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# Methyl loss from conventional and distonic isomers of $C_3H_7N^{\cdot+}$ 1

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**Abstract**

The unimolecular reactions of a number of $C_2H_5N^{\cdot+}$ and $C_3H_7N^{\cdot+}$ isomers have been investigated. Mass-analyzed ion kinetic energy (MIKE) and collision-induced dissociation (CID) experiments as well as ab initio calculations show that the *N*-methylaziridine molecular ion and the distonic radical cation $CH_2{=}N(CH_3)CH_2^{+}$ can interconvert below the threshold for unimolecular fragmentation, whereas the *N*-ethylmethylenimine molecular ion is structurally distinct. Likewise, the aziridine molecular ion can undergo ring opening below the threshold for unimolecular fragmentation. Methyl loss from the *N*-methylaziridine radical cation proceeds via isomerization to the distonic ion, whereas methyl loss from the imine radical cation is a straightforward simple cleavage. The heats of formation of the $C_3H_7N^{\cdot+}$ and $C_2H_5N^{\cdot+}$ isomers determined with four different composite methods, G2(MP2), G3, CBS-Q, and CBS-RAD, agree reasonably well, and reasonably well with the available experimental data. The distonic ions are found to be the more stable isomers on the $C_2H_5N^{\cdot+}$ and $C_3H_7N^{\cdot+}$ potential energy surfaces. (Int J Mass Spectrom 195/196 (2000) 459–466) © 2000 Elsevier Science B.V.

*Keywords:* Ab initio calculations; Metastable ions; CBS-RAD; G2(MP2); Heats of formation

## 1. Introduction

The discovery in the early eighties [1,2] that ionized methanol, $CH_3OH^{\cdot+}$, has a stable isomer, $^{\cdot}CH_2OH_2^{+}$, sparked numerous investigations in the immediately following years. It was found that distonic ions [3], i.e. radical cations with formally separated charge and radical sites, are often formed in unimolecular and bimolecular reactions of aliphatic gas-phase radical cations, and that they are in many cases key intermediates in the unimolecular reactions of radical cations [4,5]. Early systematic studies by Bouma et al. [6] demonstrated that the ring opening of gas-phase radical cations of three- and four-membered cyclic ethers yields stable distonic ions (Scheme 1).

Subsequently, work by Symons and Wren [7] showed that cyclic ethers exposed to ionizing radiation in freon matrices at low temperature also undergo spontaneous ring opening.

The ring-opened isomers of the aziridine and *N*-methylaziridine radical cations, **1** and **2** (Scheme 2), nitrogen analogs of $^{\cdot}CH_2{-}O{=}CH_2^{+}$, have not attracted similar attention. Duffield and co-workers [8] tentatively suggested that **1** and **2** were formed when ionized pyrrolidines, piperidines, and related cyclic amines dissociate in the mass spectrometer ion

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In memory of Professor Robert R. Squires and his many contributions to ion chemistry.


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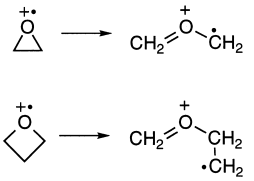
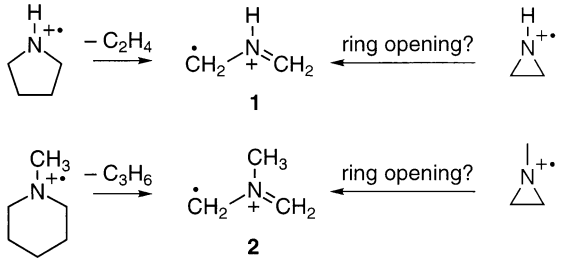


Scheme 1.

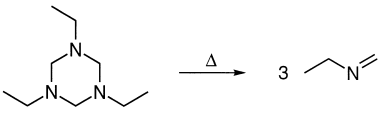
source, but they did not subject these ions to a closer experimental study.

Electron paramagnetic resonance studies by Qui and Williams [9] indicate that aziridine radical cations formed in a frozen freon matrix undergo spontaneous ring opening (to give **1**). Studies of these ions in the gas phase are less conclusive. Charge stripping experiments by Maquestiau et al. [10] indicate that gas-phase aziridine radical cations do not ring open; this conclusion was supported by early calculations by Lien et al. [11]. On the other hand, Holmes and Terlouw [12] came to the conclusion that the aziridine radical cation and **1** are indistinguishable on the basis of kinetic energy release measurements.

