of deuteriated methyl groups. This work provides further confirmation of their report.

The fact that the calculated deuterium quadrupole coupling constants and asymmetry parameters of acetic acid dimer can be fitted by a Karplus-type equation is very interesting. Heretofore, there were no reported methods for correlating deuterium quadrupole coupling constants with solid-state structural features. Further work is now in progress to refine experimental values for the parameters *A*, *B*, and *C*. It should be straightforward to extend the method to other functional groups, for example, esters, ketones, and sulfones.

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Supplementary Material Available: Listings of anisotropic thermal parameters and torsion angles for (4-chlorophenyl)acetic acid (3 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Dynamics of H_2 Elimination from the Methaniminium Cation, $[CH_2NH_2]^+$. Isotope Effects, Translational Energy Release, and Molecular Orbital Calculations

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Abstract: Various molecular orbital methods have been used to examine possible reaction mechanisms for the unimolecular decomposition $[CH_2NH_2]^+ \rightarrow [HCNH]^+ + H_2$. Measurements of deuterium isotope effects on the translational energy release indicate the nonequivalence of the two departing hydrogen atoms, as does the reported absence of hydrogen scrambling in the products of this decomposition. The semiempirical calculations and the ab initio calculations up to and including the 6-31G** level predict that the departing hydrogen atoms do become equivalent and indistinguishable and that there will be significant hydrogen scrambling. This paradox is resolved on the grounds that geometries corresponding to stationary points in these calculations would not be stationary were a degree of configuration interaction to be included. The overall conclusion reached is that the transition state for elimination for H_2 from $[CH_2NH_2]^+$ is an asymmetric nonplanar structure with a geometry not far distant from $[CH_3NH]^+$, which is not a stable minimum on the potential surface.

The power of molecular orbital calculations in the determination of stable structures of small gaseous organic ions is now well established.[1-3] Procedures for identifying cols on the potential energy surfaces are established,[4] but the significance of the findings is not always clear-cut.[5] A particular challenge arises when the results of molecular orbital calculations are to be used to elucidate reaction dynamics. In this paper, we present results of extensive ab initio and semiempirical methods of calculation pertaining to the $[CH_4N]^+$ potential energy surface, which suggest that the loss of H_2 from the methaniminium ion, $[CH_2NH_2]^+$, proceeds via a symmetrical 1,1-elimination transition structure. Experimental results concerning the reaction dynamics indicate unequivocally that the transition structure for this elimination of H_2 is asymmetric. The paradox is explored and resolved on the grounds that cols located using the GAUSSIAN 82 ab initio molecular orbital package with the 6-31G** basis set would not be features of a more accurate potential energy surface.

Interest in H_2 eliminations from small organic ions was stimulated by the proposal of Williams and Hvistendahl[6] that the large translational energy releases observed for many such reactions could be accounted for in terms of molecular orbital symmetry arguments. The elimination of H_2 was proposed to be a symmetry-forbidden synchronous[7] 1,2-elimination. Supporting the proposals were the observation that $[CH_2ND_2]^+$ ions eliminated only HD and certain measurements of isotope effects on ion abundances.[6,8] A col corresponding to a planar and almost symmetric 1,2-elimination transition structure was located in an ab initio molecular orbital study.[9] However, this result is of questionable validity as the search considered only a restricted subset of planar geometries. The proposals put forward by Williams and Hvistendahl[6] can be separated into two parts. First, there is the argument that orbital symmetry creates a hump along the reaction pathway, so that there is a reverse critical energy

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(1) Baer, T. In *Mass Spectrometry* (A Specialist Periodical Report); Johnstone, R. A. W., Ed.; Royal Society of Chemistry: London, 1981; Vol. 6; pp 1-56.

(2) Pople, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 89-106.

(3) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(4) (a) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977, Vol. 4. (b) Kato, S.; Morokuma, K. *Chem. Phys. Lett.* **1979**, *65*, 19-25.

(5) Lorquet, J. C. In *Mass Spectrometry*, (A Specialist Periodical Report); Johnstone, R. A. W., Ed.; Royal Society of Chemistry: London, 1984, Vol. 7, pp 63-78.

(6) Williams, D. H.; Hvistendahl, G. *J. Am. Chem. Soc.* **1974**, *96*, 6753-6755.

(7) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209-219.

(8) Williams, D. H. *Acc. Chem. Res.* **1977**, *99*, 7432.

(9) Saebo, S. *Chem. Phys. Lett.* **1977**, *47*, 564-568.

0002-7863/88/1510-0347$01.50/0

available for partition as kinetic energy. Second, orbital symmetry shapes the potential energy surface in such a way that much of this reverse critical energy appears as translation. Both arguments have been questioned on the basis of a dynamical theory of energy partition,[10,11] which is discussed and used below.

The dynamical theory in its simplest form[11] takes the atomic motions of a molecular system as it passes through the transition structure and gives a definite value for the partition factor representing the proportion of the reverse critical energy passing into translation. In a previous study[10] of $[CH_2OH]^+$, a transition structure geometry for H_2 loss was calculated using the semiempirical molecular orbital method MINDO/3, and the atomic motions composing the reaction coordinate were fed directly into the calculations of the partition factors. The results were compared with values for experimental energy release obtained from widths of metastable peaks at half-height.[12] Reasonable agreement was found in the cases of a series of deuterium-substituted species. Three criticisms might be leveled at this study. First, the reliability of the semiempirical method might be questioned. Second, the energy releases calculated from peak widths using the one-line formula[12] might be unreliable. Third, the "transition state" was found by restricting possibilities to planar geometries. In the present study, metastable peaks for the methaniminium cations considered have been analyzed accurately[13] to obtain translational energy release distributions. Both the forms of the distributions and their means have been considered and are explained in the present study.

