Ab initio SCF Study of the Molecular Structures and Relative Stabilities of the $C_2H_4N^+$ Cation Isomers

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The optimized molecular geometries and relative stabilities of isomers of the $C_2H_4N^+$ cations have been determined by *ab initio* SCF calculations using the 3-21G and 6-31G** basis sets. The *N*-protonated CH_3CN species ($CH_3{-}C{\equiv}NH^+$) is the most stable among the isomers considered, and this species is found to be the reaction product of the association reaction, $CH_3^+ + HCN$, determined by mass spectrometry. The protonation of the neutral C_2H_3N isomers and the isomerization and dissociation of the $C_2H_4N^+$ cationic isomers are discussed.

The positive ions $C_2H_4N^+$ generated by proton transfer from CH_3CN and CH_3NC as well as from association of CH_3^+ and HCN were detected by mass spectrometry.[1] It was shown that the species generated by association between CH_3^+ and HCN has the same structure as that produced from proton transfer to CH_3CN, whereas the protonated CH_3NC species has been definitely found to have a different structure from protonated CH_3CN. It has also been suggested that protonated CH_3NC is almost certainly $CH_3{-}N{\equiv}CH^+$, but the structure of the protonated CH_3CN species cannot be specified with complete certainty from the mass spectroscopic studies. Although the existence of the $C_2H_4N^+$ ions is thus well established, no information regarding their structures and relative stabilities is available as yet.

One of the more important contributions of *ab initio* quantum chemical studies consists in predicting the electronic structure, geometry, and relative stabilities of a transient species such as $C_2H_4N^+$. Accordingly, *ab initio* methods have been employed in recent studies on a large number of small ions, *e.g.* $C_2H_2N^+$ [2] and $CH_5N_2^+$.[3] Since the most stable structure of the ions is not simply related to the most stable neutral structure, the predictive capability of *ab initio* methods is of especially great value in the study of molecular ions.

In a previous theoretical study[4] we have reported the optimized geometries and energies of three protonated ketenimine species ($CH_3{-}C{\equiv}NH^+$, $CH_2{=}C{=}NH_2^+$, and $CH_2{=}CH{=}NH^+$) for a study of the relative nucleophilic nature of the carbon and nitrogen atoms of ketenimine and found that protonation takes place more easily at the site of the β-carbon rather than at nitrogen.

In the present *ab initio* SCF study we report completely optimized geometries, energies, and relative stabilities for all isomers of the positive $C_2H_4N^+$ ion which are considered chemically reasonable. Furthermore, the proton affinities of some C_2H_3N neutral species have been estimated from the results and rearrangement processes such as ring closure or 1,2-hydrogen shifts between two isomers have been studied in detail. Mulliken population analysis has been performed and gross atomic and bond overlap populations were calculated for the energy-optimized geometry of the isomeric ions.

Calculations

Ab initio SCF calculations of the structures and properties of the $C_2H_4N^+$ isomers have been carried out by employing the split-valence 3-21G [5] and the split-valence plus polarization function 6-31G** [6] basis sets. The molecular geometries for the

