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Reaction of $C_3H_2^+$ with Atomic Nitrogen: A Theoretical Study

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A theoretical study of the reaction of atomic nitrogen with the different isomers of $C_3H_2^+$ ($HCCCH^+$, $CCCH_2^+$, and c-$C_3H_2^+$) has been carried out. In all cases the theoretical results suggest that the predominant channel, from both thermodynamic and kinetic arguments, should correspond to production of $HCCCN^+$, followed by production of $C_2H_2^+ + CN$. In the case of the reaction with linear $C_3H_2^+$, other channels, leading to $CCCNH^+$ and $C_2 + HCNH^+$, are also exothermic but imply higher energy barriers, and therefore should be less favorable. Our results are in partial disagreement with the selected ion flow tube experiments at thermal energies, where only two channels, corresponding to $C_2H_2^+ + CN$ and $C_2 + HCNH^+$, with branching ratios of 0.85 and 0.15, respectively, were observed. Our results suggest that the reaction of nitrogen with $C_3H_2^+$ is feasible under interstellar conditions and may lead predominantly to $HCCCN^+$. This species could be a precursor of HCCCN or CCCN, two interstellar molecules.

Introduction

The study of nitrogen atom reactions with hydrocarbon ions is relevant in terrestrial ionospheric chemistry, as well as in understanding the chemistry of extraterrestrial atmospheres (for example, nitrogen is the major component of Titan's atmosphere). In addition, nitrogen chemistry is very important in the synthesis of interstellar molecules. Nearly one-third of the molecular species observed in the interstellar medium contains nitrogen.[1−3] Among them, the cyanopolyacetylenes (cyanopolyynes) family, $HC_{2n+1}N$, is one of the most interesting discovered in the interstellar medium. The list of members of this family observed in space includes $n = 1, 2, 3, 4$ and 5, the last one, $HC_{11}N$, being the largest interstellar molecule.[4] Furthermore, HCCNC and CCCNH, two new isomers of the first member of the series, HCCCN, have been discovered.[5] Another related molecule, CCCN, is present in the interstellar medium, and other isomers such as CCNC could also be of potential astrophysical interest.

Several reaction schemes have been proposed for the interstellar synthesis of cyanopolyacetylenes and related compounds. In the case of HC_3N a neutral−neutral reaction, $CN + C_2H_2$, has been suggested,[6] and experimental[7] and theoretical[8] studies on this reaction have shown that it may occur appreciably at cool interstellar temperatures. In addition, ion−molecule reactions have also been proposed.[6] The reactions of atomic nitrogen with hydrocarbon cations are among the possible processes leading to precursors of HC_3N or related molecules. Federer et al.[9] carried out an earlier experimental study, whereas Scott et al.[10] have recently investigated the reactions of $C_mH_n^+$ ions with N and N_2 using a selected ion flow tube (SIFT) operating at room temperature. One of the reactions studied by Scott et al. is $C_3H_2^+ + N$, which is quite relevant in interstellar chemistry, since two different isomers of the hydrocarbon C_3H_2 have been detected in space. Cyclopropenylidene, c-C_3H_2, is one of the most abundant interstellar hydrocarbons,[11] as well as the first interstellar organic ring. Propadienylidene (singlet vinylidenecarbene), which will be termed $CCCH_2$, was also observed in space[12] and has a linear carbon backbone and two hydrogens bonded to a terminal carbon atom.

In the present work we have carried out a theoretical study of the reaction of $C_3H_2^+$ with a nitrogen atom, determining its energetics as well as characterizing the relevant transition states. Both isomers, c-C_3H_2 and $CCCH_2^+$, derived from the hydrocarbons detected in the interstellar medium will be considered as reactants. In addition, a third isomer, $HCCCH^+$, obtained from ionization of triplet HCCCH will be considered in our work, since in the experimental study of Scott et al.[10] the ions were produced from propyne by electron impact, and a mixture of $HCCCH^+$ and c-$C_3H_2^+$ is likely to be formed. According to the authors, $HCCCH^+$ should be present in a greater amount. The existence of two isomeric forms of $C_3H_2^+$, cyclic (c-$C_3H_2^+$) and linear ($HCCCH^+$), was first demonstrated by Smith and Adams.[13] Both experiments[13] and theoretical calculations[14] indicate that the lowest-energy isomer is the cyclic structure, with the linear isomer lying about 6 kcal/mol higher in energy according to ab initio calculations.[14] The other isomer, $CCCH_2^+$, is predicted to lie about 46 kcal/mol higher than c-$C_3H_2^+$.

