Only when the association is very large ($K_A \geqslant 1000$ M^{-1}) do the results become insensitive to the parameters used. On the other hand, in this case, one may resort to use of eq I or the corresponding Fuoss–Kraus[20] or Shedlowsky[21] methods without retention of the $Ec\alpha \log c\alpha$, $J_1 c\alpha$, and $J_2(c\alpha)^{3/2}$ terms.

Analysis by the Justice method,[6a] setting $R = q$, although inconsistent with some of the derivations of the theory, gives internally consistent results in terms of the model assumed. In particular, the significance of the Bjerrum parameter q is well founded on statistical mechanical grounds.[22] The ionic distribution function shows a minimum for $R = q$, a maximum for the distance x^{-1} (the Debye atmosphere distance or average distance), and increases at shorter distances toward a. If the positions $J_1(q)$, $J_2(q)$, and $f_\pm(q)$ are correct, this would make eq III a one-parameter equation in Λ_0 and the calculations of association constants through conductance data an unambiguous process.

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Theoretical Studies of the Low-Lying Electronic States of NH_2^+ and CH_2[1]

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Abstract: Nonempirical configuration-interaction wave functions constructed from Gaussian basis functions are used to study the $^3B_1$, $^1B_1$, $^1A_1$, and $^1A_1{}^*$ states of the isoelectronic systems NH_2^+ and CH_2. The $^3B_1$ state is predicted to have a minimum-energy configuration at a bond angle of 130° for CH_2 and 140° for NH_2^+. For the $^1A_1$ state, the optimal bond angle is predicted to be 120° for NH_2^+ and 100° for CH_2. The calculated singlet–triplet energy separation ($^3B_1 - {}^1A_1$) is 1.56 eV for NH_2^+ and 0.88 eV for CH_2. Investigation of the correlation diagrams for the formation of CH_2 from the photolysis of diazomethane suggest that CH_2 is probably formed initially in the $^1A_1{}^*$ state. Since this state is predicted to be only 1.92 eV above the lower $^1A_1$ state, the possibility that the $^1A_1{}^*$ state is responsible for the stereospecific addition of CH_2 to olefins is proposed.

The importance of carbonium ions in organic chemistry has been recognized for several years;[2] however, it is only recently that the nitrogen analog, the nitrenium ion, has been established as a useful intermediate in a variety of chemical reactions.[3] The purpose of this paper is to report nonempirical quantum mechanical studies of the low-lying electronic states of the simplest nitrenium ion, NH_2^+. To our knowledge there is no direct experimental information on these states, so it is hoped that these theoretical predictions will be valuable in providing a better theoretical basis for the understanding of nitrenium ion chemistry.

As with most quantum mechanical studies, one is faced with the problem of estimating the accuracy of the calculations. To minimize this difficulty, we have carried out parallel calculations for both NH_2^+ and CH_2. Comparison of these two systems should not be taken to imply that one should expect the chemistry of these two species to be the same. In fact, Gassman[3] has pointed out that nitrenium ion chemistry is similar to carbonium ion chemistry. It appears that the presence of the positive charge plays a significant role in the chemistry of these species. To our knowledge, nitrenium ions do not exhibit carbene-like behavior.[4] Nevertheless, the electronic structure of the low-lying states of NH_2^+ and CH_2 are quite similar, and for this reason it is felt that the earlier theoretical and experimental data on CH_2 could be used to calibrate our results for CH_2 and NH_2^+.

In the case of methylene, there have been numerous theoretical studies of the ground state and several low-lying states. It is interesting to note that the accuracy of the theoretical calculations on CH_2 is such that they prompted Herzberg and Johns[5] to reinterpret the vacuum ultraviolet spectrum in terms of the predicted bent form for the $^3B_1$ ground state. In the early work by Herzberg,[6] this state was thought to be linear or nearly linear. However, most theoretical studies of this state predicted a bond angle considerably less than 180°. In Table I a number of the theoretically predicted bond angles are presented. From this table, it is clear that most of these theoretical studies are in good agreement with the rather extensive configuration-interaction calculations of

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[1] Supported in part by a research grant to Rice University from the Robert A. Welch Foundation.