We have now examined the $C_3H_7N^{\cdot+}$ ion described by Duffield and the isomeric *N*-methylaziridine molecular ions, to determine whether ring opening of the latter can take place spontaneously. Further, we have studied the loss of a methyl radical from *N*-methylaziridine molecular ions and from the distonic ion **2**, to complement previous studies of the loss of alkyl radicals from saturated $\alpha$-distonic ions [13]. Determining whether ion **2** will rearrange to the *N*-ethylmethylenimine radical cation by 1,2-methyl migration is also discussed in the investigation. The imine radical cation and **2** yield the same products upon methyl loss by simple cleavage.




Scheme 2.



Scheme 3.

To complement the experiments and to determine the heats of formation of **1**, **2** and a small set of related molecules, we have employed the G2(MP2) and CBS-Q composite ab initio methods [14,15]. In addition, we have used the G3 and CBS-RAD procedures developed recently by Curtiss et al. [16] and by Mayer et al. [17]. The CBS-RAD method was suggested to be particularly suitable for the calculation of accurate radical thermochemistry even for highly spin contaminated systems. The calculations extend a recent computational study of the $C_2H_5N^{\cdot+}$ isomers by Shaffer et al. [18].

## 2. Methods

The mass-analyzed ion kinetic energy (MIKE) and collision-induced dissociation (CID) spectra were recorded on a Jeol HX/HX110A four sector (EBEB) mass spectrometer in three-sector mode under standard operating conditions. The three isomeric $C_3H_7N$ radical cations were obtained from precursors prepared by unexceptional methods. Two different precursors were employed for **2**: *N*-methylpyrrolidine and *N*-methylpiperidine. These compounds were synthesized by the $LiAlH_4$ reduction of pyrrolidine-1-carboxylic acid ethyl ester and piperidine-1-carboxylic acid ethyl ester, respectively; $LiAlD_4$ was employed in the synthesis of the trideuteromethyl compound. *N*-methylaziridine and *N*-trideuteromethylaziridine were prepared by ring closure of 2-methylaminoethanol as described by Smith et al. [19]. Thermolysis of hexahydro-1,3,5-triazines has been shown to yield methylenimines in the hot inlet system of the mass spectrometer [20] (Scheme 3). *N*,*N*′,*N*″-triethylhexahydro-1,3,5-triazine was prepared from formaldehyde and ethylamine as described by Einhorn [21].

The 0 and 298 K heats of formation were derived from calculated electronic energies as described by Nicolaides et al. [22]. The energies presented in Table

Table 1
Calculated energies[a]

| Molecule | CBS-RAD | CBS-Q | G2(MP2) | G3 |
|---|---|---|---|---|
| $CH_3^{\cdot}$ | −39.74396 | −39.74517 | −39.74391 | −39.79329 |
| $CH_2{=}CHCH_2^{\cdot}$ | −117.00765 | −117.00983 | −117.00296 | −117.14490 |
| $CH_2{=}NCH_3^{\cdot+}$ | −133.34859 | −133.34983 | −133.34321 | −133.48497 |
| $CH_2{=}NHCH_2^{\cdot+}$ | −133.37578 | −133.37759 | −133.37053 | −133.51279 |
| Aziridine$^{\cdot+}$ | −133.32101 | −133.32283 | −133.31742 | −133.45802 |
| $CH_2{=}NCH_2CH_3^{\cdot+}$[b] | −172.58195 | −172.58410 | −172.57500 | −172.76452 |
| $CH_2{=}NCH_2CH_3^{\cdot+}$[c] | −172.58109 | −172.58298 | −172.57626 | −172.76341 |
| $CH_2{=}N(CH_3)CH_2^{\cdot+}$ | −172.60607 | −172.60840 | −172.60051 | −172.78884 |
| *N*-methylaziridine$^{\cdot+}$ | −172.56493 | −172.56660 | −172.56035 | −172.74724 |

[a] Values in Hartrees at 0 K.
[b] CCNC dihedral angle 0°.
[c] CCNC dihedral angle 120°.

1 were calculated with the GAUSSIAN 94 system of programs [23]. The required auxiliary thermochemical information was taken from the compilation by Wagman et al. [24].