To investigate the $[CH_4N]^+$ potential surface, MINDO/3 and MNDO have been taken as representatives of semiempirical methods,[14] and GAUSS 82 using basis sets of different sizes was the ab initio method[15] considered. With all of the molecular orbital methods, the reaction coordinate and vibrational modes at transition structures were calculated, and these fixed unambiguously the translational energy release distribution predicted for the reaction according to the dynamical theory. It was found that the semiempirical methods and the ab initio methods using basis sets with which it was feasible to search the surface were good enough to explain broad features of the energy release data, but were unable to give a full explanation. There was a possibility that the full explanation both of the energy release data and the reaction mechanism would have been forthcoming if the surface could have been searched with a large basis set, including electron correlation.

Details of Experiments and Calculations

Methylamine and deuterated isotopomers were produced by dropping aqueous solutions of $CH_3NH_2{\cdot}HCl$, $CD_3NH_2{\cdot}HCl$, $CD_3ND_2{\cdot}DCl$, and $CH_3ND_2{\cdot}DCl$ onto sodium hydroxide pellets and trapping the evolved gas. These amine hydrochlorides were purchased from Merck Sharpe & Dohme. In preparing CH_3ND_2 and CD_3ND_2 the deuteriochloride was dissolved in D_2O, and, before measurements were made, the inlet line and ion source of the mass spectrometer were flushed with D_2O for several hours. CH_3NHD and CD_3NDH were obtained by using an H_2O/D_2O mixture to flush the inlet system and ion source. The various methaninium ions $[CH_2NH_2]^+$, $[CH_2ND_2]^+$, $[CD_2NH_2]^+$, $[CD_2ND_2]^+$, $[CH_2NHD]^+$, and $[CD_2NHD]^+$ were formed by 70-eV electron impact of the appropriate amines.

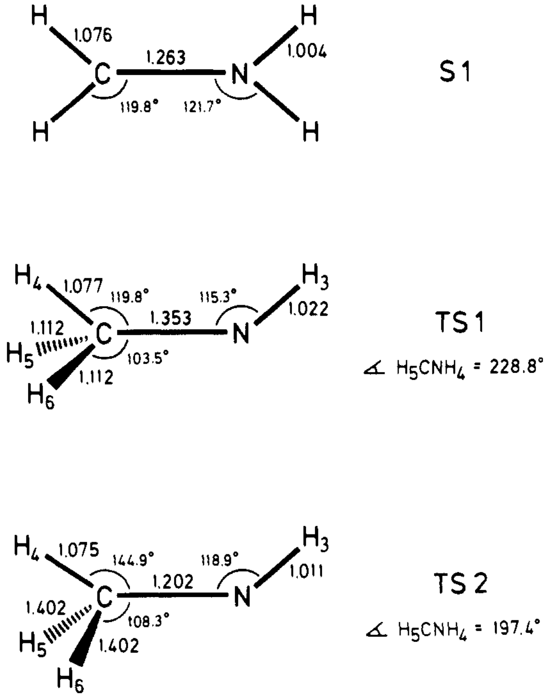

Figure 1. Geometries from ab initio calculation at the 6-31G** basis set level of $[CH_2NH_2]^+$ (S1), the exchange col (TS1), and the 1,1-elimination col (TS2).

Time-averaged mass-analyzed ion kinetic energy (MIKE) spectra[13] were measured using a large double-focusing mass spectrometer[16] with a magnetic sector of nominal radius 0.8 m and an electric sector of radius 1.0 m. The electric sector was swept in stepwise fashion (step size typically 15 mV) under computer control and signals acquired directly by the computer. The mass resolution of the mass spectrometer was typically set at about 2000. Measurements were made with the energy-defining slit between the sectors set at various widths (between 100 μm and 5 mm); the width of this slit was a factor considered in analyzing the metastable peak shapes (below).

The closed-shell ab initio Hartree–Fock self-consistent field[17] molecular orbital calculations were carried out using the GAUSSIAN 82 system of programs. Geometries were optimized with analytical gradients for the ground-state level using a split-valence plus dp-polarization basis set (6-31 G**).[15] Cols on the potential energy surface were identified on the criterion of one negative intrinsic value in the force constant matrix. Electron correlation energies were investigated by Moller–Plesset perturbation theory terminated at the fourth order (UMP4),[18] using geometries identified as wells or cols at the 6-31G** level. Starting geometries for the Hartree–Fock calculations were found using the MOPAC system of semiempirical molecular orbital programs.[19] The subroutine HADDON was modified to allow mapping of the semiempirical potential surfaces in terms of coordinates, which were quite complicated combinations of the natural valence coordinates.

Results and Discussion

a. Molecular Orbital Calculations. The results of the different ab initio and semiempirical calculations (Table I) indicate that $[CH_2NH_2]^+$ is a deep well on the potential energy surface. A calculated geometry is shown in Figure 1. The results of the different methods of calculation disagree on the question of whether or not $[CH_3NH]^+$ is a significant well on the surface. A minimum for $[CH_3NH]^+$ was found using MNDO (367 kJ mol^{-1} above the $[CH_2NH_2]^+$ energy), but no such minimum was located using MINDO/3. Using MNDO, a col was found 8 kJ

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(10) Rickard, G. J.; Cole, N. W.; Christie, J. R.; Derrick, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2904–2905.