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Table I. Summary of Some Theoretical Calculations[a]

Molecule	Bond angle $^3B_1$, deg	Well depth ($^3B_1$ − $^3\Sigma_g^-$), eV	Separation, eV ($^3B_1$ − $^1A_1$)	Separation, eV ($^1B_1$ − $^1A_1$)	Ref
CH_2	129	0.51	1.06	1.55	*b*
CH_2	140	0.13	1.39	0.53	*c*
CH_2	133	0.29	0.96	0.98	*d*
CH_2	130	0.46	0.88	0.95	This work
NH_2^+	140	0.04	1.56	0.47	This work
CH_2				(0.88)	*e*

[a] In this work the optimal geometry and corresponding energy for each state were determined from Figure 1. [b] J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 305 (1960). [c] J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969). [d] C. F. Bender and H. F. Schaefer, *ibid.*, **92**, 4984 (1970); S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971). [e] Experiment; ref 6.

Table II. Energy *vs.* Angle for Methylene[a]

θ, deg	$^3B_1$	$^1A_1$	$^1B_1$	$^1A_1$*
180	−38.9104	−38.8591	−38.8591	−38.8224
	(−38.8936)	−(38.8137)	(−38.8390)	(−38.8137)
160	−38.9158	−38.8639	−38.8595	−38.8141
	(−38.8994)	(−38.8204)	(−38.8370)	(−38.8068)
140	−38.9248	−38.8784	−38.8591	−38.7898
	(−38.9078)	(−38.8366)	(−38.8323)	(−38.7858)
120	−38.9247	−38.8923	−38.8493	−38.7512
	(−38.9069)	(−38.8516)	(−38.8191)	(−38.7500)
100	−38.9074	−38.8930	−38.8222	−38.6969
	(−38.8887)	(−38.8527)	(−38.7886)	(−38.6965)
90	−38.8900	−38.8855	−38.7994	−38.6623
	(−38.8710)	(−38.8450)	(−38.7646)	(−38.6614)

[a] The C–H bond distance is 2.0 bohrs. Energies are given in atomic units. The quantities in parentheses are the energies for the single-configuration representation of each state. For the $^3B_1$, $^1A_1$, and $^1A_1$* states, these values were obtained from SCF calculations; however, in the case of the $^1B_1$ state, the energy was determined using the orbitals from the SCF calculation on the $^3B_1$ state.

Bender and Schaefer,[7] which predicted a bond angle of 133°. In contrast to the situation for CH_2, there does not seem to be any experimental or theoretical information on the low-lying states of NH_2^+. In this study the separation between the singlet and triplet states of the nitrenium ion is of particular interest, since the chemistry of these two states is thought to be quite different. In addition, a potential energy curve for the second $^1A_1$ state of CH_2 (which we label $^1A_1$*) is reported. The possible role of this state in addition reactions is discussed.

Method of Calculation

The first step in each calculation involves the computation of an LCAO-MO-SCF wave function for the singlet closed-shell and triplet open-shell states separately. Here Roothaan's[8] restricted self-consistent-field (SCF) procedure was employed using a set of Gaussian functions for the basis set. For carbon and nitrogen, the s-type basis orbitals are the four-term 1s, three-term 2s, and three-term 3s grouped orbitals suggested by Whitten.[9] The 2p orbitals were obtained from Huzinaga's[10] 9,5 atomic basis sets. In order to provide the additional flexibility necessary to describe the molecular environment, these orbitals were subdivided by splitting out the long-range component (*i.e.*, smallest exponent) of the 3s and 2p orbitals. For hydrogen, the five-term 1s orbital reported by Whitten[9] was also subdivided by splitting out the long-range component of this orbital. In addition this orbital was scaled by a factor of 1.41465 suggested by Fink, *et al.*[11]

The configuration-interaction (CI) calculations reported here were carried out including the SCF functions ψ ($^3B_1$) and ψ ($^1A_1$) plus all configurations of the same symmetry arising from intrashell pair excitations to all possible pairs of virtual orbitals. In the case of the triplet state, the excitations from the $3a_1$ $1b_1$ orbitals were also included. The $1a_1$ orbital is predominantly a 1s orbital on the central atom, and so the correlation energy for this orbital is expected to be constant for each of the states. Also, no excitations to the highest virtual orbital were included, since this is mainly a 1s cusp orbital. For the $^1A_1$ state, the single excitations were not included, since the energy associated with these configurations was negligible.[12] For the $^3B_1$ state, all $^3B_1$ configurations arising from single excitations from the valence shell were included. The final wave functions consisted of 52 space configurations for the $^1A_1$ state and 30 space configurations for the $^3B_1$ state. All calculations were carried out using the MOLE quantum chemistry system.[13] This is a general purpose system for quantum mechanical studies of the electronic structure of molecules.

