Scheme I. Scheme I can be considered as a general mechanism, without defining individual conformers, which may become significantly simplified by the relative importance of particular rate constants. This mechanism is closely related to that already proposed by us[8] for the oxygen quenching of ketone triplets which themselves have highly localized uncoupled electrons. A putative 1,4-biradical of the type shown in Scheme I will have a lifetime no longer than a few tens of nanoseconds.[9,31] The obvious spin-allowed process is intramolecular reaction to yield products. These latter could of course be allylic hydroperoxides, endoperoxides, etc., typical $O_2(^1\Delta_g)$-derived products. Such species would, in any event, be produced because (a) significant yields of $O_2(^1\Delta_g)$ are also produced, and (b) at the high olefin concentrations necessarily employed most of that $O_2(^1\Delta_g)$ will be chemically quenched. However, there is no reason to believe that the individual biradical products and distribution thereof would be identical with those derived via $O_2(^1\Delta_g)$. Any difference would clearly be dependent on the individual olefin but in the general case would be expected to be more significant with decreasing S_Δ. We are unaware of any steady-state experiments which have addressed this specific problem.

5. Conclusions

Our results have shown that the reaction of olefin triplets with oxygen is an even more complicated function of triplet properties than has hitherto been assumed. In particular, we have provided evidence that the efficiency of the electron-exchange mechanism leading to $O_2(^1\Delta_g)$ is sensitive to the degree of distortion from planarity of the individual reacting conformer. This applies to triplets with "available" triplet energies considerably higher than the electronic excitation energy requirement of $O_2(^1\Delta_g)$. Although we recognize that the mechanistic proposals summarized in Scheme I are of necessity speculative, the key message is absolutely clear. Singlet oxygen quantum yields cannot be assumed to indicate the fraction of oxygen-quenched olefin triplets that lie more than 7882 cm^{-1} above the ground state surface.

Acknowledgment. Experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester, and the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is jointly supported by NIH Grant RR00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas at Austin. Support for this work came from SERC Grant GR/D/52169 (AAG) and NIH Grant GM24235 (MAJR).

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$(C_3H_6N)^+$ Cations in the Gas Phase: Ab Initio Molecular Orbital Calculations and Tandem Mass Spectrometry Experiments

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Abstract: Structures and energies of 26 linear or cyclic $(C_3H_6N)^+$ cations have been examined by ab initio molecular orbital calculations. The geometries of all ions were fully optimized with the 3-21G basis set; energies were improved by inclusion of polarization and electron correlation effects (CI/6-31G*//3-21 G). The seven structures predicted to be the most stable are as follows: **1** $(CH_3NCCH_3)^+$; **2**, $(CH_2CHCHNH_2)^+$; **3**, $(CH_3CH_2CNH)^+$; **4**, $(CH_3CHNCH_2)^+$; **5**, $(CH_2CHNHCH_2)^+$; **6**, $(c\text{-}CH_2CH_2NHCH)^+$; **7**, $(CH_3CH_2NCH)^+$. All other isomers have energies greater than that of **1** by ca. 100 kJ mol^{-1}. Experimental generation of five cations (**1–3**, **5** (and/or **6**), and **7**) in the source of a tandem mass spectrometer is also reported. Mass-analyzed ion kinetic energy and collisionally induced dissociation spectra have been used to characterize the five ion structures.

The positive $(C_nH_{2n}N)^+$ ions occur as major fragment ions during dissociation of unsaturated amines or as protonation or alkylation product of cyanides and isocyanides. Ions $(C_2H_4N)^+$ generated by proton transfer to CH_3CN or CH_3NC or from association of CH_3^+ and HCN have been detected by mass spectrometry.[1] The optimized molecular geometries and relative stabilities of isomers of these cations have been determined by semiempirical or ab initio calculations.[2-5] The calculations predict that $(CH_3CNH)^+$, $(CH_3NCH)^+$, $(CH_2CNH_2)^+$, and $(CH_2NCH_2)^+$ ions are the $(C_2H_4N)^+$ isomers of lowest energy.

Although the positive $(C_3H_6N)^+$ ions are present in the electron impact (EI) spectra of cyclic amines,[6] allylamine,[7] and heterocyclic compounds such as aziridine, azetidine, and ethyleneimine derivatives[8] or may be produced by protonation of C_3H_5N isomers, they have not been studied in great details.

In the present study we report first completely optimized geometries, energies, and relative stabilities of isomers **1–23** presented in Chart I. Several of those that are determined to be the most

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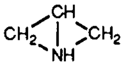
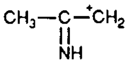
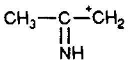
Table I. Relative Energy of $C_3H_6N^+$ Calculated at Various Theoretical Levels[a]

	ΔE					
$C_3H_6N^+$ species	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	MP4/ 6-31G*	ZPVE	MP4/6-31G* + ZPVE
$CH_3-C\equiv N^+-CH_3$ (**1**)	0	0	0	0	217	0
$CH_2=CH-{}^+CH-NH_2$ (**2**)	2	-8	6	1	225	8
$CH_3-CH_2-C\equiv{}^+NH$ (**3**)	35	48	42	43	218	43
$CH_3-{}^+CH-N=CH_2$ (**4**)	87	61	69	60	217	60
$CH_2=CH-NH-{}^+CH_2$ (**5**)	67	59	64	55	223	61
$\underline{CH_2-CH_2-{}^+CH-NH}$ (**6**)	94	65	60	56	225	63
$CH_3-CH_2-{}^+N\equiv CH$ (**7**)	79	76	68	69	218	70
$\underline{CH_2-CH_2-{}^+C}-NH_2$ (**8**)	115	94	93	92	224	98
$CH_2-{}^+C=NH-CH_3$ (**9**)	89	106	116	106	219	108
$\underline{CH_2-CH=CH-{}^+NH_2}$ (**10**)	124	121	102	99	227	108
$CH_2=C=CH-{}^+NH_3$ (**11**)	118	141	130	122	223	127
$CH_2-CH_2-N-{}^+CH_2$ (**12**)	175	132	128	125	222	129
$HC=C-CH_2-{}^+NH_3$ (**13**)	109	143	123	125	226	133
$\underline{NH-CH_2-{}^+C}-CH_3$ (**14**)	227	162	147	145	217	145
$\underline{NH_2-CH_2-C}=CH_2$ (**15**)	173	160	147	144	223	149
$CH_3-C\equiv C^+=NH_3$ (**16**)	154	187	169	171	226	180
	270	204	172	175	223	180
$CH_2-{}^+C(NH_2)CH_2$ (**18**)	209	192	199	188	215	185
$HC\equiv C-{}^+NH_2-CH_3$ (**19**)	184	219	203	204	226	212
$CH_3-{}^+CH-CH=NH$ (**20S**)	254	209	242	226	213	221
 $CH_3-\underset{\underset{NH}{\Vert}}{C}-\overset{+}{C}H_2$	303	260	294	278	213	273
$CH_2=CH-{}^+N-CH_3$ (**22S**)	332	258	297	278	213	273
$CH_2=CH-{}^+N-CH_3$ (**22T**)	191	184	354	324	205	312
 $CH_3-\underset{\underset{NH}{\Vert}}{C}-\overset{+}{C}H_2$	213	205	351	329	204	316
$CH_3-{}^+CH-CH=NH$ (**20T**)	224	215	358	335	205	322
$\underline{CH_2-NH-CH_2-{}^+CH}$ (**23**)	370	321	353	341	211	335