The energy barriers and reaction energies of the reactions under study were calculated from energies obtained with a slightly modified version of G2(MP2), in which the zero point vibrational energies were calculated at the MP2(full)/6-31G(*d*) level and scaled by 0.9646 [25]. This modification was introduced because the HF/6-31G(*d*) and MP2(full)/6-31G(*d*) calculations yield significantly different geometries in some cases. We note that geometry optimization at the MP2(full)/6-311+G(2*df*,*p*) and MP2(full)/6-31G(*d*) levels yield virtually identical results. Additionally, the CBS-RAD method [17] was employed in order to assess whether the results obtained with this method would be substantially different from the G2(MP2) results. The CBS-RAD method involves a QCISD/6-31G(*d*) geometry optimization and frequency calculation and a CCSD(T)/6-31+G(*d′*) single point energy calculation [17]. The transition states were characterized in each case by the calculation of the vibrational frequencies (one imaginary frequency) and by an intrinsic reaction coordinate calculation. The calculated transition state energies relative to the energy of **2** are presented in Fig. 1.

## 3. Results and discussion

### *3.1. Rearrangement of $C_3H_7N^{\cdot+}$: ring opening of N-methylaziridine*

The MIKE spectra of the *N*-ethylmethylenimine and *N*-methylaziridine radical cations and of **2** are summarized in Table 2. The distonic ion **2** loses a hydrogen atom in a high yield, whereas the predom-

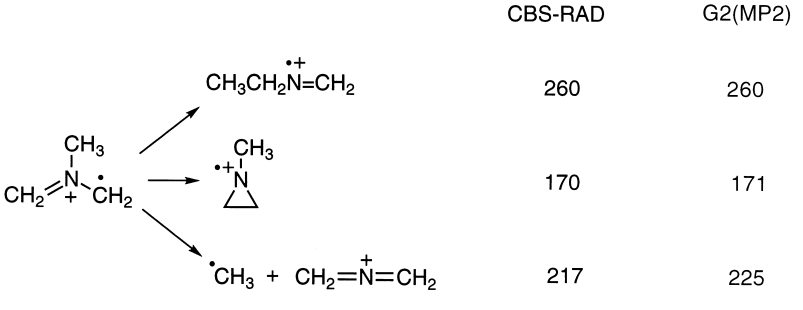



Fig. 1. Energy barriers (kJ mol$^{-1}$ at 0 K).

Table 2
MIKE spectra of $C_3H_7N^{\cdot+}$ ions and related species[a]

| Molecule | *m/z* 60 | *m/z* 59 | *m/z* 58 | *m/z* 57 | *m/z* 56 | *m/z* 45 | *m/z* 44 | *m/z* 43 | *m/z* 42 | *m/z* 41 |
|---|---|---|---|---|---|---|---|---|---|---|
| $CH_2{=}N(CH_3)CH_2^{\cdot+}$[b] | | | | $M^{\cdot+}$ | 40.5 | | | | 100.0 | 0.6 |
| $CH_2{=}N(CD_3)CH_2^{\cdot+}$[b] | $M^{\cdot+}$ | 100.0 | 19.3 | | | 1.2 | 1.0 | 0.6 | 24.0 | |
| $CH_2{=}N(CH_3)CH_2^{\cdot+}$[c] | | | | $M^{\cdot+}$ | 100.0 | | | | 31.0 | 2.0 |
| $CH_2{=}N(CD_3)CH_2^{\cdot+}$[c] | $M^{\cdot+}$ | 19.4 | 4.2 | | | 1.3 | 3.1 | | 100.0 | |
| *N*-methylaziridine$^{\cdot+}$ | | | | $M^{\cdot+}$ | 1.8 | | | | 100.0 | 1.1 |
| *N*-trideuteromethylaziridine$^{\cdot+}$ | $M^{\cdot+}$ | 1.5 | | | | | 4.0 | | 100.0 | |
| $CH_2{=}NCH_2CH_3^+$ | | | | $M^{\cdot+}$ | 67.0 | | | | 100.0 | |

[a] Relative intensity, peaks below 0.5% omitted.
[b] From *N*-methylpyrrolidine.
[c] From *N*-methylpiperidine.

inant reaction of the *N*-methylaziridine radical cation is loss of a methyl radical; only a very small proportion of the molecular ion population loses a hydrogen atom. The *N*-ethylmethylenimine molecular ion loses $CH_3^{\cdot}$ and $H^{\cdot}$ in comparable yield.