Computational Methods

Two different theoretical levels have been used in our work. First, we have used the so-called G2 method,[15] where the geometries are obtained at the second-order Moller−Plesset (MP2) level with the 6-31G(d) basis set,[16] and the electronic energy is computed, making additivity assumptions, effectively at the QCISD(T)/6-311+G(3df,2p) level. QCISD(T) stands for a quadratic configuration interaction calculation with single and double substitutions followed by a perturbative treatment of triple substitutions. The only difference with the standard G2 method is that we computed the vibrational frequencies at the MP2/6-31G(d) level instead of the HF/6-31G(d) level. Second, we have optimized the geometries of the different species using density functional theory. We have used in these calculations the B3LYP[17] exchange-correlation functional and the 6-311G(d,p) basis set.[18] Harmonic vibrational frequencies have been computed also at the B3LYP/6-311G(d,p) level to estimate the zero-point vibrational energy (ZPVE), as well as to check the

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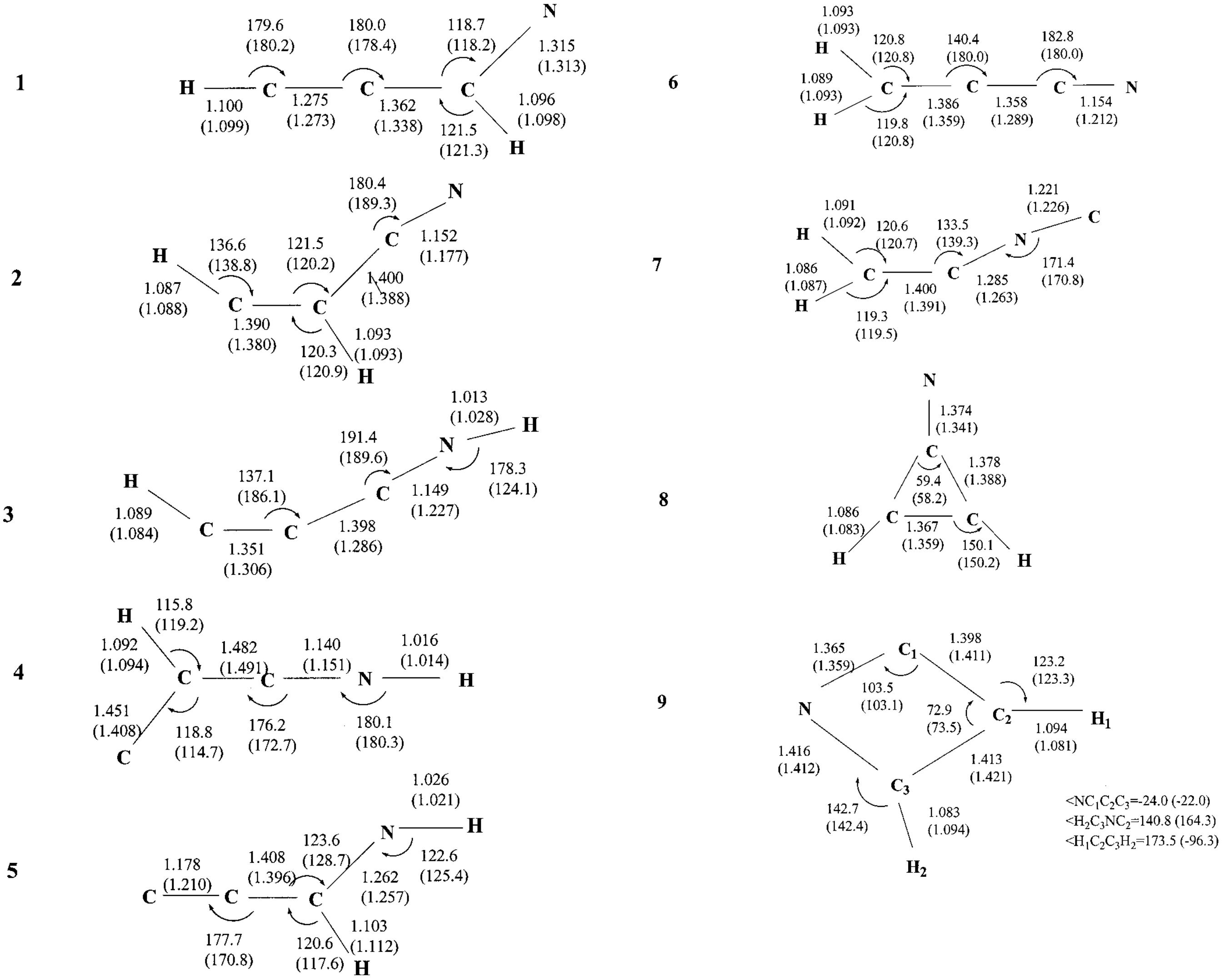