[a] Absolute total energies may be deduced from the calculated total energy of ion **1** used as reference: 3-21G//3-21G, −170.347 268; HF/6-31G*//3-21G, −171.293 623; MP2/6-31G*//3-21G, −171.820 899; MP4/6-31G*//3-21G, −171.876 330. All calculations are related to the fully optimized 3-21G geometries.

stable have been characterized experimentally by tandem mass spectrometry experiments.

Results and Discussion

I. Molecular Orbital Calculations. A. Method. Ab initio molecular calculations were carried out at the restricted (RHF) and unrestricted (UHF) Hartree–Fock level by using the MONSTERGAUSS program system.[9] The structures of all molecules were fully optimized with the 3-21G basis set without symmetry constraints. Triplet states were examined when electron resonance was thought to lead to an extra stabilization of the triplet state with regard to the singlet state. All stationary points have been characterized to correspond to local minima by having no negative eigenvalue in the computed force constant matrix. One exception was provided by structure **1**, for which it has been impossible, with the 3-21G basis set, to distinguish between the stable structure and the transition-state structure corresponding to the mutual rotation of the two methyl groups. The completely optimized structures of the singlet and triplet cations are displayed in the text.

The 3-21G optimized structures were then used for single-point calculations at the 6-31G* level with the GAUSSIAN86 program.[10] Improved energies were obtained after electron correlation correction estimated from the Møller-Plesst perturbation theory terminated at the second order (MP2) and at the fourth order including single, double, triple, and quadruple excitations (MP4, SDTQ).

Finally, zero-point vibrational energy corrections have been made from the 3-21G harmonic frequencies. To account for the overestimation of normal frequencies by Hartree–Fock calculation, the computed vibrational energies have been scaled by a factor of 0.9.[11]

The total and relative energies of the 26 $(C_3H_6N)^+$ isomers (Chart I) calculated by using various levels of theory are listed in Table I. In the following discussion, the relative stability of the $(C_3H_6N)^+$ isomers is always referred to ion **1**. The relative energy values quoted into the body of the paper are those calculated at the MP4/6-31G*//3-21G level after correction of the difference in zero-point vibrational energy (Table I, last column).

B. Nitrilium Ions. Among the $(C_3H_6N)^+$ isomers presented in Chart I, nitrilium ions **1**, **3**, and **7** hold a privileged place: the three isomers are among the most stable structures and, as will be seen, they are experimentally identifiable.

The calculated CN bond lengths are very similar for the three isomers (1.129, 1.130, and 1.125 Å for **1**, **3**, and **7**, respectively) and point to a triple-bond character. However, the nitrilium carbon atom bears most of the positive charge in the three cases.

Ions **3** and **7** may result from protonation of ethyl cyanide and ethyl isocyanide. The protonation of such species has been the subject of several experimental and theoretical studies.[1b,12-15] The

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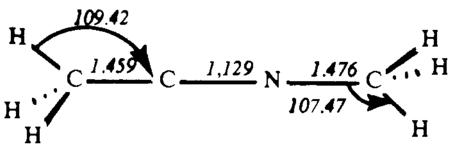
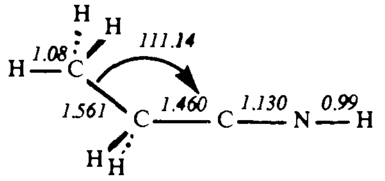


1



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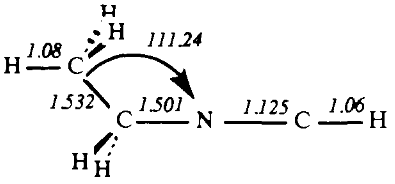


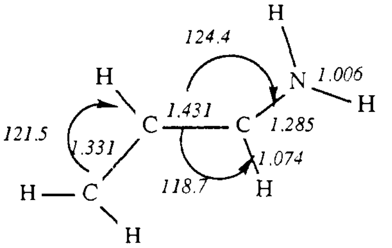
7

heats of formation derived from experimental proton affinity values are equal to 775[16] and 815 kJ/mol[17] for **3** and **7**, respectively.

For cation **1** an estimate of its heat of formation may be obtained by substracting the calculated energies of **3** and **7** relative to **1** (Table I) from their respective experimentally derived heats of formation. This procedure leads to $\Delta H^\circ_f(\mathbf{1}) = 738 \pm 7$ kJ/mol. A somewhat higher value ($\Delta H^\circ_f(\mathbf{1}) = 757 \pm 10$ kJ/mol) has been estimated from core binding energies.[3]

As will be seen in the next section, cation **1** is expected to be produced by methylation of both CH_3CN and CH_3NC.

C. Immonium Ions. The 1-substituted allyl cation **2** has an energy comparable to that of isomer **1**. A theoretical study of monosubstituted allyl cations[14] has shown that in the 1-substituted allyl cations the saturated substituents are strongly stabilizing with the order $NH_2 > OH > CH_3 > F$. For instance, the allyl cation is strongly stabilized by the amino group (strong donor). Thus the C–N bond length (1.285 Å) is shorter than a single C–N bond (1.47 Å).