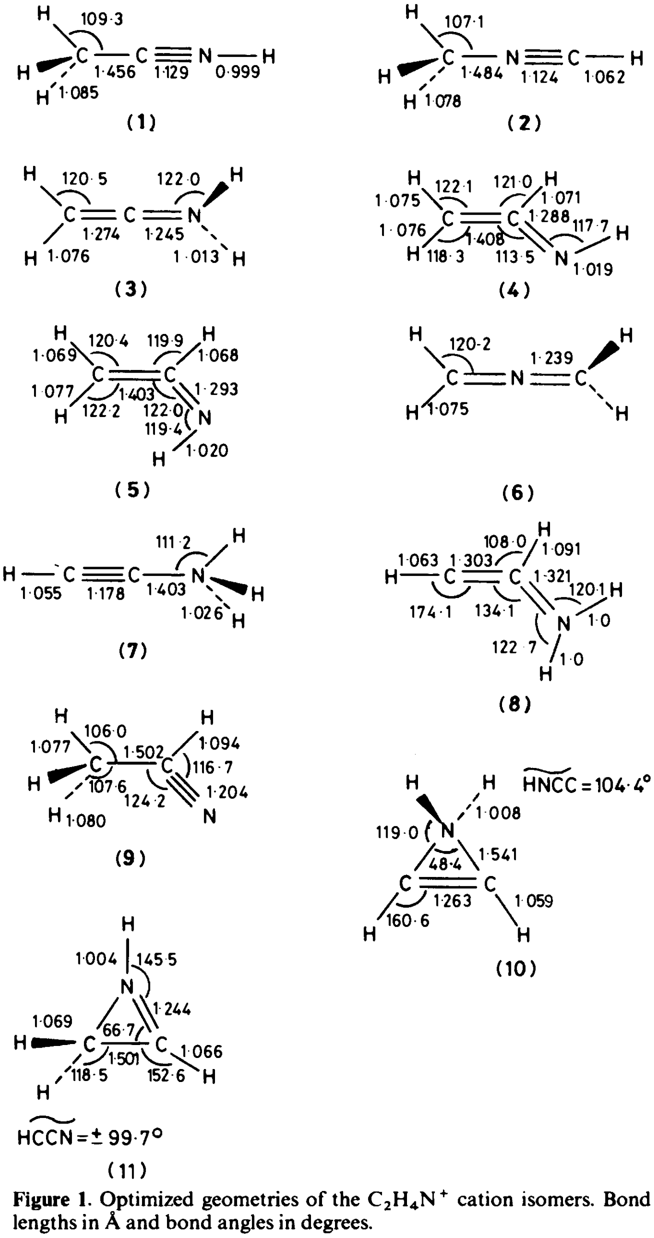


Figure 1. Optimized geometries of the $C_2H_4N^+$ cation isomers. Bond lengths in Å and bond angles in degrees.

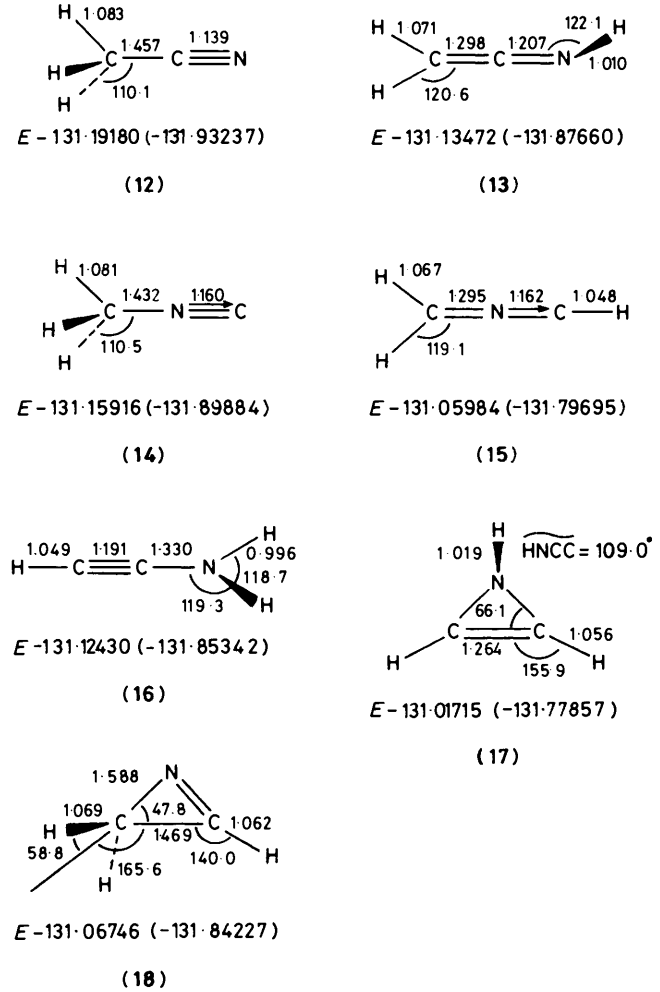
Table 1. The total and relative energies for the $C_2H_4N^+$ isomers calculated at the equilibrium geometries (Figure 1) using the 3-21G and 6-31G** basis sets