Figure 1. MP2/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) optimized geometries for the different $(NC_3H_2)^+$ minima on the triplet surface. Distances are given in angstroms and angles in degrees.

nature of stationary points. On the B3LYP geometries we have carried out single-point calculations with the CCSD(T) method[19] (coupled-cluster single and double excitation model augmented with a noniterative triple excitation correction) with the 6-311G(d,p) basis set.

All calculations in this work were carried out with the Gaussian 94 program package.[20]

Results and Discussion

$(NC_3H_2)^+$ Isomers. We will briefly comment on the $(NC_3H_2)^+$ isomers, that is, the different minimum energy structures. Given the multiplicity of the reactants, the reaction should take place in principle along the triplet surface. Therefore only the more relevant triplet $(NC_3H_2)^+$ isomers are presented in Figure 1, and their relative energies are shown in Table 1. All structures depicted in Figure 1 are intermediates in the reaction N + $C_3H_2^+$, but they are also the more stable triplet $(NC_3H_2)^+$ species. There is only a cyclic species, HNC_3H^+, that is not reported here and that is more stable than some of the structures studied in this work because it lies about 21.8 kcal/mol higher in energy than **8** at the G2 level.

In general there is a relative good agreement between the G2 and CCSD(T) relative energies, with discrepancies always lower than 2 kcal/mol between both levels of theory, except in the case of **3**, where a difference of 7.5 kcal/mol is observed for the G2 and CCSD(T) relative energies. On the other hand the B3LYP level shows larger discrepancies when compared with the G2 results.

TABLE 1: Relative Energies (kcal/mol) of Different Triplet $(NC_3H_2)^+$ Species

	level		
structure	G2	B3LYP	CCSD(T)
1	14.4	10.2	13.9
2	7.5	3.5	5.8
3	24.6	8.2	17.1
4	33.0	37.5	35.3
5	39.5	42.9	41.9
6	0.3	−8.0	−1.1
7	11.8	7.6	11.2
8	0.0	0.0	0.0
9	20.0	24.6	21.9

[a] Zero-point vibrational energy differences have been included either at the MP2 level (G2) or at the B3LYP level [B3LYP and CCSD(T)].