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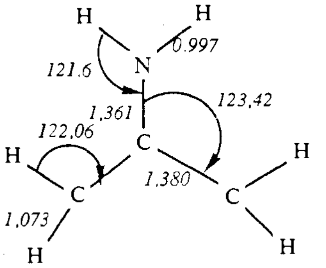
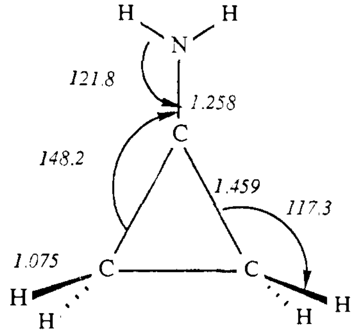


18

Introduction of the NH_2 substituent in position 2 of the allyl cation gives ion **18**. This 2-aminoallyl cation is higher in energy than both the 1-aminoallyl cation **2** and the aminocyclopropyl cation **8** by 177 and 87 kJ/mol, respectively. The large CN bond length value (1.462 Å) compared with that of the 1-allyl cation **2** (1.285 Å), and the charge distribution (C(3)H2, C(4)H2: +0.38; C(2): +0.35, 3-21G calculation) was in good agreement with a delocalization of the positive charge onto the carbon atoms exclusively.

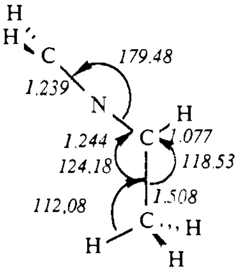


8

The stability of ion **8** with respect to its open form **18** is explainable by the donor effect of the NH_2 group directly attached to the positive center. This is illustrated by the atomic charges and by the shortening of the CN bond length (1.258 Å in **8** and 1.361 Å in **18**).

A comparison between the three structures **2**, **18**, and **8** has been done at a less accurate level by Lien et al.,[14] and good qualitative agreement is observed with our data.

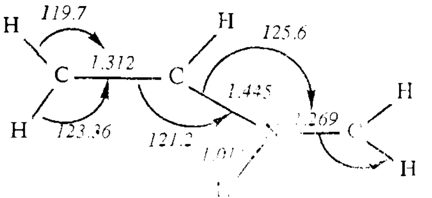
Structure **4** corresponds to an allene-type cation: the dihedral angle between the methylene group and the $CH(CH)_3$ moiety is equal to 90.0°. The two C–N bond length are comparable (1.239 and 1.244 Å).



4

The low energy of this ion relative to that of **1** (60 kJ/mol) suggests its possible experimental characterization.

Ion **5** could be produced experimentally by α-cleavage of 2-alkylaziridines[8] or piperidine and methylpiperidines.[7] The C(4)–N bond (1.269 Å) is shorter than the C(2)–N bond (1.445 Å) and close to a double-bond length as observed for the C(1)–C(2) bond. Thus ion **5** may be compared to ionized 1,3-butadiene, its isoelectronic analogue. The stability of **5** (61 kJ/mol with respect to **1**) renders the experimental observation of this species highly probable.



5

The corresponding cyclic structure **6** is the most stable of the four-membered ring isomers $(C_3H_6N)^+$. The CH–N bond length (1.278 Å) is short, indicating some stabilization of the positive charge (0.595) by the neighboring amino group. Ion **6** could be

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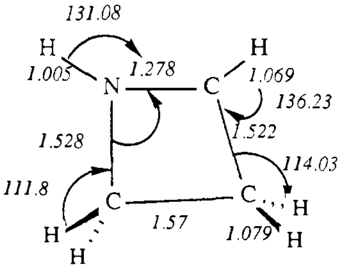
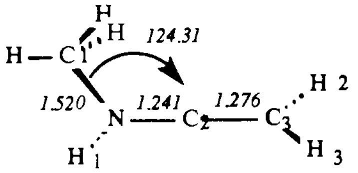


6

generated by α-cleavage from 2-alkylazetidines, but we note that its open form, ion **5**, is predicted to be of comparable stability by our molecular orbital calculations. It is thus not possible to exclude a competitive formation of **5** and **6**, by dissociative ionization of 2-alkylazetidines.

The ketene iminium ion **9** is an allene-type molecule (bond lengths C–N and C–C are quite equivalent: 1.241 and 1.276 Å). With a positive charge of +0.56 (3-21G calculation) the central carbon atom (C2) is the most electrophilic site.

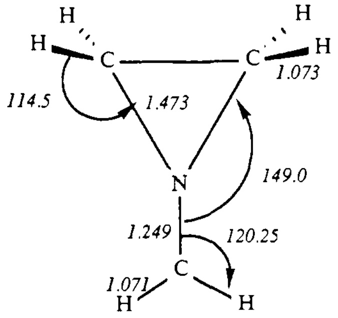


9

$< C_1NC_2H_2 = 89.7$

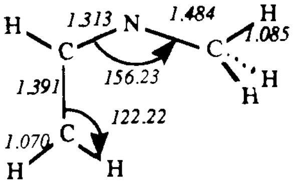
$< H_1NC_2H_3 = 89.9$

The positive charge of the cyclic ion **12** is located on the exocyclic methylene group (CH_2 +0.58). The C–N bond is short (1.249 Å), indicating a stabilization by the π-donating effect of the nitrogen atom.

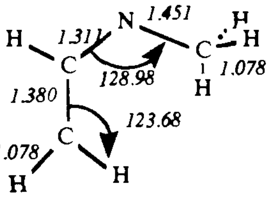


12

D. Carbenium Ions. Structure **22** may be represented under two mesomeric forms: $CH_2—CH{=}NCH_3$ (carbenium) ↔ $CH_2{=}CH—NCH_3$ (nitrenium). The nitrenium character of ion **22** suggests a favorable triplet state.



22 T

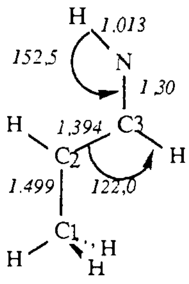


22 S

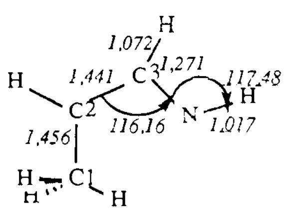
A minimum (ΔE = 312 kJ/mol, structure **22T**) was located on the triplet hypersurface lying 39 kJ/mol above the singlet ion **22S**. The C–N–C angle in the triplet state **22T** is widened to 156.2°, whereas it was 129.0° in the singlet state **22S**.