Molecule	E(3-21G) (a.u.)	E(6-31G**) (a.u.)	ΔE(3-21G)/ kcal mol $^{-1}$	ΔE(6-31G**)/ kcal mol $^{-1}$
(1)	−131.508 75	−132.246 19	0.0	0.0
(2)	−131.489 72	—132.228 72	11.9	11.0
(3)	−131.487 45	−132.223 20	13.4	14.4
(4)	−131.399 17	−132.155 93	68.8	56.6
(5)	−131.385 39	−132.142 58	77.4	65.0
(6)	−131.474 73	−132.221 57	21.3	15.4
(7)	−131.448 55	−132.179 05	37.8	42.1
(8)	−131.396 87	−132.143 37	70.2	64.5
(9)	−131.379 76	−132.128 54	80.9	73.8
(10)	−131.409 77	−132.165 78	62.1	50.5
(11)	−131.411 15	−132.176 73	61.2	43.6

stationary points and the transition states have been optimized by the force method using the 3-21G basis set with analytical slope[7] as implemented in the MONSTERGAUSS program system.[8] We have considered eleven stationary states for the $C_2H_4N^+$ isomers and three transition states resulting from rearrangement between two isomers of interest. Furthermore, seven neutral C_2H_3N isomers have been treated independently in order to estimate the proton affinities. The transition state was obtained by minimizing the gradient norm while ensuring that the matrix of the second derivatives of the energy had one negative eigenvalue. In order to insure that the calculated relative stabilities are not an artefact of the geometry optimization procedure using the rather smaller 3-21G basis set, the extended 6-31G** basis set calculations have been included throughout to obtain reasonable isomerization energies.

Results and Discussion

Optimized Geometries and Relative Stabilities of $C_2H_4N^+$.—The total SCF and relative energies for the $C_2H_4N^+$ isomers calculated at equilibrium geometries, using the 3-21G and 6-31G** basis sets, are summarized in Table 1. It is shown that two levels of approximation were in agreement with each other in that the *N*-protonated CH_3CN species ($CH_3{-}C{\equiv}NH^+$) is the most stable among the $C_2H_4N^+$ isomers considered in this study. The protonated CH_3NC species ($CH_3{-}N{\equiv}CH^+$) is found to lie *ca.* 11 kcal mol^{-1} above the $CH_3{-}C{\equiv}NH^+$ species, whereas the *C*-protonated $CH_3{-}CH{\equiv}N^+$ species, which turned out to be the most unstable species among the $C_2H_4N^+$ isomers, lies much higher than the most stable isomer by more than 80 kcal mol^{-1}. The optimized geometries calculated by the SCF gradient method employing the 3-21G basis set for the 11 isomers listed in Table 1 are shown in Figure 1.


E - 131·19180 (-131·93237)

(12)

E - 131·13472 (-131·87660)

(13)

E - 131·15916 (-131·89884)

(14)

E - 131·05984 (-131·79695)

(15)

E -131·12430 (-131·85342)

(16)

E - 131·01715 (-131·77857)

(17)

E -131·06746 (-131·84227)

(18)

Figure 2. Optimized geometries and energies (E) of the neutral C_2H_3N isomers. Energies in a.u., bond lengths in Å, and bond angles in degrees. For **(15)** we only considered the linear structure. Energies from the 3-21G and 6-31G** basis set (values in parentheses) calculations.