The two more stable species, **6** and **8**, are very close in energy. **8** is predicted to lie lower at the G2 level by only 0.3 kcal/mol, whereas at the CCSD(T) level **6** is predicted to lie 1.1 kcal/mol below **8**. Probably the G2 energy result is more reliable and **8** should be the lowest-lying triplet species, but in any case both species are almost isoenergetic. **8** can be viewed as the result of the interaction of N with the cyclic species c-$C_3H_2^+$, whereas **6** is produced by the interaction of N with $CCCH_2^+$ through the terminal carbon atom. It is worth noting that the interaction in both cases takes place through a carbon atom bearing an unpaired electron, but it is much more favorable in the case of formation of **6**. Even though $CCCH_2^+$ lies much higher in energy than c-$C_3H_2^+$ (about 45 kcal/mol at the G2 level), the result of the interaction with nitrogen, **6**, is nearly isoenergetic with **8**. The reason is mainly that in $NCCCH_2^+$(**6**) multiple N−C bonding is feasible, whereas in the case of $NC_3H_2^+$(**8**) multiple N−C bonding should result in breaking the cyclic C_3 unit. This is reflected in the much shorter C−N bond distance for **6** compared with **8**.

1 can be considered as the result of the interaction of nitrogen with the third $C_3H_2^+$ isomer, linear $HCCCH^+$. The interaction produces a considerable distortion of the geometry and, compared with the other products of the interaction between N and $C_3H_2^+$ isomers, is the less favorable. **1** lies about 14.4 kcal/mol higher than **8** at the G2 level, whereas $HCCCH^+$ is found 6 kcal/mol above c-$C_3H_2^+$ at the same level of theory. Even more stable than **1** are other isomers such as **2** and **7**. **2** that can be viewed as the result of the interaction of $C_2H_2^+$ with CN (notice the relatively short C−N distance and the long C_2−C_3 distance) and lie only 7.5 kcal/mol above **8** at the G2 level. On the other hand, **7** is the analogue of **6** with nitrogen in central position. The less-stable triplet species are those with N−H bonding (**3**, **4**, and **5**), whereas the global minimum of $(NC_3H_2)^+$ is singlet $HCCCNH^+$. Surprisingly, even more stable than these species is a four-member ring, **9**, which in principle should not be very favorable for a first-row atom such as nitrogen.

Reaction of N with $C_3H_2^+$. The geometries of the different transition states are given in Figure 2. All transition states, with the exception of TS5 and TS18, have one imaginary frequency associated with the corresponding reaction coordinate. Furthermore, TS18 was only obtained at the MP2 level, because at the B3LYP level hydrogen elimination is a direct process without involving any transition state. Our attempts to obtain TS18 at the B3LYP level led to very large C−H distances. TS5 and TS18 are in fact second-order saddle points, since both have two imaginary frequencies, one of them corresponding to migration of hydrogen in the case of TS5 or to hydrogen elimination for TS18, and the second one for an out-of-plane bending in both cases. All attempts to obtain these transition states in nonplanar geometries failed. Nevertheless we have included the relative energies of these second-order saddle points as an estimate of the values for the true transition states. In the case of TS18 the reported B3LYP and CCSD(T) values are obtained by using the MP2 geometry.

The reaction of nitrogen atoms with the linear isomer of $C_3H_2^+$ will be considered first. The energy profile for this reaction is rather complicated because of several possible reaction pathways. Therefore it is divided into Figures 3 and 4, where the results for selected levels of theory, namely G2 (which should be the most reliable one), B3LYP, and CCSD(T), are shown.

We have found four different exothermic channels for this reaction:

$$N(^4S) + C_3H_2^+(^2\Pi_g) \rightarrow CN(^2\Sigma) + C_2H_2^+(^2\Pi_u) \quad (1)$$