Finally, ion **20** has been also investigated.

The singlet (**20S**) and triplet (**20T**) states of the cation $(CH_3CHCH{=}NH)^+$ have very different relative energies (221 and 322 kJ/mol, respectively). As expected, the value of the H–N–C angle is larger for the triplet state than for the singlet state.

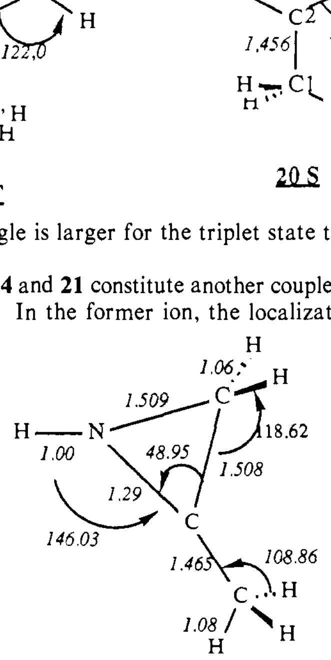


20 T



20 S

Cations **14** and **21** constitute another couple of closed and open structures. In the former ion, the localization of the positive charge is on C(2) (+0.47), the CN bond (length = 1.29 Å) is equivalent to a C=N double bond, and thus ion **14** offers another illustration of the π-donor effect of the NH_2 group toward a positive charge. The open form of ion **14** is more stable in its singlet state (ion **21S**) than in its triplet electron configuration (ion **21T**). The energy difference equals 43 kJ/mol. The bond angle H–N–C is increased when passing from **21S** (117.4°) to **21T** (150.8°).



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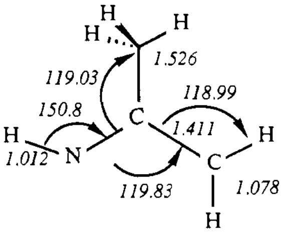
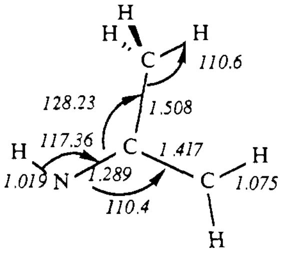
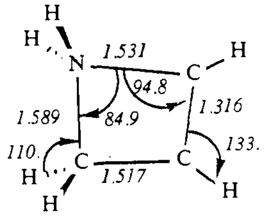


21 T



21 S

E. Ammonium Ions. Ion **10** is the most stable of ammonium ions in this series. The carbon–nitrogen bond lengths (1.589 and 1.531 Å) are longer than a C–N single bond (as expected for cyclic ions). The ring opening of this ion (**10**) gives ion **2**, which is lower in energy by 100 kJ/mol.

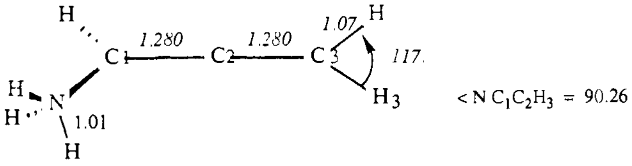


10

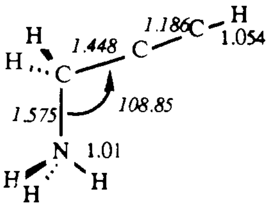
With its orthogonal arrangement of the two π bonds, ion **11** is also an allenic structure. The positive charge is located in the ammonium group (NH_3 +0.55).

Ion **13** is the most stable $(C_3H_6N)^+$ ion containing a C≡C triple bond. Significant positive charge is located on the amonium group

(NH_3 +0.56) as was observed in the case of ion **11**.

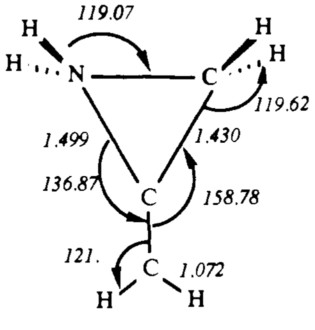


11



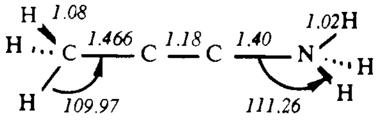
13

Ion **15** has a three-membered cyclic ammonium structure, and the positive charge is located on the exocyclic methylene group (CH_2: +0.42; NH_2: +0.15).



15

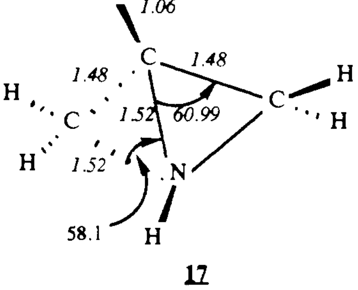
Ion **16** is the second acetylenic ammonium ion with **13**. Significant positive charge is located on the ammonium group (+0.55), but a nonnegligible part is also present on C(2).



16

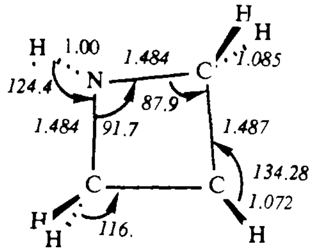
The heat of formation of ion **16** has been deduced from core binding energies.[3] The value, 883 ± 10 kJ/mol, is only roughly comparable to an estimate of 918 ± 7 kJ/mol based on the experimental heats of formation of **3** (775 kJ/mol) and **7** (815 kJ/mol) and the calculated relative energies (Table I).

A value of 957 kJ/mol has been proposed for the heat of formation of ion **17** by using the experimental proton affinity of 1-azabicyclo[1.1.0]butane (887 kJ/mol[16b]) and an incremental estimate of the $\Delta H°_f$ of the latter. With the procedure used above to derive heats of formation of **1** and **16** we obtain $\Delta H°_f(\mathbf{17})$ = 918 kJ/mol.