Isomers **(8)**, **(3)**, and **(10)** are considered in a previous theoretical study which dealt with the structures and relative energies of the $C_2H_2X^+$ isomers (X = F, NH_2, Cl, and SH) by the STO-3G and 4-31G basis sets.[9] The molecular geometries were partially optimized using the STO-3G basis set and partially taken from the geometrical parameters of $C_2H_3^+$. The energy was also calculated for this geometry with the 4-31G basis set. In accord with the present study, the acetylenic isomer, $CH_2{=}C{=}NH_2^+$ **(3)**, which lies about 13.4 (3-21G) and 14.4 kcal mol^{-1} (6-31G**) above the most stable $CH_3{-}C{\equiv}NH^+$ isomer, was also found to be the most stable one among these three isomers followed by the cyclic **(10)** and the vinyl **(8)** isomers. The partially optimized geometries from the STO-3G basis set reported in the previous study were, however, appreciably different from those of the present study. Among other things, the C=C distance was overestimated by *ca.* 0.03 Å and the C=N distance was underestimated by *ca.* 0.04 Å in the previous study.

In a recent synthetic study, De Kimpe *et al.*[10] reported the Friedel–Crafts reactions of α-chloroaldimines (Cl⋗C–CH=N–) and mentioned the important role of the α-imidoylcarbenium ion (⋗C=CH$^+$=N–) as a possible reaction intermediate, but the structure of this ion could not be deduced from experiment. With respect to this study, it is worthwhile noting from Table 1 that the calculated energy of the two isomers of α-imidoylcarbenium ion lies more than 56 kcal mol^{-1} above the most stable $CH_3{=}C{=}NH^+$ isomer, and the energy difference between two conformers **(4)** and **(5)** is calculated as 8.6 (3-21G) or 8.4 kcal mol^{-1} (6-31G**), **(4)** being more stable. The geometries of these species are also given in Figure 1.

Proton Affinities and the Neutral C_2H_3N *Isomers.*—In order to study the proton affinities of the C_2H_3N isomers, an independent SCF geometry optimization for these neutral species, which are all metastable isomers of methyl cyanide (CH_3CN), has been carried out. The optimized geometries and the SCF energies are summarized in Figure 2. The calculated proton affinities of the neutral C_2H_3N isomers are shown in Table 2.

Table 2. Proton affinities of the C_2H_3N isomers[a]

Molecule	3-21G	6-31G**
(12)	−198.9	−196.9
(13)	−221.3	−217.5
(14)	−207.4	−207.0
(15)	−267.7	−266.4
(16)	−203.5	−204.3
(17)	−246.4	−243.0
(18)	−215.7	—209.9

[a] The calculated protonation energies refer to $E(C_2H_4N^+) - E(C_2H_3N)$ in kcal mol^{-1}.