$$\rightarrow HCNH^+(^1\Sigma_g) + C_2(^3\Pi_u) \quad (2)$$

$$\rightarrow HCCCN^+(^2\Pi) + H(^2S) \quad (3)$$

$$\rightarrow CCCNH^+(^2\Pi) + H(^2S) \quad (4)$$

In their SIFT experiments, Scott et al. only observed two product channels, 1 and 2, with branching ratios of 0.85 and 0.15, respectively. Our calculations predict that channel 1 presents a higher exothermicity than channel 2, but production of $HCCCN^+$ ($^2\Pi$ ground state) is more exothermic than any of the channels observed in the SIFT experiments. In the case of production of $CCCNH^+$, all levels of theory predict a higher exothermicity than for production of CN + $C_2H_2^+$ when the $^2\Sigma$ ground state is taken into account. However, the ground state of $CCCNH^+$ does not correlate with the intermediates of the reaction, and the $^2\Pi$ state should be considered. In that case the products in channel 4 lie even higher in energy than CN + $C_2H_2^+$. Nevertheless, the most important result of the thermochemical analysis is that all levels of theory agree in that production of $HCCCN^+$ is clearly the most exothermic channel. An analysis of the possible barriers associated with the different channels is then necessary.

When a nitrogen atom approaches $HCCCH^+$, structure **1** is initially formed. Several processes may then occur. One of the obvious possibilities is hydrogen elimination, leading to the most stable product $HCCCN^+$ + H:

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS1} HCCCN^+ + H \quad (a)$$

This path involves transition state TS1, which has a quasi-linear HCCCN backbone. The C−H distance for the breaking bond is much longer at the B3LYP level than at the MP2 one, a fact that is observed for all transition states corresponding to hydrogen atom elimination. Another possibility is isomerization of structure **1** into **2** through migration of the hydrogen atom. In this case two different channels might be followed, one of them leading to the same products as path a ($HCCCN^+$ + H), and the second one corresponding to fragmentation into CN + $C_2H_2^+$. These two processes can be schematically represented as follows:

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS2} \mathbf{2} \xrightarrow{TS3} HCCCN^+ + H \quad (b)$$

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS2} \mathbf{2} \xrightarrow{TS4} C_2H_2^+ + CN \quad (c)$$

It should be pointed out that TS4 has only been obtained at the MP2 level. Our attempts to obtain this transition state at the B3LYP level led to the transition state corresponding to the degenerate rearrangement of **2** through migration of the CN unit to the contiguous carbon atom. Consequently we have computed the B3LYP and CCSD(T) electronic energies on the MP2 geometry, including the MP2 ZPVE to estimate the relative energy of TS4 at those levels of theory.

In all cases the transition states involved in paths a, b, and c lie below the reactants. Therefore, if $HCCCH^+$ is present in the interstellar medium, all are feasible processes under interstellar conditions (low temperature and low density, which preclude reactions that are endothermic or proceed through significant activation barriers). It is clear that isomerization into **2** seems to be slightly favored over direct hydrogen elimination from **1** (TS2 lies slightly lower in energy than TS1). Nevertheless, even if the reaction proceeds preferentially through structure **2**, formation of $HCCCN^+$ should be predominant over production of CN + $C_2H_2^+$, because TS4 lies higher in energy than TS3. The energy barrier from structure **2** for production of CN + $C_2H_2^+$ is nearly 70 kcal/mol at both G2 and B3LYP levels [∼76 kcal/mol at the CCSD(T) level], whereas it is estimated to be about 51 kcal/mol for production of $HCCCN^+$ at the same levels of theory [∼54 kcal/mol at the CCSD(T) level].

