium ion NH_2^+. The calculations show that the ground state is a linear or almost linear triplet ($^3B_1$) with a very flat potential energy curve for H–N–H bending. About 45 kcal/mol above it is the lowest singlet state ($^1A_1$) with an HNH angle $\theta \sim 115°$. These results are very similar to those obtained elsewhere for CH_2. The population analysis suggests that the singlet NH_2^+ will react like a carbonium ion and that the triplet NH_2^+ will react like a triplet methylene. These results are in agreement with and lend interpretative support to the experimental work of Gassman on heterolytic solvolyses of *N*-haloamines.

In view of the extensive studies on the structure and chemistry of carbonium ions and carbenes, it is rather surprising that very little is known about the nitrenium or imidonium ion $R_1N^+R_2$. Recently, in his study of the heterolytic solvolyses of the nitrogen–halogen (N–X) bond in organic *N*-haloamines, Gassman proposed the nitrenium ion as a reaction intermediate to account for the observed reaction products and kinetic data.[3] Solvolysis experiments further suggest that the nitrenium ion exists in both singlet and triplet states and that the cleavage of the N–X bond first forms the singlet nitrenium ion which then is converted into a triplet state through spin–orbit interaction.[4]

Since the nitrenium ion is isoelectronic with carbene R_1CR_2, one might expect that, if the effect of the net positive charge on the one molecule is not too large, the two systems would have similar energy schemes, *e.g.*, the same ordering of lower triplet and singlet states and the same dependency of the energy on the HNH or HCH angle. Walsh's rule predicts for both CH_2 and NH_2^+ that the singlet is bent and the triplet is linear or nearly so.[5] Walsh does not make a prediction as to which state is lower.

On the other hand, it is reasonable to expect that a (singlet) nitrenium ion resembles a carbonium ion in its chemical behavior,[3] except that the former would be more reactive or unstable due to the larger electronegativity of the nitrogen atom and, therefore, greater reluctance to accommodate a positive charge.

Extensive *ab initio* molecular orbital calculations have been carried out for the lower electronic states of methylene (CH_2)[6] and the ground state of methyl cation (CH_3^+)[7] for several bond angles.[7a] The valence bond (VB) calculation for CH_2[6a] with scaled near-Hartree–Fock atomic orbitals and restricted canonical structures led to the ground state $^3B_1$ having an HCH angle of $\theta = 138°$. This state is energetically lower than the lowest singlet state $^1A_1$ for all the angles studied ($\theta \geqq 80°$). The SCF–CI calculation[6c] for $^3B_1$ with a Gaussian basis set comparable to the Slater double ζ set gives the equilibrium angle of $\theta = 135°$.

Unfortunately the existing calculations[7c,8] for NH_2^+ deal only with the lowest singlet ($^1A_1$) state in the SCF approximation. It appears that an extensive calculation for the lower electronic states of NH_2^+ for several $\angle HNH = \theta$ values would allow us to compare the energy levels and structure of NH_2^+ with that of CH_2 and CH_3^+ and thereby obtain some insight into the electronic structure of the proposed nitrenium ion intermediates in the solvolysis reactions.

In the present paper we carried out *ab initio* LCAO–SCF–CI (configuration interaction) calculations for NH_2^+. The results indicate that the order of lower states and the angular dependency of their energies are in fact qualitatively similar to that of CH_2 and that the positive charge is mostly distributed on H as in CH_3^+. Implications of these results will be discussed.

Method

The LCAO–SCF–CI method was used throughout the paper. The basis sets are the minimal (MZ) and double zeta (DZ) Slater-type sets. Exponents used (shown in Table I) for N are obtained from Slater's rules for MZ and Clementi's for DZ.[9] Exponents for H were chosen arbitrarily; the MZ exponent is larger than the commonly accepted value 1.18 considering the contraction of orbital due to the positive charge of the molecule.

Table I. Orbital Exponents Used

Atom	Orbital	Exponents MZ	Exponents DZ
H	1s	1.20	1.00000, 1.5000
N	1s	6.70	6.11863, 8.93843
	2s	1.95	1.39327, 2.22157
	2p	1.95	1.50585, 3.26741

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[2] Alfred P. Sloan Research Fellow, 1970–1972.