(11) Christie, J. R.; Derrick, P. J.; Rickard, G. J. *J. Chem. Soc., Faraday Trans. 2* **1978**, *2*, 304–308.

(12) Cooks, R. G.; Beynon, J. H.; Caprioli, R.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.

(13) Slit widths, ion losses due to collisions with electric sector walls and entrance plates, z-axial discrimination, the translational energy distribution of the parent ion beam, the size of the field-free region within which decomposition occurs, and the contributions from decomposition within the electric sector have all been allowed for. The method is similar in its approach to that described by: Mendez Amaya, A.; Brenton, A. G.; Szulejko, J. E.; Beynon, J. H. *Proc. R. Soc. London, Ser. A* **1980**, *373*, 13–25, and is described by: Rumpf, B. A. Ph.D. Thesis, University of New South Wales, 1985; and Rumpf, B. A.; Derrick, P. J. *Int. J. Mass Spectrom. Ion Proc.*, in press.

(14) (a) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–1293. (b) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

(15) (a) Binkley, J. S.; Frisch, M. J.; De Frees, D. J.; Raghavachar, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(16) (a) Darcy, M. G.; Rogers, D. E.; Derrick, P. J. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *27*, 335–347. (b) Cullis, P. G.; Neumann, G. M.; Rogers, D. E.; Derrick, P. J. *Adv. Mass Spectrom.* **1980**, *8*, 1729–1734.

(17) Roothaan, C. C. *J. Rev. Mol. Phys.* **1951**, *23*, 69.

(18) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244–4245.

(19) Stewart, J. J. P. Quantum Chemistry Exchange Program No. 455, Chemistry Department, Indiana University, Bloomington, IN.

Table I. Calculated Energies Using ab Initio and Semiempirical Methods. Scaled Zero-Point Vibrational Energies from ab Initio Calculations at the 6-31G** Basis Set Level (After Reduction by 10%)

structure	RHF(6-31G**) (hartrees)	MP4/SDTQ/6-31G** (hartrees)	MNDO (kJ mol^{-1})	MINDO/3 (kJ mol^{-1})	zero-point energy (kJ mol^{-1})
S1[CH_2NH_2]$^+$	−94.394 715	−94.723 508	782.8	732.2	137.5
S2[CHNH]$^+$	−93.165 300	−93.469 229	951.4	838.5	67.3
S3[$CHNH_3$]$^+$	*b*	*b*	1120.5	*a*	*b*
S4[CNH_2]$^+$	−93.101 678	−93.390 080	1164.4	963.2	65.8
S5[CH_2N]$^+$	−93.059 966	−93.351 773	1242.6	*a*	58.9
S6[H_2]	−1.131 334	−1.164 558	2.9	0.4	24.9
TS1[CH_3NH]$^+$	−94.232 998	−94.558 953	*a*	1028.0	117.5
TS2[(H_2)CHNH]$^+$	−94.227 629	−94.570 305	1189.1	*a*	111.0
TS3[CH(H)NH_2]$^+$	−94.202 522	−94.540 076	1253.9	1003.3	121.5
TS4[(H_2)CNH_2]$^+$	*a*	*a*	1269.4	*a*	*a*
TS5[$CH_2N(H)_2$]$^+$	−94.187 747^c	−94.524 017^c	1282.4^c	*a*	98.7
TS6[CHNH(H_2)]$^+$	−94.127 133	−94.473 677	*a*	*a*	105.4
TS7[C(H)NH]$^+$	−93.038 463	−93.351 278	1369.8	*a*	47.0
TS8[CH(H)N]$^+$	−93.058 604	−93.356 357	1278.6	*a*	56.2
		Relative Calculated Energies			
S1[CH_2NH_2]	0	0	0	0	
S2[CHNH]$^+$ + H_2	257.6	235.6	171.5	106.7	
S3[CHNH]$^+$	*b*	*b*	337.7	*a*	
S4[CHN_2]$^+$ + H_2	424.7	443.5	384.5	231.4	
S5[CH_2N]$^+$ + H_2	534.2	544.1	462.7	*a*	
TS1[CH_3NH]$^+$	424.7	432.2	*a*	295.8	
TS2[(H_2)CHNH]$^+$	438.8	402.4	406.3	*a*	
TS3[(H_2)CHNH]$^+$	504.8	481.8	471.1	271.1	
TS4[(H_2)CNH2]$^+$	*a*	*a*	486.6	*a*	
TS5[$CH_2N(H)_2$]$^+$	543.6	523.9	499.6	*a*	
TS6[CHNH(H_2)]$^+$	702.8	656.2	*a*	*a*	
TS7[C(H)NH]$^+$ + H_2	590.8	545.4	589.9		
TS8[CH(H)N]$^+$ + H_2	537.8	532.1	498.7	*a*	