The CID spectra of the three radical cations are summarized in Table 3. The methyl and hydrogen atom loss reactions give rise to metastable peaks and are therefore not included [26]. The spectra of the *N*-methylaziridine molecular ion and **2** are virtually identical, indicating that these two species interconvert. The CID spectrum of the *N*-ethylmethylenimine molecular ion is different, indicating that the imine molecular ion does not isomerize to **2** or to the *N*-methylaziridine molecular ion. These results indicate that the *N*-methylaziridine molecular ion can undergo spontaneous ring opening upon ionization whereas the *N*-ethylmethylenimine molecular ion is a structurally distinct species.

Table 3
CID spectra of $C_3H_7N^{\cdot+}$ ions[a]

| *m/z* | *N*-methylaziridine$^{\cdot+}$ | $CH_2{=}N(CH_3)CH_2^{\cdot+}$[b] | $CH_2{=}N(CH_3)CH_2^{\cdot+}$[c] | $CH_2{=}NCH_2CH_3^+$ |
|---|---|---|---|---|
| 12 | 0.2 | 0.2 | 0.2 | 0.4 |
| 13 | 0.5 | 0.7 | 0.4 | 0.5 |
| 14 | 1.5 | 2.6 | 1.5 | 1.7 |
| 15 | 9.7 | 11.4 | 8.4 | 4.2 |
| 25 | 0.4 | 0.4 | 0.4 | 1.0 |
| 26 | 3.0 | 3.2 | 3.0 | 6.1 |
| 27 | 7.4 | 7.8 | 7.0 | 14.7 |
| 28 | 14.0 | 12.2 | 15.3 | 27.5 |
| 29 | 2.3 | 2.0 | 4.1 | 13.6 |
| 30 | 4.1 | 4.0 | 4.9 | 4.4 |
| 38 | 2.0 | 2.4 | 2.0 | 1.8 |
| 39 | 3.3 | 3.7 | 3.3 | 2.5 |
| 40 | 11.6 | 12.3 | 10.6 | 7.2 |
| 41 | 21.4 | 22.4 | 23.5 | 15.3 |
| 51 | 1.0 | 1.1 | 0.9 | 1.3 |
| 52 | 2.7 | 2.5 | 2.3 | 2.6 |
| 53 | 0.7 | 0.5 | 0.8 | 0.8 |
| 54 | 8.2 | 6.7 | 7.0 | 5.3 |
| 55 | 5.6 | 3.6 | 4.2 | 3.9 |

[a] Peak intensity relative to sum of intensities, metastable peaks ignored.
[b] From *N*-methylpyrrolidine.
[c] From *N*-methylpiperidine, high resolution mass spectrometry showed a considerable $^{13}C$ contribution from *m/z* 56 resulting in a peak at *m/z* 28.5 (omitted from the Table).