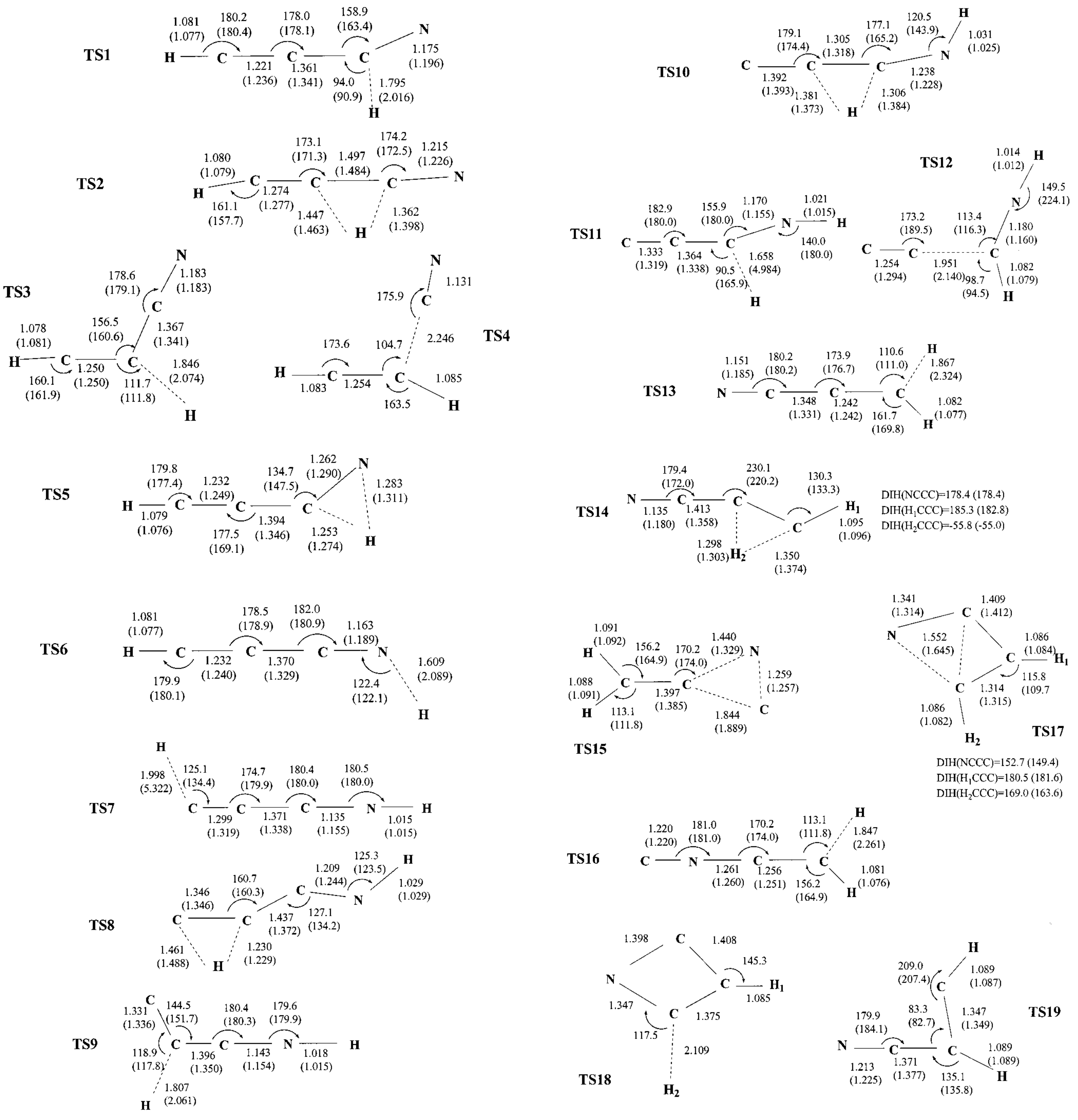

Figure 2. MP2/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) optimized geometries for the relevant transition states involved in the reaction of N with $C_3H_2^+$. Distances are given in angstroms and angles in degrees.

Concerning the performance of the different levels of theory in predicting the relative energies of transition states, it is readily seen in Figure 3 (but also in Figures 4−6) that, compared with the G2 results, B3LYP tends to overestimate those relative energies, whereas CCSD(T) tends to underestimate them. However, it is generally observed that the relative energy ordering of the different transition states is essentially the same at the three levels of theory.