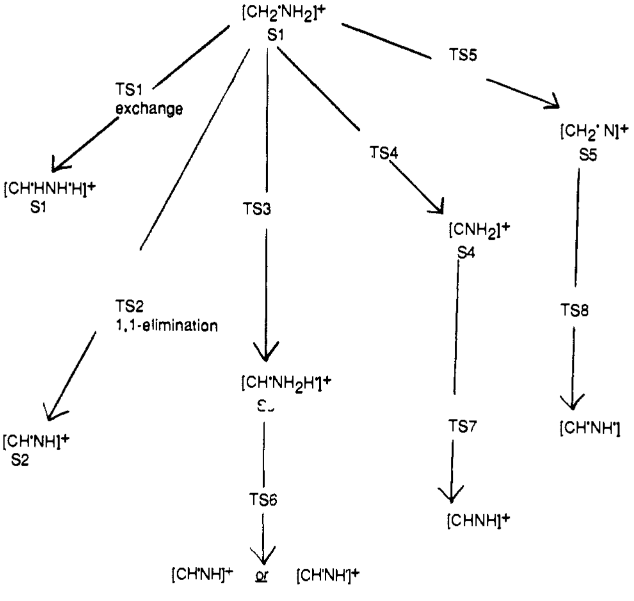
[a] Did not optimize. [b] Did not search. [c] Two negative frequencies.

mol^{-1} above the [CH_3NH]$^+$ minimum and is identified as a 1,2-hydrogen shift transition structure connecting the [CH_3NH]$^+$ minimum to [CH_2NH_2]$^+$. A minimum for [CH_3NH]$^+$ could not be found using ab initio calculations at the 6-31G** level. With smaller basis sets, including 6-31G, there was a minimum and a nearby col. With both MNDO and the ab initio calculations using smaller basis sets, there was a second col close to the [CH_3NH]$^+$ minimum, which is taken to be a transition structure between [CH_3NH]$^+$ and the decomposition products [CHNH]$^+$ and H_2. The 1,1-elimination transition structure is symmetrical and the two departing H atoms are indistinguishable. An equivalent col was found using the 6-31G** basis set, and will be referred to as the 1,1-elimination transition structure (TS2). Its geometry is shown in Figure 1. In this case, however, the transition structure cannot be assumed to connect to [CH_3NH]$^+$ since using this basis set no minimum was found for the latter. The computing time, which would have been required, precluded searching the potential energy surface at the higher level MP4/SDTQ/6 31G**. Single-point calculations were carried out at this level, using geometries determined at the 6-31G** basis set level.

A col (TS 1 in Table I and Scheme I) representing a transition structure for hydrogen exchange between the C and N atoms of [CH_2NH_2]$^+$ is found in the results of those molecular orbitals schemes (6-31G** and MINDO/3) that do not provide a stable [CH_3NH]$^+$ minimum. The geometry of this transition structure TS1 obtained from the ab initio calculation at the 6-31G** level is shown in Figure 1. Evidently, TS1 is [CH_3NH]$^+$-like in structure. A significant finding is that, when using the highest level basis set investigated and including some configuration interaction (MP4/SDTQ/6-31G**), the energy of the geometry TS1 is greater than that of the geometry TS2. The geometries TS1 and TS2 are not cols at this level, i.e., do not have a single imaginary frequency.

All the different types of ab initio and the semiempirical calculations agree that [CHNH]$^+$, [CNH_2]$^+$, and [CH_2N]$^+$ are all wells on the potential energy surface and that, of these three geometries, [CHNH]$^+$ is the lowest in energy (Table I and Scheme I). Cols, which we take to be transition structures between [CH_2NH_2]$^+$ and [CNH_2]$^+$ and [CH_2N]$^+$ structures, have been located and their energies are given in Table I. Similarly, cols for isomerization of [CNH_2]$^+$ and [CH_2N]$^+$ have been located (Table I and Scheme I). The isomer [$CHNH_3$]$^+$ (S3) is also predicted to be stable, and cols associated with it have been located [Table I and Scheme I].

Scheme I. Minima and Cols Located by Molecular Orbital Calculations



A plot of the MINDO/3 potential energy surface of [CH_4N]$^+$ in the region of the col exchange (TS1) and 1,1-elimination col (TS2) is shown in Figure 2. The unusual coordinates have been chosen to reveal the proximity and relationship of these two cols to each other. It can be seen that the valleys from the exchange col to [CH_2NH_2]$^+$ are narrow, while that over the elimination col is broad. The plots of this same region obtained using the 6-31G** ab initio method would be similar.

The results of all the different ab initio and semiempirical calculations agree that deep wells for the reactant [CH_2NH_2]$^+$