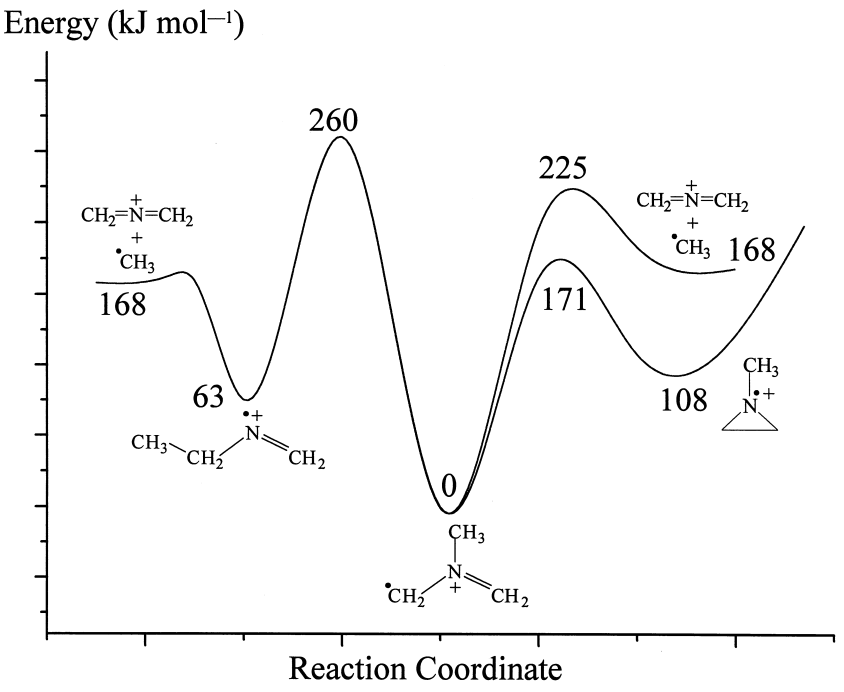



Fig. 2. Schematic presentation of the investigated region of the $C_3H_7N^{+}$ potential energy surface [G2(MP2)].

The computational and experimental results agree. The energy barrier for the rearrangement of **2** to the *N*-ethylmethylidenimine molecular ion (260 kJ $mol^{-1}$) [G2(MP2)] is substantially higher than the energy barrier for the lowest energy unimolecular fragmentation (methyl loss, 225 kJ $mol^{-1}$). The energy barrier for ring closure of **2** to the *N*-methylaziridine molecular ion (171 kJ $mol^{-1}$) is lower (Fig. 2), allowing these two species to interconvert prior to fragmentation. Rearrangement to the imine would be endothermic by 63 kJ $mol^{-1}$ and the endothermicity of the ring closure is 108 kJ $mol^{-1}$.

The geometries of the transition states for the rearrangements optimized at the QCISD/6-31G(*d*) level (CBS-RAD) and the MP2(full)/6-31G(*d*) level are similar. The QCISD/6-31G(*d*) geometries are depicted in Fig. 3(a) and (b). The barriers and reaction energies obtained with the CBS-RAD and G2(MP2) methods are also similar (Fig. 1); they agree within 1 kJ $mol^{-1}$.

### *3.2. Methyl loss from three $C_3H_7N^{+}$ isomers*

The loss of methyl from **2** and from the *N*-methylaziridine molecular ion gives rise to broad metastable peaks [Fig. 4(a) and (b)]. The corresponding *N*-trideuteromethyl substituted ions cleanly lose a $CD_3$ radical, also resulting in a broad metastable peak. The similarity in peak shapes could be taken to indicate that **2** and the *N*-methylaziridine molecular ion lose methyl in a similar manner. The computational results lend support to this suggestion. The loss of a methyl radical from **2** is found to be a direct C–N cleavage with an energy barrier of 225 kJ $mol^{-1}$ [G2(MP2)] (217 kJ $mol^{-1}$ with the CBS-RAD method) and the reverse reaction, the addition of a methyl radical to $CH_2$=N=$CH_2^{+}$, has an energy barrier of 57 kJ $mol^{-1}$ [G2(MP2)] (Fig. 2). The transition state geometry [QCISD/6-31G(*d*)] is depicted in Fig. 3(c). The existence of an energy barrier for the reverse reaction is consistent with the presence of the broad

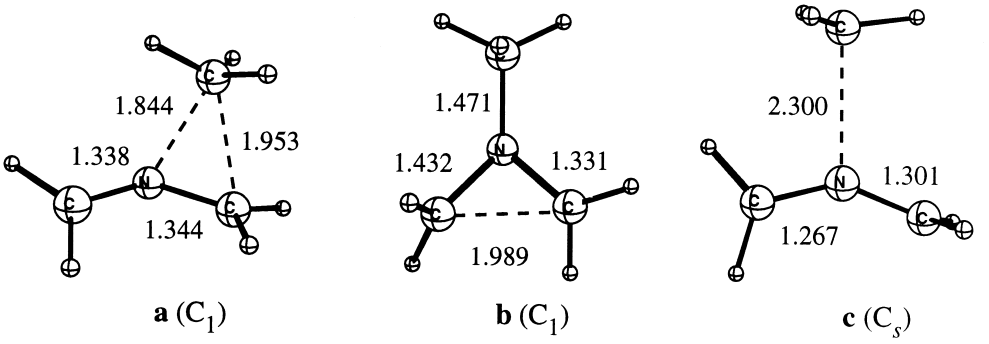



Fig. 3. QCISD/6-31G(*d*) optimized geometries of the transition states for rearrangement of the distonic ion to the imine radical cation (**a**), for ring closure of the distonic ion (**b**), and for methyl loss from the distonic ion (**c**).

peak. Our results show that a direct loss of methyl from the *N*-methylaziridine molecular ion requires considerably more energy than does rearrangement to **2** followed by methyl loss.