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Table II. Total Energies (au) as Functions of θ

	$^3B_1$		$1\,^1A_1$		$^1B_1$		$2\,^1A_1$
θ, deg	MZ	DZ	MZ	DZ	MZ	DZ	MZ
180	−55.12441	−55.27317	−55.02137	−55.18867	−55.02137	−55.18867	−54.96586
170	−55.12486		−55.02200		−55.02190		−54.96611
160	−55.12594		−55.02453		−55.02312		−54.96552
150	−55.12689	−55.27183	−55.03000	−55.19078	−55.02412	−55.18614	−54.96134
140	−55.12676		−55.03801		−55.02318		−54.95189
130	−55.12455		−55.04669		−55.02098		−54.93700
120	−55.11928	−55.25783	−55.05400	−55.20108	−55.01472	−55.16813	−54.91684
110	−55.11000		−55.05824		−55.00403		−54.89131
100	−55.09563		−55.05795		−54.98783		−54.85997
90	−55.07487	−55.20993	−55.05175	−55.18811	−54.96476	−55.11273	−54.82210
80	−55.04596		−55.03818		−54.93303		−54.77745
No. of config	124	446	115	333	88	307	115

Table III. Equilibrium Energy, the Inversion Barrier Height, and Equilibrium Angle for Lower Electronic States[a]

	NH_2^+		CH_2	
State	MZ	DZ	~MZ[b]	~DZ[c]
$^3B_1$	−1.6, 1.6 (146°)	0, 0 (180°)	−4.8, 4.8 (138°)	−6.7, 6.7 (135°)
$^1A_1$	41.3, 23.4 (106°)	45.0, 8.0 (115°)	27.1, 21.3 (108°)	
$^1B_1$	62.9, 1.7 (150°)	53.0, 0 (180°)	46.7, 1.6 (148°)	

[a] First entry is the total energy in kilocalories per mole relative to $^3B_1$ at $\theta = 180°$, the second entry is the inversion barrier, and the number in parentheses is the equilibrium angle. [b] From ref 6a, calculation VB (III) (Harrison and Allen). [c] From ref 6c (Bender and Schaefer).

Table IV. Atomic Population and Charge Distribution

State	Atomic orbitals	$\theta = 180°$	150°	120°	90°
$^3B_1$	Hs	0.4468	0.4604	0.4797	0.4939
	Nσ	6.1063	6.0791	6.0405	6.0121
	Nπ	1.0001	1.0001	1.0001	1.0001
	Net charge H	+0.5532	+0.5396	+0.5203	+0.5061
	Net charge N	−0.1064	−0.0792	−0.0406	−0.0122
$^1A_1$	Hs	0.4251	0.4471	0.4902	0.5251
	Nσ	6.1497	6.6378	6.8887	6.8761
	Nπ	1.0001	0.4680	0.1309	0.0737
	Net charge H	+0.5749	+0.5529	+0.5098	+0.4749
	Net charge N	−0.1498	−0.1058	−0.0196	+0.0502
$^1B_1$	Hs	0.4251	0.4418	0.4661	0.4835
	Nσ	6.1497	6.1163	6.0677	6.0329
	Nπ	1.0001	1.0001	1.0001	1.0001
	Net charge H	+0.5749	+0.5582	+0.5339	+0.5165
	Net charge N	−0.1498	−0.1164	−0.0678	−0.0330

For the SCF and CI calculations the program package POLYCAL–CI[10] was used. The SCF–MO's obtained for the lowest triplet ($^3B_1$) configuration $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)$ are used in the CI calculations. Here $1a_1$ is essentially N1s, $2a_1$ and $1b_2$ are the N–H σ bonds, $3a_1$ is the N lone pair in the molecular plane, and $1b_1$ is N2pπ. The vacant MO's are $4a_1$ and $2b_2$, the N–H σ antibonding orbitals. In DZ there are more vacant orbitals which do not correspond to any valence orbitals. In the CI calculation with MZ set all the configurations are included except for those in which two electrons are simultaneously excited from the lowest MO ($1a_1$). With the DZ set we "freeze" the lowest MO ($1a_1$) completely and allow no more than two electrons to be excited simultaneously. However, because MO's $3a_1$ and $1b_1$ are either degenerate (linear case) or almost degenerate (bent cases), neither the excitation $3a_1 \rightarrow 1b_1$ nor $1b_1 \rightarrow 3a_1$ is counted as an excitation. This selection results in 307–446 spin eigenfunctions (not Slater determinants but linear combinations of Slater determinants) in each symmetry representation discussed in this paper, and the results should include all the essential parts of the correlation energy within the used basis set.