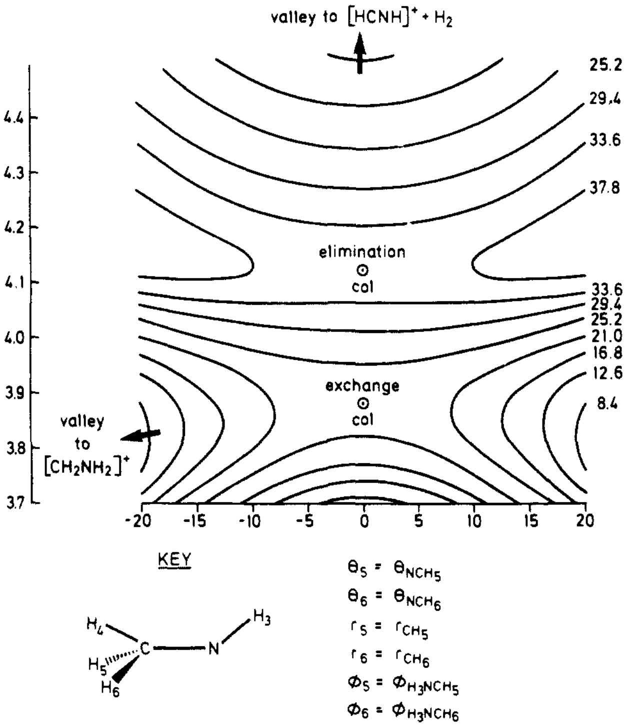


Figure 2. Plot of the $[CH_4N]^+$ potential surface in the neighborhood of $[CH_3NH]^+$ geometries, according to MINDO/3. The x coordinate is $(\theta_5 - \theta_6)$/degrees and the y coordinate is $(r_5 + r_6)/\text{Å} + 0.2(\theta_5 + \theta_6 + \phi_5 - \phi_6)$/radians. Interval between adjacent potential energy contours is 4.2 kJ mol^{-1}; absolute values are arbitrary. All geometric variables other than the two plotted are optimized for minimum potential energy.

and for the products $[CHNH]^+$ and H_2 are separated by a broad and relatively flat plateau on the potential energy surface. Considering the plot of the potential energy surface (Figure 2) the minimum energy pathway from $[CH_2NH_2]^+$ in the direction of products leads up the side of the plateau to the H-exchange col TS1, and hence back to $[CH_2NH_2]^+$. The overall effect of this exchange is to shift one H atom originally attached to the N atom to the C atom and one H atom originally attached to the C atom to the N atom, i.e., $[CH'_2NH_2]^+ \rightarrow [CH'HNH'H]^+$. If the system were to follow the minimum energy pathway, there would be no decomposition to $[CHNH]^+$ and H_2. Decomposition would, however, be expected as a consequence of perambulatory motion around and about the minimum energy pathway. Sufficient motion in directions transverse to the minimum energy pathway would cause the system to spill over the broad col of the 1,1-elimination transition structure. Some degree of hydrogen exchange or "scrambling" would be expected to occur within $[CH_2NH_2]^+$ ions with sufficient internal energy to decompose. This prediction runs contrary to experimental findings. The transition structure for elimination of H_2 would be symmetrical and the departing H atoms would become indistinguishable in the transition structure. The types of potential surface which need to be considered can be summarized as in Figure 3. There are two symmetric surfaces, one with a minimum at $[CH_3NH]^+$ (indicated by MNDO and ab initio calculations with smaller basis sets) and the other without the minimum (indicated by MINDO/3 and the 6-31G** calculation). Experiment shows the surface to be asymmetric, as will now be discussed. The possibilities for transition state structures for H_2 elimination are summarized in Figure 4.

b. Translational Energy Release. The metastable peak for elimination of H_2 from $[CH_2NH_2]^+$ gives the distribution $P(E_t)$ of translational energy shown in Figure 5. The calculated distribution shown (Figure 5) is based on the 1,1-elimination (TS2) transition structure and is discussed below. The mean of the experimental distribution is 0.903 eV. Metastable peaks were measured for loss of H_2, HD, and/or D_2 from different deuterium-substitution methaniminiums and were each analyzed to

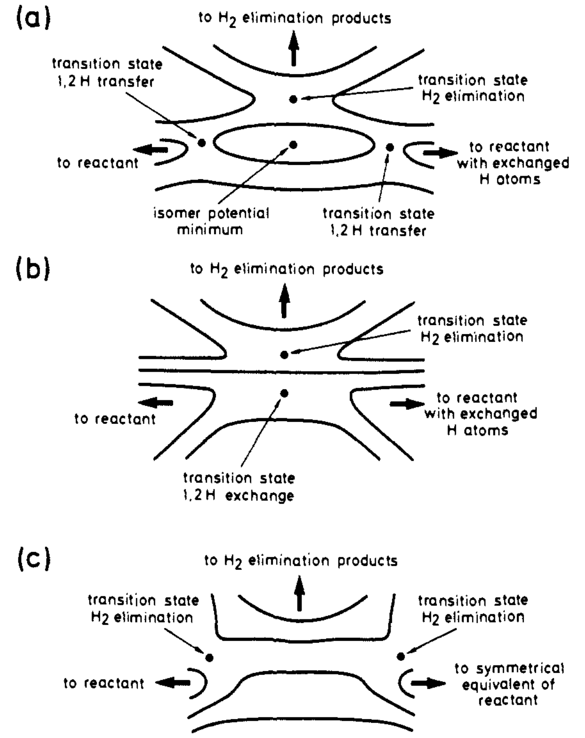


Figure 3. Three types of potential surface for loss of H_2 from $[CH_4N]^+$, shown schematically in terms of the coordinates defined in Figure 2: (a) symmetrical transition state, stable isomer; (b) symmetrical transition state, no isomer; (c) unsymmetrical transition state.