In this study the sensitivity of energy separations to changes in bond length was not investigated, since this point was considered in some detail by O'Neil, Schaefer, and Bender[7] in their studies of CH_2. Thus, for all the calculations the N–H and C–H bond distances were fixed at 2.0 bohrs.

Results and Discussion

Since CH_2 and NH_2^+ both have eight electrons, the electron configuration for the linear form of these molecules is

$$\Phi = (1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2 \qquad (1)$$

This electron configuration gives rise to three electronic states, $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$. These states correlate with the $^3B_1$, $^1B_1$, $^1A_1$, and $^1A_1$* states of the nonlinear AH_2 molecule. The corresponding electron configurations for these states are

$$\Phi(^3B_1) = (1a_1)^2(2a_1)^2(1b_2)^2(3a_11b_1 - 1b_13a_1) \qquad (2)$$

$$\Phi(^1B_1) = (1a_1)^2(2a_1)^2(1b_2)^2(3a_11b_1 + 1b_13a_1) \qquad (3)$$

$$\Phi(^1A_1) = (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 \qquad (4)$$

$$\Phi(^1A_1^*) = (1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2 \qquad (5)$$

where the $3a_1$, $1b_1$ orbitals are triplet coupled in eq 2 and singlet coupled in eq 3. Configuration-interac-

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(7) C. F. Bender and H. F. Schaefer, *J. Amer. Chem. Soc.*, **92**, 4984 (1970); S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971).

(8) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 1791 (1960); **23**, 69 (1951).

(9) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

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(11) W. H. Fink, J. L. Whitten, and L. C. Allen, in preparation.

(12) For instance, adding ten single-excitation configurations to the double excitations for the $^1A_1$ state gives energy improvements of less than 0.0003 au for CH_2 at all bond angles.

(13) S. Rothenberg, P. Kollman, M. E. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem., Symp.*, **3**, 715 (1970).

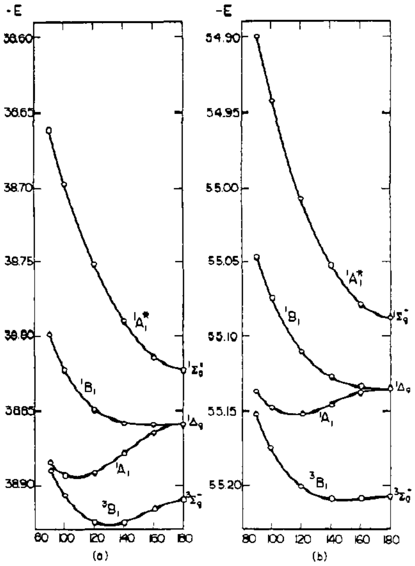

Figure 1. Potential energy curves for the molecules (a) CH_2 and (b) NH_2^+.

tion calculations have been carried out for each of these states for several HAH bond angles ranging from 90 to 180°, using the methods described in the previous section. The resulting potential energy curves for each of these states are displayed in Figure 1. The calculated points are presented in Tables II and III.

Table III. Energy *vs.* Angle for Nitrenium Ion[a]

θ, deg	$^3B_1$	$^1A_1$	$^1B_1$	$^1A_1^*$
180	−55.2086 (−55.1916)	−55.1350 (−55.0830)	−55.1357 (−55.0899)	−55.0878 (−55.0830)
160	−55.2096 (−55.1934)	−55.1373 (−55.0880)	−55.1342 (−55.0877)	−55.0797 (−55.0743)
140	−55.2102 (−55.1941)	−55.1458 (−55.0999)	−55.1280 (−55.0812)	−55.0532 (−55.0482)
120	−55.2013 (−55.1848)	−55.1530 (−55.1090)	−55.1109 (−55.0649)	−55.0080 (−55.0041)
100	−55.1748 (−55.1569)	−55.1472 (−55.1032)	−55.0753 (−55.0324)	−54.9434 (−54.9386)
90	−55.1526 (−55.1339)	−55.1367 (−55.0922)	−55.0478 (−55.0023)	−54.9023 (−54.8960)

[a] The N–H bond distance is 2.0 bohrs. Energies are given in atomic units. The quantities in parentheses are the energies for the single-configuration representation of each state. For the $^3B_1$, $^1A_1$, and $^1A_1^*$ states, these values were obtained from SCF calculations; however, in the case of the $^1B_1$ state, the energy was determined using the orbitals from the SCF calculation on the $^3B_1$ state.