To obtain an idea of the electron distribution within the molecule, Mulliken's gross population was calculated from the DZ–CI wave functions. The calculation was performed using a general purpose one-electron expectation value program, ONEXP.[10]

Results

The energies of the four lowest states of the nitrenium ion resulting essentially from $(3a_1)^{2-n}(1b_1)^n$, n = 0, 1, 2 configurations are calculated by the SCF–CI method with both MZ and DZ basis sets for different θ and are given in Table II. The number of spin eigenfunctions included in each CI calculation is also listed. The energies of each state are plotted against θ in Figure 1. The interpolated equilibrium angles and the energies of each state are tabulated in Table III. Both MZ and DZ results give identical ordering of states, *i.e.*, $^3B_1 < {}^1A_1 < {}^1B_1$ for the whole range of angles stud-

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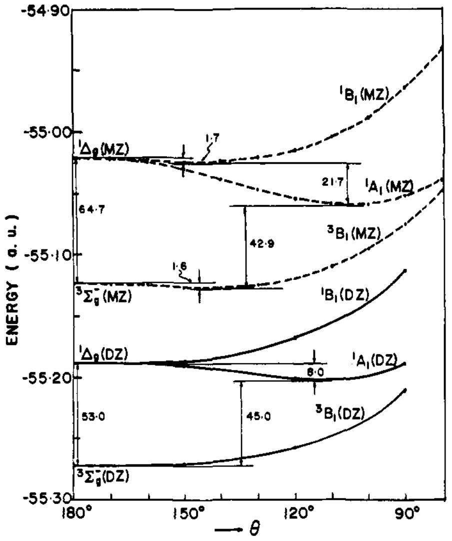


Figure 1. Energies of lower electronic states of NH_2^+ as a function of the HNH angle θ calculated by the SCF–CI method with both the MZ and DZ basis sets. The numbers inside the figure are in kilocalories per mole.

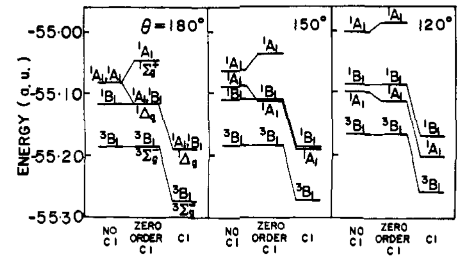


Figure 2. Effects of configuration interaction on the energies of lower states of NH_2^+ calculated with the DZ basis set.

ied ($\theta > 80°$), ${}^3B_1$ being the ground state. The ${}^1A_1$ state is bent in both calculations ($\theta = 106°$ for MZ and 115° for DZ). Both B_1 states (${}^3B_1$ and ${}^1B_1$) show an extremely flat energy curve; in MZ both states are bent to $\theta \simeq 150°$ with an almost identical inversion barrier of 1.6–1.7 kcal/mol, but in DZ, for both states, the linear structures are found most stable. In either case the barrier is so small that the amplitude of the bending vibration must be large.

The gross populations calculated from the DZ–CI wave functions are shown in Table IV for the three lower states. It is quite remarkable that for every state and angle studied the net positive charge remained localized on the protons with the nitrogen possessing a slight negative charge. This resembles methyl cation (CH_3^+) in which each hydrogen atom carries a net charge of +0.29 to +0.32 (depending on the out-of-plane angle), while the carbon net charge is only +0.13 to +0.04.[7a] It should also be noted that the charge distribution does not vary substantially from one state to another, that the charge on the hydrogens is somewhat reduced as the ion becomes more bent, and that the angular dependency of this charge is somewhat greater for the ${}^1A_1$ state.