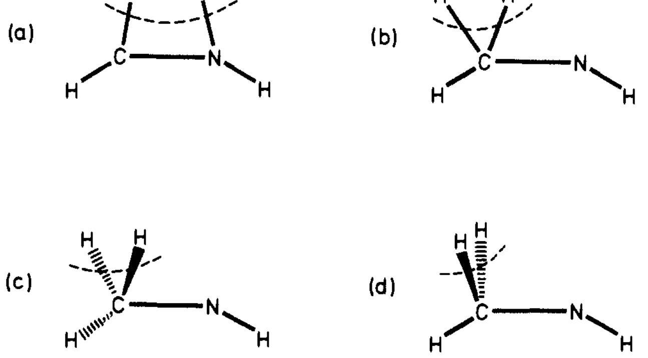


Figure 4. Possibilities for transition-state structures for loss of H_2 from $[CH_4N]^+$: (a) symmetrical planar, ruled out by molecular orbital calculations and experimental results; (b) planar, ruled out by molecular orbital calculations; (c) unsymmetrical, indicated by experimental results; (d) nonplanar symmetrical, indicated by a wide variety of molecular orbital calculations.

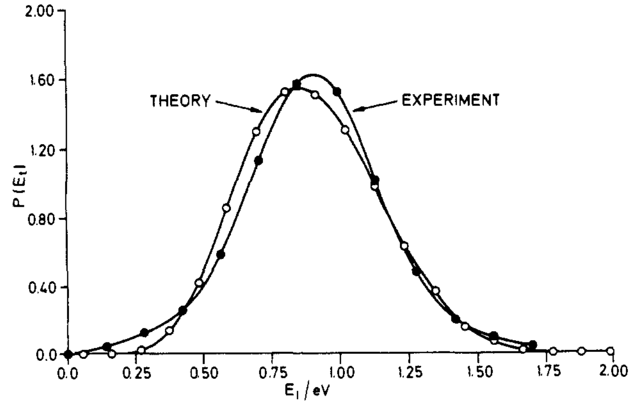


Figure 5. The translational energy release distribution derived through analysis of the metastable peak for loss of H_2 from $[CH_2NH_2]^+$. Theoretical distribution calculated by means of the extended dynamical theory for a 1,1-elimination transition structure (TS2).

Table II. Isotope Effects on Energy Releases

ion	loss	exptl	calcd[a]
$[CH_2NH_2]^+$	H_2	1.000	1.000
$[CH_2ND_2]^+$	HD	1.000	1.044
$[CD_2NH_2]^+$	HD	0.989	0.954
$[CD_2ND_2]^+$	D_2	0.984	0.993
$[CH_2NHD]^+$	H_2	0.967	0.984
$[CH_2NHD]^+$	HD	1.120	1.060
$[CD_2NHD]^+$	HD	0.932	0.931
$[CD_2NHD]^+$	D_2	1.075	1.019
$[CDHNH_2]^+$	H_2	0.90[b]	
$[CDHNH_2]^+$	HD	1.00[b]	1.060

[a] Using 1,1-elimination transition structure TS2. [b] Values from Hvistendahl and Uggerud (ref 21).

obtain the translational energy release distribution.[13] The effects of deuterium substitution can be discussed in terms of the means of the distributions, since the shape of a distribution was found to be not significantly affected by substitution of deuterium. In Table II, the means of the experimental distributions are given relative to that for $[CH_2NH_2]^+$ as 1.000. The theoretical energy releases, which are expressed relative to that for $[CH_2NH_2]^+$, were obtained by means of the dynamical theory.[10-12] The transition structure employed in calculating the energy releases in Table II was the 1,1-elimination transition structure (TS2) from ab initio calculations at the 3-21G level. Allowance has been made for the different reverse critical energies for the variously deuterium-substituted methaniminiums.

The calculated distributions of translational energy release (Figure 5) were obtained using a recent extension of the dynamical theory.[20] As in the basic theory,[10-12] the energy release is considered to depend on the individual internal atomic motions of the transition structure. The extended method differs, however, in that allowance is made for zero-point motion. The calculated distribution of energy releases reflects the spread of motions due to zero-point energy. The motions due to zero-point vibration were obtained directly by ab initio calculation at the 3-21G level. The calculated distributions of energy release were found to be rather insensitive to the basis set level used in calculating zero-point motions. The calculated isotope effects (Table II), however, were sensitive to the level of sophistication of the basis set employed as discussed below.

The agreement between the experimental translational energy release distribution and that calculated using the 1,1-elimination transition structure is good. The agreement between the experimental isotope effects and those calculated using the 1,1-elimination transition structure (Table II) is satisfactory in some respects, but there are disagreements and these are significant. The agreement between experiment and calculation on isotope effects was found to be improved if the basis set used to calculate the atomic motions was made larger, but the disagreements referred to (below) remained. The isotope effects (Table II) can be analyzed as follows. Consider replacing the "active" (i.e., to be eliminated) H atom on the N atom by a D atom. Compare, therefore, $[CH_2NH_2]^+$ to $[CH_2NHD]^+$ losing HD, $[CD_2NHD]^+$ losing HD to $[CD_2ND_2]^+$, $[CH_2NHD]^+$ losing H_2 to $[CH_2ND_2]^+$, and $[CD_2NH_2]^+$ to $[CD_2NHD]^+$ losing D_2. Experimentally there is found to be an increase in energy release by an average factor of 1.08, and theoretically an increase by an average factor of 1.05. Replacing the "inactive" H atom on the N atom by a D atom decreases the experimental energy release by an average factor of 0.93, based on comparison of $[CH_2NH_2]^+$ to $[CH_2NHD]^+$ losing H_2, $[CD_2NHD]^+$ losing D_2 to $[CD_2ND_2]^+$, $[CD_2NHD]^+$ losing HD to $[CH_2ND_2]^+$, and $[CD_2NH_2]^+$ to $[CD_2NHD]^+$ losing HD. The theoretical energy releases show the same trend, with a decrease by an average factor of 0.98. Experimentally, the replacement of both H atoms on the C atom by D atoms decreases the energy release by an average of 0.97, which is less than the decrease (0.93) on replacing the "inactive" H atom on the N atom.