The rest of explored channels for the reaction of nitrogen with $HCCCH^+$ starts with isomerization of **1** into **3** through migration of hydrogen to the nitrogen atom. This isomerization involves TS5, which has a relative energy quite similar to TS1 and TS2, and therefore should be a competitive process. Once isomer **3** is obtained, two different channels are opened leading to $HCCCN^+$ and $CCCNH^+$, corresponding to direct elimination of a hydrogen atom bonded either to nitrogen or to carbon, respectively:

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS5} \mathbf{3} \xrightarrow{TS6} HCCCN^+ + H \qquad (d)$$

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS5} \mathbf{3} \xrightarrow{TS7} CCCNH^+ + H \qquad (e)$$

It is readily seen in Figure 4 that TS6 lies much lower in energy than TS7 (between 20 and 30 kcal/mol depending on the theoretical method), and therefore production of $HCCCN^+$ should be not only thermodynamically but also kinetically favored over production of $CCCNH^+$.

A third possibility (path f) for the evolution of **3** is further isomerization through migration of the hydrogen atom bonded

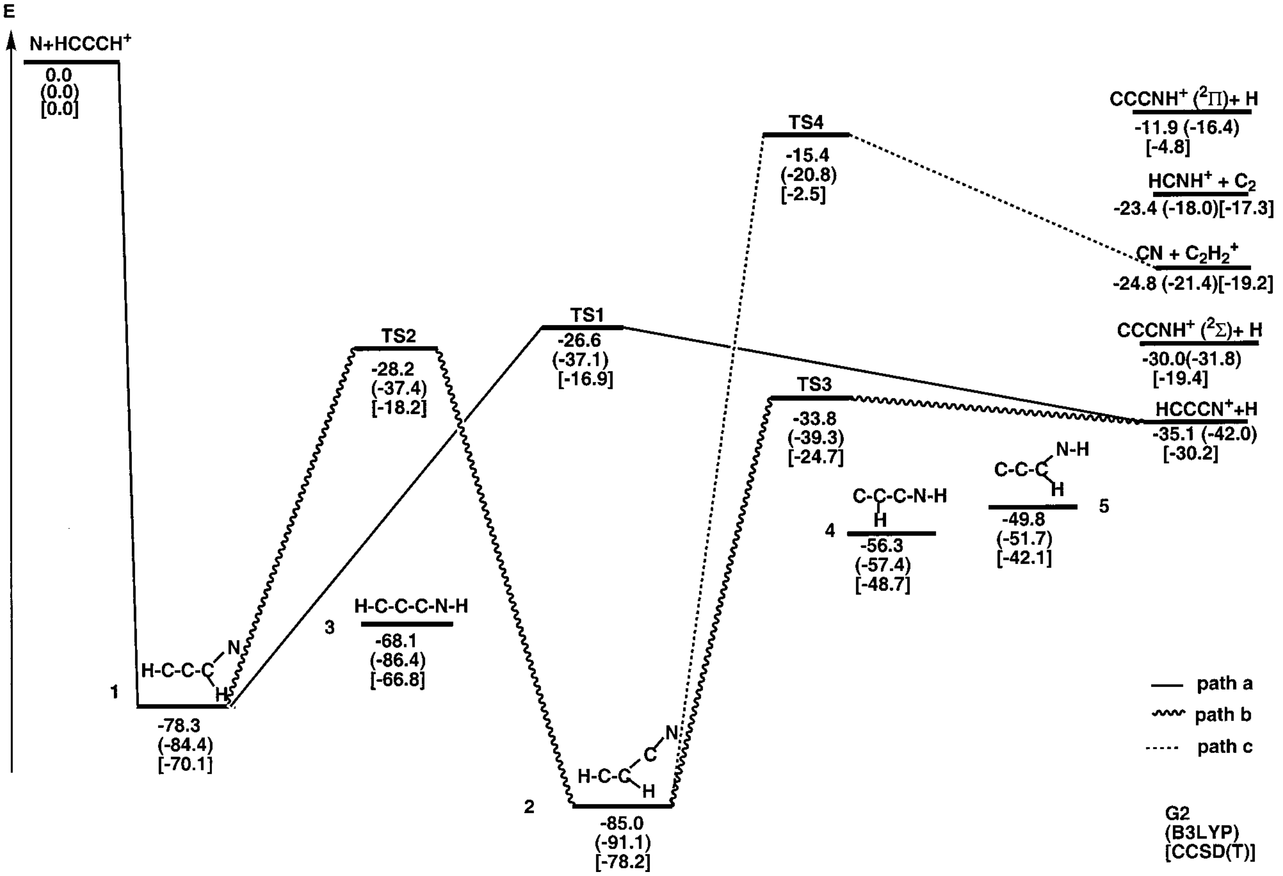

Figure 3. Energy profile (first part), in kcal/mol, for the reaction of N with $HCCCH^+$ at the G2, B3LYP, and CCSD(T) levels (including zero-point vibrational energy differences).