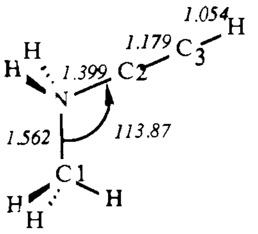
17

Ring opening of the pyramidal cation **17** leads to structure **23**; however, this latter carbenium ion is situated 145 kJ/mol above **16**.



23

Finally ion **19** is the last ammonium structure examined; one may note that the ammonium group is likely free of charge (+-0.09).



19

II. Mass Spectrometry. A. Experimental Part. Mass-analyzed ion kinetic energy (MIKE) and collisionally induced dissociation (CID) mass spectra have been used to differentiate and to establish the structure of the $(C_3H_6N)^+$ isomers. These techniques have been applied to $(C_3H_6N)^+$ ions generated by different methods:

(a) Methylation of methyl cyanide (**24**) or methyl isocyanide (**25**):

$$CH_3CN + CH_3^+ \rightarrow C_3H_6N^+$$

24

$$CH_3NC + CH_3^+ \rightarrow C_3H_6N^+$$

25

(b) Protonation of ethyl cyanide (**26**) or ethyl isocyanide (**27**):

$$C_2H_5CN + H^+ \rightarrow C_3H_6N^+$$

26

$$C_2H_5NC + H^+ \rightarrow C_3H_6N^+$$

27

(c) Electron-impact-induced fragmentation of molecules **28–35** (Chart II).

The $(C_3H_6N)^+$ ions produced in the source or in the first field-free region (FFR) of an EBE mass spectrometer[18] were characterized by collisions with helium in the third field-free region. The corresponding CID spectra are reported in Tables II and III. The unimolecular (MIKE) spectra of most of the $(C_3H_6N)^+$ ions generated from **24–35** exhibit a major peak at m/z 28; the most reasonable set of products being $(HCNH)^+ + C_2H_4$ ($\Delta H°_f$ = 1000 kJ/mol, using $\Delta H°_f$ = $((HCNH)^+)$ = 947 kJ/mol[16b]). Analysis of the metastable peak shape for the transition m/z 56 → m/z 28 leads to the kinetic energy release values quoted in Table IV.

B. Discussion. At least five structures are inferred from the experimental results presented in Tables II–IV namely ions **1**, **2**, **3**, **5** (and/or **6**), and **7**.

Dimethyl Nitrilium Ion 1. Methylations of methyl cyanide and methyl isocyanide clearly lead to the same $(C_3H_6N)^+$ ion structure. Characteristic features of the two first CID spectra of Table II are that (i) m/z 40 (loss of CH_4) dominates the m/z 36–42 region, (ii) negligible signals appear at m/z 29 and 30, and

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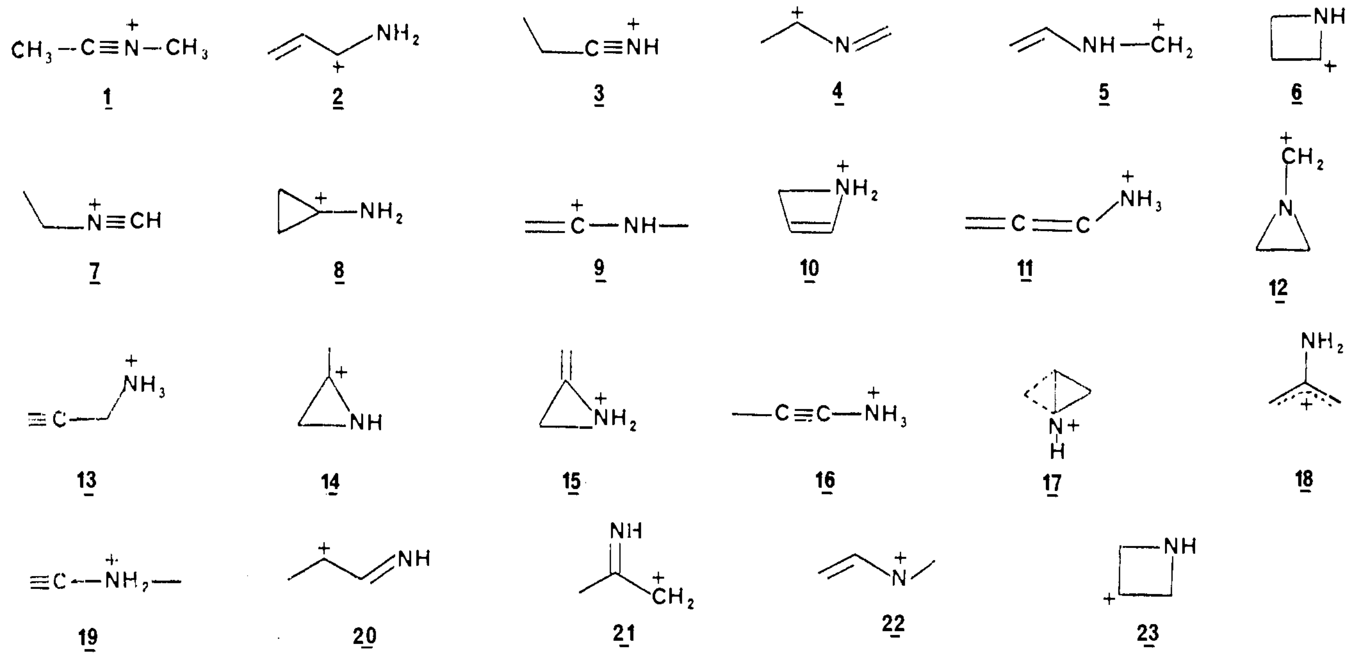
[18] Maquestiau, A.; Van Haverbek, Y.; Flammang, R.; Finet, D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 765.

Chart I



(iii) the ions m/z 15 are the most abundant in the **24**–**35** series.