Consider $[CH_2NH_2]^+$ compared to $[CD_2NH_2]^+$, $[CH_2NHD]^+$ losing HD to $[CD_2NHD]^+$ losing D_2, $[CH_2NHD]^+$ losing H_2 to $[CD_2NHD]^+$ losing HD, and $[CH_2ND_2]^+$ to $[CD_2ND_2]^+$. The calculations seems to have overestimated the role of the H atoms on the carbon. The role of the "active" H atom on the nitrogen is also underestimated. The shortcoming is revealed clearly, when the "active" and "inactive" H atoms on the C atom are distinguished. Experimentally, replacing the "active" H atom on the C atom by a D atom does not alter the energy release (Table II). Theoretically, there is an increase in energy release on replacing the "active" H atom on the C atom by a D atom equal to that on replacing the "active" H atom on the N atom, as must always be the case when considering a 1,1-elimination transition structure since the "active" H atoms are equivalent and indistinguishable. Experimentally, the replacement of the "active" H atom on the N atom increases the energy release, whereas replacing the "active" H on carbon does not. The experimental results establish that the two departing ("active") H atoms do not become equivalent at the transition structure.[22]

Conclusion

It is our view that the molecular orbital calculations that we have been able to perform have failed to describe correctly the essential features of the potential surface. Their universal prediction of a transition-state structure with the departing hydrogen atoms symmetrically equivalent cannot be reconciled with experimental results without modifying the usual assumptions of transition-state theory.

The conclusion that can be drawn from the single-point MP4/SDTQ/6-31G** calculations is that the geometries corresponding to stationary points in the lower level calculations are far from stationary when this degree of configuration interaction is included, and their energies are differently ordered. All calculations indicate a very flat region of potential surface near the $[CH_3NH]^+$ geometry, and a detailed topography which is very finely balanced. It seems that in this case a qualitatively correct picture will only emerge when potential surface mapping is done with a molecular orbital method that includes a moderate degree of configuration interaction in the calculation as well as polarization functions in the basis set.

The experimental evidence is quite unambiguous in pointing to an asymmetric transition state. Any structure in which the two departing hydrogen atoms are equivalent can revert with equal probabilities to reactant, or to reactant with hydrogen atoms exchanged. The lowest energy structure with this symmetry must, of necessity, be either a col for 1,2 hydrogen atom exchange or a minimum corresponding to a stable $[CH_3NH]^+$ structure. In either event, a symmetrical H_2 elimination col would necessarily imply that hydrogen atom exchange could occur as a lower energy process than hydrogen molecule elimination. Experimentally, no scrambling of hydrogen isotope labels can be observed. Similarly, it is clear from both our results and those of Hvistendahl and Uggerud[21] that the average kinetic energy released in translation differs according to whether the departing hydrogen originally bonded to the nitrogen atom is substituted with deuterium, or the atom originally bonded to the carbon. But this translational energy arises from the reverse critical energy, and can only depend on the shape of the potential surface between transition state and products. If the two departing atoms were symmetrically equivalent in the transition state, there could be no such distinction in the observed kinetic energy release.

The transition state for elimination of H_2 from $[CH_2NH_2]^+$ is a completely asymmetric, nonplanar structure with a geometry not far distant from $[CH_3NH]^+$ (which is *not* a stable minimum on the potential surface). This reaction, which is concerted but

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(20) A full mathematical description is given in: Rumpf, B. A. Ph.D. Thesis, University of New South Wales, 1985.

(21) Hvistendahl, G.; Uggerud, E. *Org. Mass Spectrom.* **1985**, *20*, 541-542.

(22) The TS2 geometry from the 6-31G** level and the atomic motions were adjusted using a computer-based optimization procedure so as to give an exact fit to the experimental energy releases (Rumpf, B. A. Ph.D. Thesis, University of New South Wales, 1985). The adjusted geometry was completely asymmetric and the departing H atoms were nonequivalent.

not synchronous,[7] involves one of the hydrogen atoms originally bonded to the nitrogen moving quite close to the carbon atom before departing with another hydrogen atom from the carbon atom in the form of H_2. The important caveat emphasized by this study is that ab initio calculations at the 6-31G** level and semiempirical MNDO and MINDO/3 calculations are not necessarily reliable in their predictions as to the symmetries and geometries of cols on the potential energy surfaces of small organic cations. The case of $[CH_2NH_2]^+$ shows that consideration of correlation effects can be essential in mapping reaction pathways of small organic cations by means of molecular orbital calculations.

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Registry No. $CH_3NH_2{\cdot}HCl$, 593-51-1; $CD_3NH_2{\cdot}HCl$, 7436-22-8; $CH_3ND_2{\cdot}DCl$, 14779-55-6; $CD_3ND_2{\cdot}DCl$, 14779-52-3: $[CH_2NH_2]^+$, 54088-53-8; $[CH_2ND_2]^+$, 111772-38-4; $[CD_2NH_2]^+$, 111772-39-5; $[CD_2ND_2]^+$, 111772-40-8; $[CH_2NHD]^+$, 111772-41-9; $[CD_2NHD]^+$, 111772-42-0; $[CH_3NH]^+$, 49784-84-1; $[CHNH]^+$, 38263-97-7; $[CNH_2]^+$, 86784-42-1; $[CH_2N]^+$, 53518-13-1; D_2, 7782-39-0.