The loss of a methyl radical from *N*-ethylmethylenimine molecular ion gives rise to a narrow peak ($T_{0.5}$ = 3 meV) in the MIKE spectrum. Correspondingly, the calculations indicate that the imine radical cation loses methyl by straightforward simple cleavage without an energy barrier in excess of the reaction endothermicity.

The metastable peaks that correspond to loss of methyl from ion **2** and from the *N*-methylaziridine molecular ion (Fig. 4) appear to consist of unequal amounts of a broad and a narrow component. It is not yet clear why the peaks are composite. One possible reason would be that the *N*-methylaziridine molecular ion can lose $CH_3^{\cdot}$ without prior ring opening. However, our calculations make that possibility unlikely (see previous text). A bimodal energy distribution of the reacting ions as a consequence of a cul-de-sac rearrangement [27] is another possibility; we are currently investigating these matters in more detail.

### *3.3. Heats of formation of $C_3H_7N^+$ and $C_2H_5N^+$ isomers*

The heats of formation (Table 4) obtained with the four composite methods agree quite well, and reasonably well with the available experimental data. We note that the spin contamination for the distonic ions **1** and **2** is considerable ($\langle S^2 \rangle$ is close to 1.0); nevertheless the G2(MP2) method yields very much the same results as CBS-RAD which was designed to

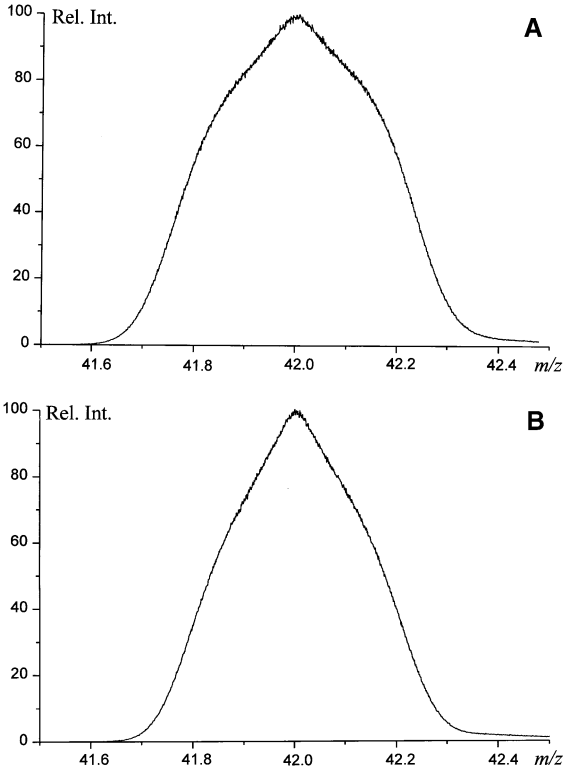



Fig. 4. Metastable peak for (a) loss of methyl from the distonic ion **2** and (b) loss of methyl from the *N*-methylaziridine molecular ion.

Table 4
Heats of formation calculated with four different composite methods[a]

| Molecule | Experiment | CBS-RAD[b] | | CBS-Q[b] | G2(MP2)[b] | G3[b] |
|---|---|---|---|---|---|---|
| | 298 K | 0 K | 298 K | 298 K | 298 K | 298 K |
| $CH_3^{\cdot}$ | 147[d] | 153 | 150 | 147 | 149 | 142 |
| $CH_2{=}CHCH_2^{\cdot}$ | 171[d], 165[e] | 186 | 174 | 169 | 180 | 165 |
| $CH_2{=}NCH_3^{+}$ | 979[c] | 981 | 973 | 964 | 967 | 964 |
| $CH_2{=}NHCH_2^{+}$ (**1**) | | 909 | 894 | 889 | 893 | 889 |
| Aziridine$^{\cdot+}$ | 1014[c] | 1053 | 1037 | 1033 | 1032 | 1033 |
| $CH_2{=}NCH_2CH_3^{\cdot+}$[f] | | 946 | 926 | 921 | 925 | 920 |
| $CH_2{=}NCH_2CH_3^{\cdot+}$[g] | | 948 | 928 | 924 | 928 | 923 |
| $CH_2{=}N(CH_3)CH_2^{+}$ (**2**) | | 883 | 862 | 856 | 861 | 855 |
| *N*-methylaziridine$^{\cdot+}$ | 964[c] | 990 | 969 | 965 | 965 | 964 |

[a] Values in kJ mol$^{-1}$.
[b] The same integrated heat capacity was determined with all four methods.
[c] From [31].
[d] From [28].
[e] From [29].
[f] CCNC dihedral angle 0°.
[g] CCNC dihedral angle 120°.

alleviate the problems that can arise in the case of severe spin contamination [17].