Formation of a common $(C_3H_6N)^+$ ion structure by methylation of **24** and **25** is expected if the methylation occurs on terminal nitrogen or carbon atom, respectively:

$$\underset{\mathbf{24}}{CH_3CN} \rightarrow \underset{\mathbf{1}}{(CH_3{-}C{\equiv}N{-}CH_3)^+} \leftarrow \underset{\mathbf{25}}{CNCH_3}$$

Structure **1** is thus proposed for the corresponding $(C_3H_6N)^+$ product ion. The CAD spectrum of $(CD_3CNCH_3)^+$ ions produced by the reaction of CH_3I with CD_3CN shows peaks at m/z 15 and 18 in the ratio 3/2. This experimental indication may be interpreted by an easier C–N bond cleavage rather than a C–C bond rupture from **1** under collisional activation. This is in keeping with the associated thermochemistry: CH_3CN elimination is favored by 100 kJ/mol over CH_3NC loss, both reactions being endothermic:

$$\begin{tikzcd}[column sep=small, row sep=tiny]
 & CH_3CN + (CH_3)^+ \quad 1167\ \text{kJ/mol} \\
(CH_3CNCH_3)^+\ (738\ \text{kJ/mol}) \arrow[ur, "1"] \arrow[dr, "1"'] & \\
 & (CH_3)^+ + CNCH_3 \quad 1266\ \text{kJ/mol}
\end{tikzcd}$$

During the revision of this manuscript we became aware of an experimental study on $(C_3H_6N)^+$ ions generated by ion–molecule reactions involving acetonitrile and adding support for the facile generation of nitrilium structure **1**.[26]

Nitrilium Ions 3 and 7. The protonation of molecules **26** and **27** leads to two different products. Accordingly the CID spectrum of $(\mathbf{26} + H)^+$ ions presents two significant peaks at m/z 28 and 41, whereas the CID spectrum of $(\mathbf{27} + H)^+$ ions is dominated by peak at m/z 27; the two structures are consequently easily distinguishable.

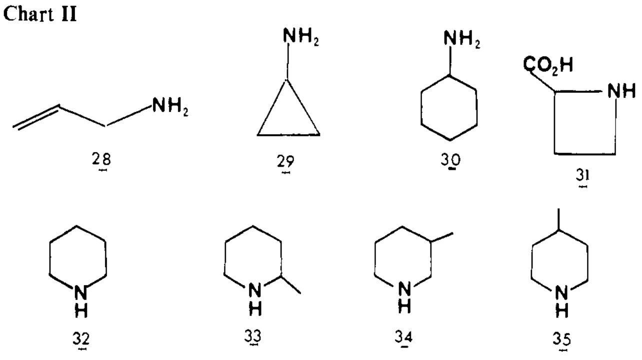
Protonation of ethyl cyanide (**26**) and ethyl isocyanide (**27**) is expected to give rise to $(C_3H_6N)^+$ ions of structures **3** and **7**, respectively. A similar interpretation was given for the protonation of methyl cyanide and methyl isocyanide:[1]

$$\underset{\mathbf{26}}{C_2H_5CN} \rightarrow \underset{\mathbf{3}}{(C_2H_5CNH)^+}$$

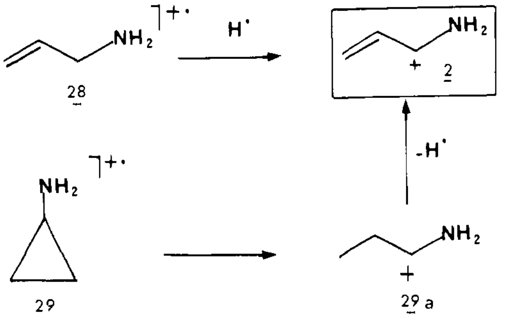
$$\underset{\mathbf{27}}{C_2H_5NC} \rightarrow \underset{\mathbf{7}}{(C_2H_5NCH)^+}$$

Immonium Ion 2. Precursors **28** and **29** give a common $(C_3H_6N)^+$ ion. The two CID spectra are identical and characterized by peaks at m/z 39 (NH_3 loss) and m/z 30 (C_2H_2 loss); no significant signal appears in the m/z 12–17 range. In the homologous series of $(C_3H_5O)^+$ ions, the $(CH_2{=}CHCHOH)^+$ structure is characterized by a CID spectrum containing peaks corresponding to H_2O and C_2H_2 eliminations. By analogy structure **2** $(CH_2{=}CHCHNH_2)^+$ may be assigned to the $(C_3H_6N)^+$ ions coming from dissociation of the ionized molecules **28** and **29**. This assignment is also the most reasonable in view of the structure of these precursors as depicted in Scheme I.

Chart II



Scheme I



According to Scheme I, ion **2** may be produced by direct C–H bond cleavage from either molecular cation $(\mathbf{28})^{\cdot+}$ or distonic ion $(\mathbf{29a})^{\cdot+}$ obtained by ring opening of $(\mathbf{29})^{\cdot+}$. This latter reaction occurs probably without significant critical energy as observed in the case of oxygenated derivatives of cyclopropane[19] and as indicated by MNDO calculations.[20] The formation of **2** from

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(19) Bouchoux, G.; Flammang, R.; Maquestiau, A. *Org. Mass Spectrom.* **1985**, *20*, 154.

Table II. CID Spectra[a] of $[C_3H_6N]^+$ Ions Produced in the Source of the Mass Spectrometer from Precursors **24**–**35**

	m/z[b]																							
precursor	55	54	53	52	51	50	42	41	40	39	38	37	36	30	29	28	27	26	25	16	15	14	13	12
$(CH_3CN/CH_3)^+$ (**24**)	339	100	14	41	17	3	7	22	30	13	9	<1		1	5	33	24	15	10			15	3	1
$(CH_3NC/CH_3)^+$ (**25**)	265	100	14	39	14	2	8	21	30	13	8	<1		2	8	40	28	17	5		13	3	1	
$(C_2H_5CN/H)^+$ (**26**)	227	100	14	48	27	5	2	40	32	21	12	5			29	93	51	21	3		2	1		
$(C_2H_5NC/H)^+$ (**27**)	[238]	35	5	27	24	4	10	52	60	23	14	2			[115]	[570]	100	43	6	1	7	5	2	1
$CH_2{=}CHCH_2NH_2$ (**28**)	[228]	100	9	34	10	2	3	11	7	24	12	8	1	13	[19]	[106]	20	10	2		1	<1		
$c\text{-}C_3H_5NH_2$ (**29**)	[156]	100	7	35	11	2	3	12	7	25	14	8	1	11	[18]	[106]	20	10	2		1	<1		
	96	100	8	35	11			8	6	20	12	6		11	14	60	19	10						
cyclohexylamine (**30**)	[112]	100	7	24	7	1	2	7	5	15	8	4	<1	7	[15]	[69]	13	7	1		1	<1		
azetidine (**31**)	[182]	100	8	26	14	2	3	21	14	11	6	2	1	26	22	[201]	40	18	3		2	1		
piperidine (**32**)	[274]	100	10	31	16	3	3	[35]	20	12	6	2		39	[22]	[144]	51	22	3		5	3		
2-Me-piperidine (**33**)	[160]	100	9	30	14	4	4	[49]	21	13	5	2		28	[21]	[127]	44	21	3		4	3	1	
3-Me-piperidine (**34**)	[389]	100	9	26	11	2	4	[30]	15	12	7	3		25	[22]	[133]	35	18	3		3	2	<1	
4-Me-piperidine (**35**)	[241]	100	9	26	11	2	4	[26]	16	10	5	2		30	[23]	[158]	42	21	4		4	2	1	