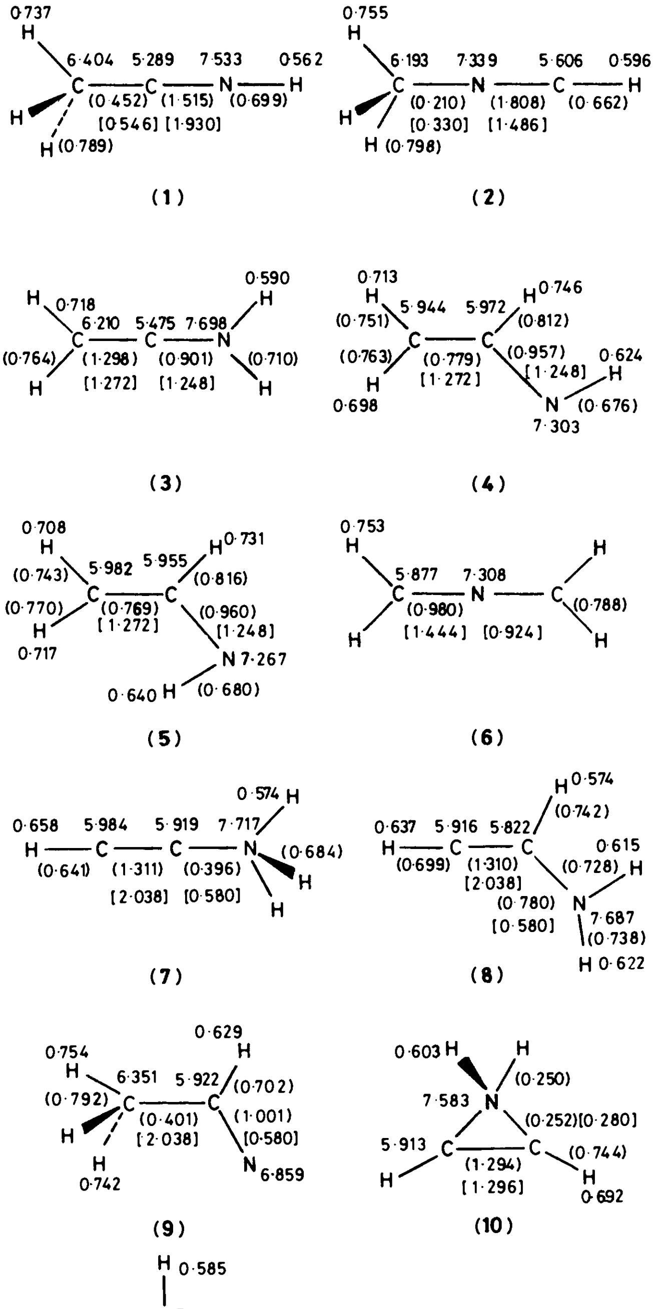
A theoretical study of proton addition to oxirane, aziridine, and 2-azirene **(17)** has been reported previously by Catalan and Yarez.[11] The molecular geometries both for the neutral and protonated species were optimized by the minimal STO-3G basis set, and it was concluded that the changes in geometrical parameters produced by the protonation were not significant. This observation is only partially confirmed by the present split-valence basis set calculation. While the geometrical parameters which describe the three-membered ring system change relatively little, the bond angle ∠CCH and the dihedral angles ∠HNCC and ∠HCCN are found to change significantly in going from the neutral to protonated species, as Figures 1 [**(10)** and **(11)**] and 2 [**(17)** and **(18)**] show. The calculated protonation energy of 239.2 kcal mol^{-1} of a previous study (6-31G basis set) for 2-azirene **(17)** is comparable with 243.0 kcal mol^{-1} of the present study (6-31G** basis set).

It has been established that minimal basis sets significantly overestimate protonation energies,[12] whereas the extended basis set gives results which are in good agreement with experimental values. The experimental protonation energies for aziridine and oxirane were reported as 220.1 and 185.0 kcal mol^{-1},[13] respectively, and the calculated values of 237.6 and 193.2 kcal mol^{-1} by the 6-31G basis set[11] were found to be in good agreement with them. Unfortunately, there are no experimental proton affinities reported as yet for the C_2H_3N isomers considered in this study. But according to previous theoretical and experimental studies of similar systems, it may be concluded that the calculated proton affinities listed in Table 2 are very close to the experimental values.

In a recent study, Guillemin *et al.*[14] reported, for the first time, the syntheses of ketenimine **(13)** and Δ^1-azirine **(18)** by flash vacuum thermolysis and/or gas-solid phase multistep sequences. As also shown in a previous theoretical study,[4] the SCF energies of ketenimine and Δ^1-azirine are calculated to lie more than 35 and 71 kcal mol^{-1} above the stable CH_3CN molecule, respectively, and both of them are, for example, more unstable than CH_3NC.

The results of the Mulliken population analysis for the eleven isomers of $C_2H_4N^+$ considered in this study are shown in Figure 3. The calculated gross atomic charges and overlap populations indicate that it would be difficult to represent these isomers in terms of a few simple resonance hybrids. The change of overlap populations in going from neutral to protonated species would be of some interest.