Structure and Bonding in Cycloalkanes and Monosilacycloalkanes

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Abstract: The structural parameters and vibrational frequencies are predicted for the cycloalkanes C_nH_{2n} and silacycloalkanes $SiC_{n-1}H_{2n}$, n = 3–6, using the 3-21G* basis set and SCF wave functions. Bent bond lengths are predicted by tracing the paths of maximum electron density connecting atomic centers. Strain energies and heats of formation are predicted for these compounds and some smaller acyclic alkylsilanes by using MP2/6-31G(d) energies at the 3-21G* geometries and the appropriate homodesmic reactions.

I. Introduction

The concept of strain in small ring compounds has played an important role in chemistry since it was introduced more than a century ago. The nature of ring strain, its role in reactivity, and the importance of substituent effects have been the subject of several recent reviews.[1] The vast majority of attention, both experimentally and theoretically, has been devoted to cyclic compounds containing atoms in the first two periods of the periodic table, most particularly cyclopropane and cyclobutane and their derivatives.[2] Recently, however, several papers dealing with strain in cyclic molecules containing one or more silicon atoms in the ring have appeared in the literature.[2] Since the introduction of strained rings into a molecular environment can have a profound effect on the chemistry of the overall system, interest in strained cyclic compounds in which one or more carbons is replaced by a main group metal is likely to increase. Thus, it is important to develop a systematic understanding of how such substitutions affect molecular properties and chemical behavior.

This paper is the first in a series in which ab initio electronic structure theory is applied to investigations of small cyclic compounds with one or more carbon atoms replaced by a main group metal. In this first paper we examine the molecular structures, vibrational frequencies, and strain energies in the smallest cycloalkanes C_nH_{2n} (n = 3, 4, 5, 6) and their monosila analogues.

Also considered in this work are two important properties of strained ring compounds: bent bond lengths and heats of formation. The notion[3] that ring bonds are curved away from the bond axis has been explored in a quantitative manner recently by the groups of Bader[4,5] and Politzer.[6] These authors find that the bent bond distances can deviate significantly from the straight line distances connecting the two nuclei. One expects particularly large deviations in very highly strained systems. The heats of formation of the cycloalkanes are known experimentally, but the same is not the case for their silicon analogues. Thus, it is of interest to make use of theory to predict these values.

Table I. Homodesmic Reactions for Strained Rings

c-$(CH_2)_3$ + $3CH_3CH_3$ → $3CH_3CH_2CH_3$	(R1)
c-$(CH_2)_4$ + $3CH_3CH_3$ → n-C_4H_{10} + $2C_3H_8$	(R2)
c-$(CH_2)_5$ + $3CH_3CH_3$ → n-C_5H_{12} + $2C_3H_8$	(R3)
c-$(CH_2)_6$ + $3CH_3CH_3$ → n-C_6H_{14} + $2C_3H_8$	(R4)
c-$(CH_2)_2SiH_2$ + $3CH_3CH_3$ → $CH_3SiH_2CH_3$ + $2C_3H_8$	(R5)
c-$(CH_2)_3SiH_2$ + $3CH_3CH_3$ → $CH_3SiH_2CH_2CH_3$ + $2C_3H_8$	(R6)
c-$(CH_2)_4SiH_2$ + $3CH_3CH_3$ → $CH_3CH_2SiH_2CH_2CH_3$ + $2C_3H_8$	(R7)
c-$(CH_2)_5SiH_2$ + $3CH_3CH_3$ → $CH_3SiH_2CH_2CH_2CH_2CH_3$ + $2C_3H_8$	(R8)

In section II, the computational procedures used in this work are summarized. The calculated geometries and frequencies, strain

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(1) (a) Greenberg, A.; Liebman, J. F. *Chem. Rev.* **1976**, *76*, 311. (b) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978. (c) Greenberg, A.; Stevenson, T. A. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1986; Vol. 3, Chapter 5.

(2) (a) Tribble, M. T.; Allinger, N. L. *Tetrahedron* **1972**, *28*, 2147. (b) Oulette, R. J.; Baron, D.; Stolfo, J.; Rosenblum, A.; Weber, P. *Tetrahedron* **1972**, *28*, 2163. (c) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419. (d) Cartledge, R. K. *J. Organomet. Chem.* **1982**, *225*, 131. (e) Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1706. (f) Dabisch, T.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1986**, 896.

(3) Coulson, C. A. *Valence*; Oxford: London, 1961.

(4) (a) Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040. (b) Tal, Y.; Bader, R. F. W.; Erkku, J. *Phys. Rev. A* **1980**, *21*, 1. (c) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 631.

(5) (a) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061. (b) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, T. T.; McDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069. (c) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811.

(6) (a) Politzer, P.; Abrahmsen, L.; Sjoberg, P.; Laurence, P. R. *Chem. Phys. Lett.* **1983**, *102*, 74. (b) Politzer, P.; Domelsmith, L. N.; Abrahmsen, L. *J. Phys. Chem.* **1984**, *88*, 1752. (c) Politzer, P.; Jayasuriya, K.; Zilles, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 121.

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0002-7863/88/1510-0352$01.50/0