[a] Triple sector EBE instrument equipped with a collision cell (He) in the third FFR and a MSS CI source. Typical conditions were 8-kV accelerating voltage, 500-μA electron emission, and 200-eV electron energy. Values in brackets refer to peaks also observed in the unimolecular dissociation mass spectra of metastable $(C_3H_6N)^+$ ions. [b] No ions of m/z 17 were observed.

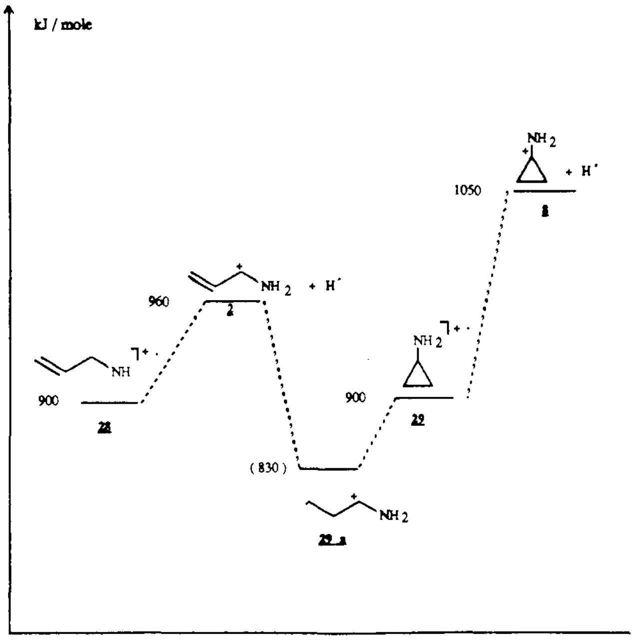
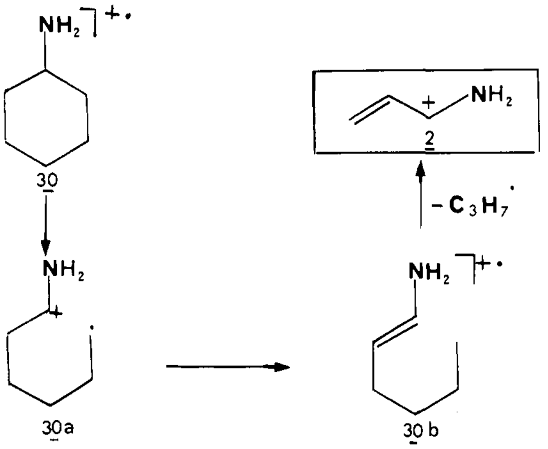


Figure 1. Potential energy profile associated with the fragmentation of ionized allylamine and cyclopropylamine. Relevant thermochemical data (in kJ/mol): $\Delta H°_f(\mathbf{28}) = 55$;[22] $\Delta H°_f(\mathbf{29}) = 72$;[22] IE(**28**) = 845;[23] IE(**29**) = 830 (i.e., estimated to be identical with IE(isopropylamine) as suggested by the equality IE(cyclopropanol) = IE(isopropanol)[23]); $\Delta H°_f(\mathbf{2}) = 746$; $\Delta H°_f(\mathbf{8}) = 836$; $\Delta H°_f(H^{\cdot}) = 218$; $\Delta H°_f(\mathbf{6a}) = 828$ (estimated from $\Delta H°_f(CH_3CH_2CHNH)^+ = 636$[24] and a primary CH bond dissociation energy of 410[25]).

Scheme II



ionized **28** and **29** is endothermic by approximately 60 kJ/mol; the formation of **8** by direct dissociation of $(\mathbf{29})^{\cdot+}$ would require around 150 kJ/mol. This large energy difference in forming **2** or **8** renders improbable a competitive formation of both structures at least for low internal energy precursors. A potential energy diagram associated with Scheme I is proposed in Figure 1.

The CID spectra of $(C_3H_6N)^+$ ions issued from the dissociation of ionized **28** and **29** in the first FFR of the triple sector mass spectrometer were also measured (Table III). Except for ions of m/z 28, 29, and 55, produced also by unimolecular processes, the spectra are similar to those obtained with the source-produced $(\mathbf{28} - H)^+$ and $(\mathbf{29} - H)^+$ ions. This is in favor of a common structure(s) for $(C_3H_6N)^+$ ions produced from long- and short-lived molecular ions $(\mathbf{28})^{\cdot+}$ and $(\mathbf{29})^{\cdot+}$, thus strongly supporting the formation of ions of the lone **2** structure.

In the case of cyclohexylamine (**30**), formation of fragment ion **2** is also expected on the basis of the mechanism presented in Scheme II.

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(20) Bouchoux, G.; Hoppilliard, Y. *Int. J. Mass Spectrom. Ion Proc.* **1983**, *55*, 47.