The heat of formation of the allyl radical (Table 4) was determined for comparison; allyl is a neutral conjugated radical that is isoelectronic with the distonic ion **1**. In addition, an unrestricted treatment of the wave function of this species results in a large spin contamination that could make the CBS-RAD method particularly suited for this system. The experimental value [28,29] is in reasonable agreement with the G3, CBS-RAD, and CBS-Q values but the result obtained with the G2(MP2) method differs by a substantial amount (Table 4).

### 3.4. $C_2H_5N^{\cdot+}$ ions

Maquestiau and co-workers [10] have shown that the charge stripping of $^{\cdot}CH_2$–NH=$CH_2^{+}$ (**1**) and aziridine molecular ions results in significantly different yields of doubly charged parent ions (*m/z* 21.5); this result was taken to indicate that aziridine molecular ions do not ring open spontaneously [10]. However, such a difference could reflect that charge stripping experiments, to a large extent, sample the stable ions [30], i.e. the fraction of ions that have energy below the isomerization threshold and therefore retain their structure. Calculations indicate that the aziridine molecular ion resides in a minimum; the barrier for ring opening is 35 kJ mol$^{-1}$ [G2(MP2)]. With the exception of the peak at *m/z* 21.5, we find that the CID spectra of **1** and the aziridine molecular ion (Table 5) are identical. This result is in agreement with the conclusions of Holmes and Terlouw [12].

Table 5
CID spectra of $C_2H_5N^{\cdot+}$ ions[a]

| *m/z* | Aziridine$^{\cdot+}$ | $CH_2{=}NHCH_2^{\cdot+}$[b] | $CH_2{=}NHCH_2^{\cdot+}$[c] |
|---|---|---|---|
| 12 | 0.8 | 0.8 | 0.5 |
| 13 | 1.2 | 1.5 | 2.0 |
| 14 | 4.3 | 4.7 | 4.1 |
| 15 | 19.0 | 21.0 | 22.5 |
| 16 | 0.7 | 0.2 | 0.2 |
| 20.5 | 2.0 | 2.0 | 1.6 |
| 21 | 0.5 | 0.7 | 1.2 |
| 26 | 1.5 | 2.2 | 1.7 |
| 27 | 6.4 | 7.7 | 6.5 |
| 29 | 1.6 | 1.7 | 1.9 |
| 38 | 6.8 | 7.8 | 7.3 |
| 39 | 12.6 | 14.9 | 12.3 |
| 40 | 39.3 | 35.0 | 39.1 |

[a] Peak intensity relative to sum of intensities, metastable peaks ignored.
[b] From pyrrolidine. Peak at *m/z* 21.5 omitted from the Table; see text.
[c] From piperidine. Peak at *m/z* 21.5 omitted from the Table; see text.

## 4. Concluding remarks

The experimental and computational results show that the *N*-methylaziridine molecular ion can undergo spontaneous ring opening to **2** below the threshold for fragmentation. Likewise, the ring opening of the aziridine molecular ion can take place below the threshold for fragmentation. We note with satisfaction that the three-membered first row heterocycles—oxirane, aziridine, and *N*-methylaziridine—exhibit consistent behavior in that they all undergo ring opening subsequent to ionization.

The unimolecular loss of a methyl radical from ion **2** proceeds by direct C–N cleavage, whereas the methyl loss from the *N*-methylaziridine radical cation takes place subsequent to ring opening. The corresponding metastable peaks indicate the presence of an appreciable energy barrier for the reverse reaction; this is corroborated by the computational results.

The agreement between the four composite computational methods is good, regardless of the high spin contamination encountered in some cases. Use of the computationally demanding CBS-RAD method does not appear to be warranted for the systems included in the present study.

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