N-Protonation on CH_3CN brings about a decrease in the overlap populations both for the C–N and C–C bonds, whereas *C*-protonation on CH_3NC makes the N–C bond stronger and the C–N bond weaker. Also, *N*- and *C*-protonation on ketenimine have different changes in overlap population. While the C–N bond becomes weaker in both cases, the overlap population of the C–C bond in the *N*-protonated species ($CH_2{=}C{=}NH_2^+$) becomes slightly larger and that of the *C*-protonated species ($CH_2{=}CH{=}NH^+$) becomes much smaller compared with ketenimine. For the cyclic isomers, **(10)** and **(11)**, the protonation has only a small effect on the C–C and C–N overlap populations.



(1) **(2)** **(3)** **(4)** **(5)** **(6)** **(7)** **(8)** **(9)** **(10)** **(11)**

Figure 3. Gross atomic charges and overlap populations (values in parentheses) of the $C_2H_4N^+$ cation isomers. Values in [ ] are the overlap populations of the corresponding neutral C_2H_3N isomers.

Isomerization and Dissociation of the $C_2H_4N^+$ *Isomers.*—The 1,2-hydrogen shift and ring-closure reactions of **(4)** resulting in

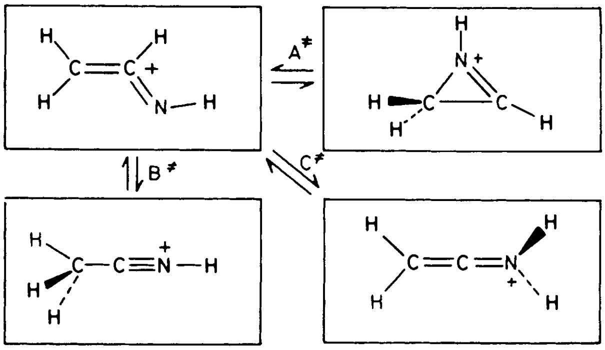


Figure 4. The 1,2-hydrogen shift and ring-closure reactions of $CH_2{=}CH{=}NH^+$ species. A‡, B‡, and C‡ represent the transition states.

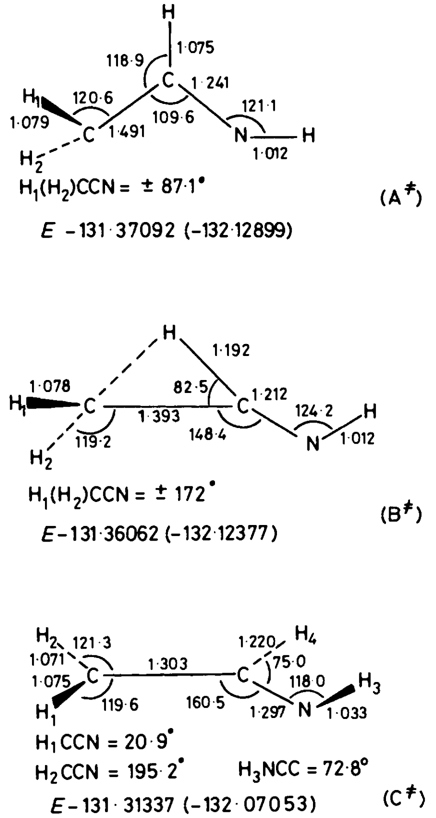
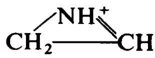
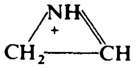


Figure 5. Optimized geometries and energies of the transition states (A‡, B‡, and C‡) for the isomerizations shown in Figure 4. Energies (*E*) in a.u., bond lengths in Å, and bond angles in degrees. Energies from the 3-21G and 6-31G** basis set (values in parentheses) calculations.