The lowest singlet state, $^1A_1$, has two electrons in a lone-pair orbital which is basically an sp^2 hybrid orbital in the molecular plane. From Figure 1 it can be seen that this state has a minimum at 100° for CH_2 and 120° for NH_2^+. The two B_1 states have two singly occupied orbitals which are sp^3 like. The $^3B_1$ state has a rather flat minimum around 140° for both NH_2^+ and CH_2. This is considerably larger than the 109° angle typical of sp^3 hybrids. For CH_2, our CI results indicate a shallow well of 0.0004 au at 160°, while the $^1B_1$ results for NH_2^+ predict a linear geometry for this state. However, for both of these systems the bending force constant for the $^1B_1$ state of the molecule appears to be small.

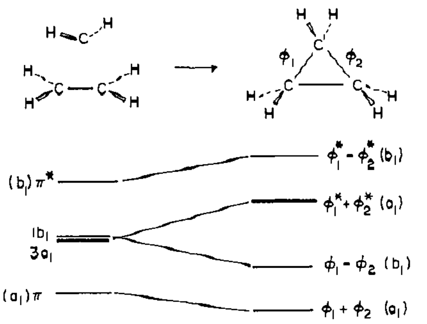

Figure 2. Correlation diagram for the symmetric addition of CH_2 to $CH_2{=}CH_2$.

In this study we have also calculated the $^1A_1^* - {}^1A_1$ separation. The point of interest here is the possibility that the $^1A_1^*$ state may be responsible for the stereospecific addition of CH_2 to olefins. Since the $^1A_1^*$ state has two electrons in the lone-pair orbital perpendicular to the molecular plane, the stereospecific addition of this state to olefins would be consistent with orbital symmetry arguments.[14] Furthermore, the CH_2 formed by photolysis of diazomethane is expected to be in the $^1A_1^*$ state, assuming that nitrogen is formed in the ground state. The experimental studies of Herzberg[6] support this conjecture, since no CH_2 absorption characteristic of the lower $^1A_1$ state has been found immediately after the production of CH_2 by flash photolysis of diazomethane. Since both CH_2N_2 and N_2 are thought to be in singlet states, spin conservation[6] would suggest that CH_2 is first formed in a singlet state. Furthermore, on the basis of orbital correlation, if the lone pair at one end of the nitrogen molecule correlates with the N–C σ bond in the CH_2N_2 system, one would expect that the $^1A_1$ and $^1B_1$ states of CH_2 would be quite unfavorable, since the $3a_1$ orbital on CH_2 correlates with the antibonding N–C σ bond. The $^1A_1^*$ state would seem to be more acceptable owing to the correlation of the $1b_1$ orbital with the N–C bonding π orbital. The situation here is analogous to the case of the photolysis of N_2O. For this system Warneck[15] has pointed out that atomic oxygen is generated in the ^1S state rather than the ^1D state. Any CH_2 formed from photolysis in the $^1A_1^*$ state would have enough excess energy to dissociate into CH + H. However, in the presence of an olefin and a cooling gas, this process must compete with the addition reaction and the relaxation of CH_2. The evidence that the $^1A_1^*$ state of CH_2 leads to stereospecific addition to the double bond is the following. In the addition of methylene to ethylene to form cyclopropane, the newly formed localized σ orbitals ϕ_1 and ϕ_2 can be transformed to symmetry orbitals $\phi_1 + \phi_2$ and $\phi_1 - \phi_2$ of a_1 and b_1 species in the point group C_{2v} for cyclopropane. The correlation diagram for the reaction is sketched in Figure 2. The initial π orbital of ethylene correlates with the a_1 orbital $\phi_1 + \phi_2$, and only the $1b_1$ out-of-plane orbital of methylene can correlate with the b_1 $\phi_1 - \phi_2$ orbital. Thus, only the excited $^1A_1^*$ state of methylene is symmetry allowed for the symmetric addition to the double

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bond. This process was ignored by Hoffmann[14] because the $^1A_1^*$ state is energetically unfavorable. Our limited CI calculations on $^1A_1$ states of CH_2 indicate that the $^1A_1^* - {}^1A_1$ energy separation is only 1.92 eV. Thus, the possible role of the $^1A_1^*$ state in the reaction cannot be ruled out, particularly when this state seems to be the one that is photochemically produced.