Table III. CID Spectra of $(C_3H_6N)^+$ Ions Produced in the First Field-Free Region from Metastable Precursors **28**, **29**, and **32–35**

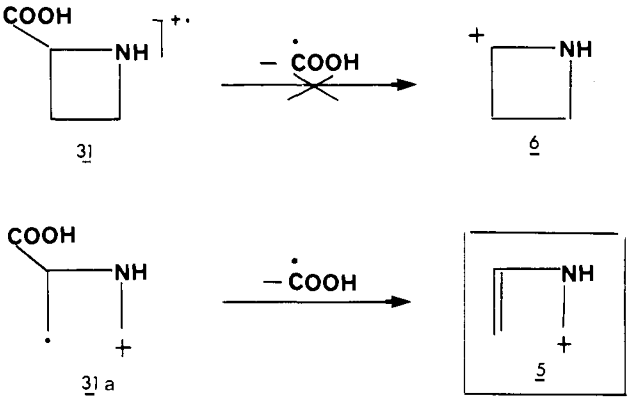
	m/z																	
	55	54	53	52	51	42	41	40	39	38	37	30	29	28	27	26	25	25
$CH_2{=}CHCH_2NH_2$ (**28**)	149	100	8	28	8	5	9	6	19	9	5	10	16	67	19	10	1	1
$CH_2CH_2CHNH_2$ (**29**)	152	100	8	26	6	5	9	5	18	8	5	12	17	67	20	11	1	2
piperidine (**32**)	135	72	10	19	7	4	18	10	5	3		28	18	100	35	18	1	4
2-Me-piperidine (**33**)	185	63	11	28	11	4	35	17	7	2		33	20	100	39	20	2	7
3-Me-piperidine (**34**)	141	59	7	16	6	3	16	10	7	2		31	16	100	37	16	1	6
4-Me-piperidine (**35**)	204	63	8	18	8	4	18	14	6	2		35	18	100	43	18	2	6

Table IV. Kinetic Energy *T* (millielectronvolts) Released during Unimolecular Dissociation *m/z* 56 → *m/z* 28

precursor	$T_{0.5}$	$\langle T \rangle$
26	58	160
27	4	
28	30	160
31–35	45 ± 4[a]	170 ± 20

[a] Composite metastable peak.

Scheme III



The spectral data agree only roughly with this proposal. The metastable peak associated with the fragmentation *m/z* 56 → *m/z* 28 for precursor **30** is simple Gaussian and possesses a mean *T* value of 158 meV as observed for **28**; however, the $T_{0.5}$ value is larger (48 meV). Similarly the CID spectrum of $(\mathbf{30} - C_3H_7^{\bullet})^+$ is very close to that of $(\mathbf{29} - H^{\bullet})^+$ and $(\mathbf{28} - H^{\bullet})^+$. With the results in hand it is not possible to conclude if the slight differences observed are due to a different energy content of a single $(C_3H_6N)^+$ structure **2** or to the presence of a small amount of a second species beside **2**.

Immonium Ions 5 and 6. Precursors **31–35** produce $(C_3H_6N)^+$ ions that give identical spectral characteristics. In the CID spectra the importance of peak at *m/z* 30 (C_2H_2 loss) is noteworthy (the presence of a peak at *m/z* 41 must be attributed to the presence of $C_4H_8^{\bullet+}$ ions in the *m/z* 56 beam).

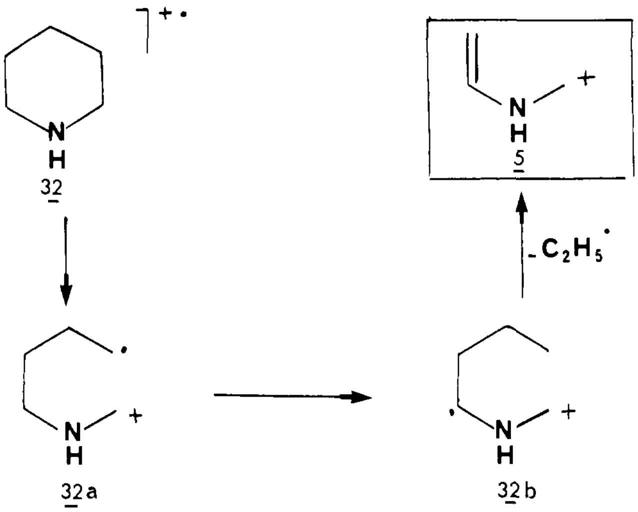
Azetidine (**31**) is expected to give the cyclic ion **6** whereas piperidine and its methyl derivatives **32–35** were proposed to be at the origin of ion **5**, the open form of **6**[8] (Schemes III and IV).

As noted before, the calculations presented above predict that **5** and **6** have similar stabilities.

The direct elimination of COOH from ionized **31** giving **6** may be in competition with the ring opening leading to distonic ion **31a**, which may further dissociate into **5** + COOH (Scheme III).

The fragmentation of ionized piperidine follows a ring opening and a 1,4-H migration via the distonic ions **32a** and **32b** as depicted in Scheme IV. Obviously a similar picture may account for the behavior of methylated molecular ions **33–35**. Note that **32b** is the open form of ionized 2-propylaziridine, the high stability of such structure is well established in the oxygenated series.[21]

Scheme IV



Finally, Table III reveals that metastable ions from **32** to **35** generate also $C_3H_6N^+$ ions of identical structure, probably **5**, but there is no irrefutable argument excluding a further cyclization **5** → **6**.

Conclusion

The calculations presented in this study bring a large amount of information concerning the stationary points on the $(C_3H_6N)^+$ potential energy surface. Six of the first structures predicted to be the most stable by calculations have been experimentally identified by tandem mass spectrometry:

Dimethylnitrilium ion (**1**, $(CH_3CNCH_3)^+$) is generated by methylation of either methyl cyanide or methyl isocyanide.

Dissociation ionization of unsaturated amines such as allylamine, cyclopropylamine, and cyclohexylamine gives rise to immonium ion **2** ($(CH_2{=}CH{-}CHNH_2)^+$).

The protonation of ethyl cyanide or ethyl isocyanide leads to nitrilium ions **3** ($(C_2H_5CNH)^+$) or **7** ($(C_2H_5NCH)^+$).

The generation of immonium **5** ($CH_2NHCH{=}CH_2$) or its cyclic form **6** is occurring from dissociative ionization of azetidine, piperidine, and its methyl derivatives.

A seventh structure, not yet experimentally characterized, ion **4**, is also expected to be in the same energy range.

Acknowledgment. We are indebted to Professor N. M. M. Nibbering for providing us with a manuscript of ref 26 prior to publication.

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(21) Bouchoux, G.; Hoppilliard, Y.; Jaudon, P. *Org. Mass Spectrom.* **1987**, *22*, 98, and references therein.

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