(**1**) and (**3**), and (**11**), respectively, are shown in Figure 4. The geometries and SCF energies of the calculated transition states (A‡, B‡, and C‡) are shown in Figure 5. The calculated energy barrier for the C–C 1,2-hydrogen shift, $CH_2{=}CH{=}NH^+ \longrightarrow CH_3{-}C{\equiv}NH^+$, amounts to 21.2 (3-21G) and 16.9 (6-31G**) kcal mol^{-1}, and the corresponding barrier for the C–N hydrogen shift, $CH_2{=}CH{=}NH^+ \longrightarrow CH_2{=}C{=}NH_2^+$, amounts to 53.8 (3-21G) and 53.6 (6-31G**) kcal mol^{-1}, respectively. The barrier to the ring closure, $CH_2{=}CH{=}NH^+ \longrightarrow$ , is found to be almost the same as that of the C–C hydrogen shift, 17.7 (3-21G) and 16.9 (6-31G**) kcal mol^{-1}.

Generally, the effect of electron correlation would appreciably reduce the activation energies of the 1,2-hydrogen shift. The isomer $CH_2{=}CH{=}NH^+$, which was proposed by De Kimpe *et al.*[10] as a possible reaction intermediate in the Friedel–Crafts reaction, should be a very instable species and might easily be transformed into the more stable $CH_3{-}C{\equiv}NH^+$ isomer. However, the relative stability could change in solution, depending on the solvent effect and substituents.

Table 3. Dissociation energies of the $C_2H_4N^+$ isomers[a]

$C_2H_4N^+$ isomers	Dissociation fragments	3-21G	6-31G**
$CH{\equiv}C{-}NH_3^+$	$HC{\equiv}C^+ + NH_3$	−241.6	−229.1
$CH{=}CH{=}NH_2^+$	$HC{\equiv}CH + NH_2^+$	−111.7	−117.4
$CH_3{-}C{\equiv}NH^+$	$CH_3^+ + HNC$	−100.3	−94.3
$CH_3{-}C{\equiv}NH^+$	$CH_3^+ + HCN$	−91.3	−83.4
$CH_3{-}N{\equiv}CH^+$	$CH_3^+ + HCN$	−79.4	−72.4
$CH_3{-}CH{\equiv}N^+$	$CH_3^+ + HCN$	−10.4	−9.6
	$H_2C{=}NH + HC^+$	−148.8	−153.2

[a] In kcal mol^{-1}

The dissociaton energies of some of the $C_2H_4N^+$ isomers to their possible fragments are summarized in Table 3. It can be noted that all these dissociation reactions are endothermic. The association reaction, $CH_3^+ + HCN \longrightarrow C_2H_4N^+$, has been invoked to explain the existence of some interstellar molecules,[1] and knowledge of the structure of the $C_2H_4N^+$ species would be useful for theoretical modelling of the molecular rate constant and for kinetic modelling of other products produced in reactions involving this ion. The exothermicity of the above reaction is estimated as 95 kcal mol^{-1} by the mass spectral experiment. The calculated dissociation energy of 91.3 (3-21G) or 83.4 (6-31G**) kcal mol^{-1} for the reaction, $CH_3{-}C{\equiv}NH^+ \longrightarrow CH_3^+ + HCN$, as shown in Table 3, is in good agreement with the experimental value. The dissociation energies for the other possible reactions, $CH_3N{\equiv}CH^+ \longrightarrow CH_3^+ + HCN$ (79.4 and 72.4 kcal mol^{-1}) and $CH_3CH{\equiv}N^+ \longrightarrow CH_3^+ + HCN$ (10.4 and 9.6 kcal mol^{-1}), are found to be appreciably smaller in magnitude than that of $CH_3{-}C{\equiv}NH^+ \longrightarrow CH_3^+ + HCN$. Therefore, it seems quite reasonable to assume that the structure of the $C_2H_4N^+$ isomer which is responsible for the above association reaction would be the $CH_3{-}C{\equiv}NH^+$ species. The effect of electron correlation on the calculated dissociation energy would be large, but the qualitative conclusions derived from the SCF calculations would remain valid.

Acknowledgments

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