In contrast to the carbene, the nitrenium ion may be produced from the heterolytic cleavage of an $>$N–Cl bond under solvolytic conditions, giving a chloride ion and an electron-deficient species $>N{:}^+$, the nitrenium ion.[3] The ion should be formed in the $^1A_1$ state, with the lone pair in the *N*-chloramine correlating with the $3a_1$ orbital in the nitrenium ion. Gassman[3] has pointed out that the $^1A_1$ state should exhibit carbonium ion like behavior, while the $^3B_1$ state would be expected to resemble a nitrogen cation radical in its chemical reactivity. Using these ideas and the fact that spin–orbit interaction should convert the $^1A_1$ nitrenium ion to the $^3B_1$ ion, he has established the existence of the nitrenium ion by observation of triplet–singlet product ratios as halogenated solvents are added to the reaction. Thus, two states of the nitrenium ion are of particular interest in its chemistry.

Our CI calculations indicate that the $^3B_1 - {}^1A_1$ separation for the NH_2^+ molecule is 1.56 eV. This is about twice as large as the $^3B_1 - {}^1A_1$ separation predicted for CH_2. Our value of 0.88 eV for the singlet–triplet splitting in CH_2 compares quite favorably with the more extensive calculations of O'Neil, Schaefer, and Bender,[7] which predict a separation of 0.96 eV. The experimental value of the ($^3B_1 - {}^1A_1$) separation is not known for either CH_2 or NH_2^+; however, in view of our agreement with Schaefer and Bender for the $^3B_1 - {}^1A_1$ separation in CH_2 and the excellent agreement with the experimental value for the ($^1B_1 - {}^1A_1$) separation in CH_2 (see Table I), we believe the reported value for NH_2^+ is probably accurate to 0.2 eV.

Conclusions

In this paper, nonempirical configuration-interaction results have been reported for the low-lying states of NH_2^+ and CH_2. Analysis of these results suggests several points which are of potential value in understanding and interpreting the chemistry of these and related species. First of all, the singlet–triplet separation ($^1A_1 - {}^3B_1$) for NH_2^+ is predicted to be about twice as big as the singlet–triplet separation for CH_2. Secondly, the $^1A_1^*$ state of CH_2 is implicated as the active state in the stereospecific addition of CH_2 to olefins.

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Conformational Characteristics and Flexibility of Branched Polyethylenes

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Abstract: The mean-square unperturbed radii of gyration of branched polyethylenes are calculated in the rotational isomeric state approximation. Tri- and tetrafunctional branching is considered, as well as the effects of branch spacing, type, and distribution on the calculated radii. Regardless of the branching functionality, it is found that the mean-square radius of gyration of the backbone of branched polyethylene is nearly identical with the radius of linear polyethylene of the same degree of polymerization as the branched polymer's backbone, providing the branches are spaced 20 or more bonds apart. This result reduces the calculation of the mean-square unperturbed radii of gyration of branched polyethylenes to the taking of the appropriate sums and differences of the radii of gyration of linear portions of the branched polymer. Since the radius of linear polyethylene has been previously calculated as a function of chain length, it is possible to closely approximate the radius of any given branched polyethylene without specifically conducting any further conformational calculations. Examples of the calculated radii of gyration of several widely differing branched polyethylenes are presented and compared to their freely jointed values. A recent solution–viscosity study of ethyl-branched polyethylenes reports an increase in the backbone flexibility relative to linear polyethylene as the branch content is increased. For reasonable ranges of the rotational state statistical weights, it is possible to predict this observed increase in backbone flexibility only if the rotational states are displaced *ca.* 10° from the symmetric positions 0 and ±120°. Displacements of this magnitude from the threefold symmetric locations are in agreement with spectroscopic measurements and potential energy calculations performed on *n*-butane and higher alkanes.

Chain branching, together with molecular weight distribution, tacticity in vinyl polymers, and degree of cross linking in network polymers, is a molecular parameter knowledge of which is crucial to the understanding of the physical properties of polymers.[1] Many experimental studies[2–12] seeking to determine the

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