In Figure 2 we show the effects of CI in the DZ calculation at θ = 180, 150, and 120°. The "No CI" results are for the following wave functions: ${}^1A_1$, $\psi_1 = A\{(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)_2\}$, $\psi_2 = A\{(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2\}$, ${}^{1,3}B_1$, $\psi_3 = A\{(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1\ {}^{1,3}\theta\}$, where ${}^{1,3}\theta$ is the two-electron singlet (or triplet) spin function, and A is an antisymmetrizer. For $\theta = 180°$, ψ_1 and ψ_2 are degenerate and have to be intermixed to satisfy the symmetry requirement. This mixing is allowed for all angles and is called the "zero-order CI" result. It is noted that at 150° where ψ_1 and ψ_2 are no longer degenerate, the "zero-order CI" is necessary to obtain the correct ordering of states ${}^3B_1 < {}^1A_1 < {}^1B_1$. At 120°, where the correct ordering is obtained with a "no CI," the "zero-order CI" brings the ${}^1A_1$ state down by 0.015 au by mixing ψ_2 in by 12%. The relative energies of these three states after "zero-order CI" are not very different from the full CI results for all the angles. The above results suggest the importance of "zero-order CI" in predicting orders and energies of several states arising from the distribution of electrons among nearly degenerate MO's.

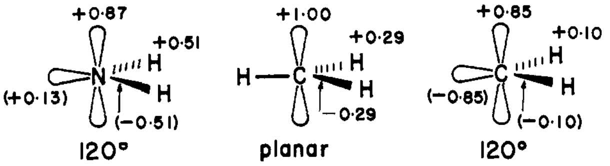
Discussion

The results of our calculations described in the previous section lead us to conclude that the ordering of states in NH_2^+ is ${}^3B_1 < {}^1A_1 < {}^1B_1$ for values of θ between 180 and 80° and that the equilibrium geometry of ${}^1A_1$ is bent (~110°) while ${}^3B_1$ and ${}^1B_1$ are linear or slightly bent with a very flat potential energy curve with respect to change in the H–N–H angle. The details of the ${}^3B_1$ and ${}^1B_1$ curves such as the equilibrium H–N–H angle and the inversion barrier height will be sensitive to the SCF basis set used as well as to the correlation energy. It appears that a larger basis set and an even more extensive CI treatment of the correlation energy are necessary to obtain accurate structural parameters.

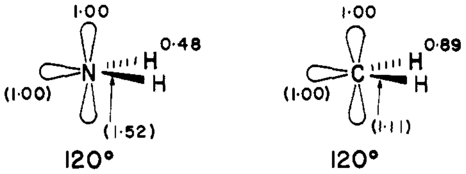
It is now interesting to compare our NH_2^+ results with existing CH_2 calculations. Table III summarizes the available results. The present DZ result compared with a comparably accurate result of CI calculations by Bender and Schaefer[6c] suggests that NH_2^+ would be less bent, if at all, than CH_2 in the ground-state ${}^3B_1$. Harrison and Allen used the valence bond method with a minimal number (7) of atomic orbitals, each of which is near the Hartree–Fock limit.[6a] Boys and Foster[6b] used the CI method with eight AO's, and obtained results similar to Harrison and Allen. Since these calculations are done with a minimal (or subminimal) number of AO's, a comparison should be made with our MZ results. We find great similarities between NH_2^+ and CH_2, *e.g.*, the order of the states, the equilibrium geometries (Table III), and the shape of potential energy curves (Figure 1 and ref 6a and 6b). One difference we notice is the energy separation between the equilibrium ground triplet state (${}^3B_1$) and the equilibrium lowest singlet state (${}^1A_1$): about 45 kcal/mol for NH_2^+ and about 32 kcal/mol for CH_2. The calculated vertical excitation energy from ${}^3B_1$ to ${}^1A_1$ is 2.28 eV if ${}^3B_1$ is linear and 0.10 eV or so less if ${}^3B_1$ is bent to ~140°. This is to be compared with 1.77 eV for CH_2.[6a] Qualitatively we may conclude that CH_2 and NH_2^+ have very similar energy level structures.

On the other hand the charge distribution of NH_2^+ is similar to that of CH_3^+. We would like to make a qualitative comparison of anticipated reactivities between NH_2^+, CH_2, and CH_3^+[7a] based on the structure and the charge distribution. No charge distribution for CH_2 is available, and so we carried out the MZ–CI calculation identical with the NH_2^+ calculation with

R(C–H) = 2.0 au, ∠HCH = 120°, and exponents $\zeta_{\mathrm{H1s}} = 1.18$, $\zeta_{\mathrm{C1s}} = 5.7$, and $\zeta_{\mathrm{C2s}} = \zeta_{\mathrm{C2p}} = 1.625$. For the lowest singlet state the net charge distributions are summarized



The unpaired and bonding σ AO's on N and C cannot be unequivocally separated in the MO calculation. So the values obtained, assuming that the N–H or C–H bond contains two electrons, are shown in parentheses. All three species have a 2pπ orbital completely or almost completely unoccupied, and qualify as an electrophile. Electrophilic attacks by these reagents are anticipated to take place with the 2pπ orbital pointing toward the substrate. This is shown to be the case by the extended Hückel method for the case of CH_2.[11] Of the three molecules, CH_2 would be expected to be the weakest electrophile. To compare the reactivity between CH_3^+ and NH_2^+ we have to consider two factors: the net charge in the 2pπ orbital and the electron affinity of the cation. For the planar CH_3^+ the 2pπ net charge is +1, while for NH_2^+ it is a strong function of the HNH angle θ. At θ = 120°, around where the calculated energy minimum of the $^1A_1$ state of NH_2^+ is found, the charge is +0.87 and the effect of deviation from 1.0 would be small. Then NH_2^+ would be a stronger electrophile because of its larger electronegativity. Interesting would be the reactivity of the singlet RN^+R' in which the bond angle on N is sterically fixed at an angle close to 180°, at which the charge in 2pπ is reduced to zero. Another finding worth noticing is a larger charge on H in NH_2^+ than in CH_3^+, which could have some implication on the chemistry of substituent groups R_1 and R_2.



For the ground triplet state ($^3B_1$) the gross populations (not the net charges) are shown above. The numbers in parentheses are again obtained from the assumption above. The values shown are for θ = 120°, but they are essentially independent of the angle from 180 to 90° (Table IV). The triplet NH_2^+ will behave as a biradical like the triplet CH_2 as is experimentally proposed by Gassman,[4] but the former would be more electrophilic than the latter due to its electron deficiency.

A recent study[12] on difluoroamino radical NF_2 using photoelectron spectroscopy and INDO calculations suggests that the ground state of NF_2^+ is $^1A_1$ with an equilibrium angle around 103°. The bent structure of NF_2^+ is predicted also by Walsh's rule.[5] The difference in the ground states between NH_2^+ ($^3B_1$) and NF_2^+ ($^1A_1$) would be accountable considering the extent to which the N2p$_y$ orbital (y being the direction in the molecular plane and on the bisector of the XNX angle) is involved in bonding as the angle ∠XNX decreases from 180°. In NF_2^+ N2p$_y$ would interact strongly with F2p lone-pair orbitals, while in NH_2^+ the interaction of N2p$_y$ with H1s is limited. Thus, in NF_2^+ the separation between this orbital and the N2pπ orbital will be substantial, resulting in the $^1A_1$ ground state. In the case of $R_1N^+R_2$, where R_1 and R_2 are alkyl groups, the separation would be expected a little larger than in NH_2^+ but not as large as in NF_2^+.

The finding that the energy separation between the triplet ($^3B_1$) and the singlet ($^1A_1$) states decreases as the HNH angle θ decreases is interesting. This suggests that if the nitrenium ion is formed in a ring structure where it is clamped at both ends near its singlet equilibrium angle or even smaller, the singlet state gains an extra stability and hence the singlet reaction could predominate in such cases. Most of the reactions successfully studied by Gassman[3] are actually those of ring compounds, presumably because of the reason stated above.

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