to carbon to reach structure **4**. Hydrogen elimination now proceeds through transition state TS9 leading again to $CCCNH^+$.

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS5} \mathbf{3} \xrightarrow{TS8} \mathbf{4} \xrightarrow{TS9} CCCNH^+ + H \quad (f)$$

Finally, two other channels are originated from subsequent isomerization of structure **4** into **5**, followed by either hydrogen elimination (leading to $CCCNH^+$) or by fragmentation into $C_2 + HCNH^+$:

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS5} \mathbf{3} \xrightarrow{TS8} \mathbf{4} \xrightarrow{TS10} \mathbf{5} \xrightarrow{TS11} CCCNH^+ + H \quad (g)$$

$$N + HCCCH^+ \rightarrow \mathbf{1} \xrightarrow{TS5} \mathbf{3} \xrightarrow{TS8} \mathbf{4} \xrightarrow{TS10} \mathbf{5} \xrightarrow{TS12} C_2 + HCNH^+ \quad (h)$$

However, none of the last three channels, (f), (g), and (h), should be competitive, because although TS8 is close in energy to TS6, TS9, TS10, TS11, and TS12 all lie quite higher in energy.

We now summarize the results obtained for the reaction of atomic nitrogen with the linear isomer $HCCCH^+$. We may conclude that theoretical calculations suggest that the most favorable channel, from both thermodynamic and kinetic arguments, should be the production of $HCCCN^+$. The most competitive channel seems to be that leading to $C_2H_2^+ + CN$, although all theoretical levels predict a smaller exothermicity and a higher energy barrier than for production of $HCCCN^+$. Production of $C_2 + HCNH^+$ is even less favorable, because it involves considerable rearrangement within the intermediate initially formed and proceeds through transition states that are relatively higher in energy. Finally, production of $CCCNH^+$ is only feasible in its $^2\Pi$ state, and should not be competitive, because it is less exothermic and all pathways leading to this species imply higher energy barriers.

Our results partially agree with the results from SIFT experiments,[10] since production of $C_2H_2^+ + CN$ is predicted to be dominant over formation of $C_2 + HCNH^+$, and the experimental branching ratios are 0.85 and 0.15, respectively. In addition, the reaction enthalpies for these two processes agree quite well with the values reported by Scott et al.,[10] namely 21.5 and 18.2 kcal/mol, respectively. In particular these values are in almost perfect agreement with our B3LYP results for these processes (21.4 and 18.0 kcal/mol). However, our prediction that $HCCCN^+$ should be the most favorable product is in clear disagreement with the experimental findings, because this channel is not observed in the SIFT experiments. We may suggest two possible explanations for this contradiction: either fragmentation of the most exothermic product, $HCCCN^+$, takes place or the reaction proceeds in a very different way at ~0 K than at thermal energies.

We now consider the reaction of N with $CCCH_2^+$, which is the less stable of the three $C_3H_2^+$ isomers, but which might be of relevance in interstellar chemistry. The energy profile for this reaction is shown in Figure 5. The reaction is initiated by formation of structure **6**, which is one of the most stable $(NC_3H_2)^+$ species. Once again, direct hydrogen elimination leads to the most exothermic product, $HCCCN^+$:

$$N + CCCH_2^+ \rightarrow \mathbf{6} \xrightarrow{TS13} HCCCN^+ + H \quad (i)$$

Another possibility is isomerization into structure **2**, followed either by hydrogen elimination to give $HCCCN^+$ or fragmenta-

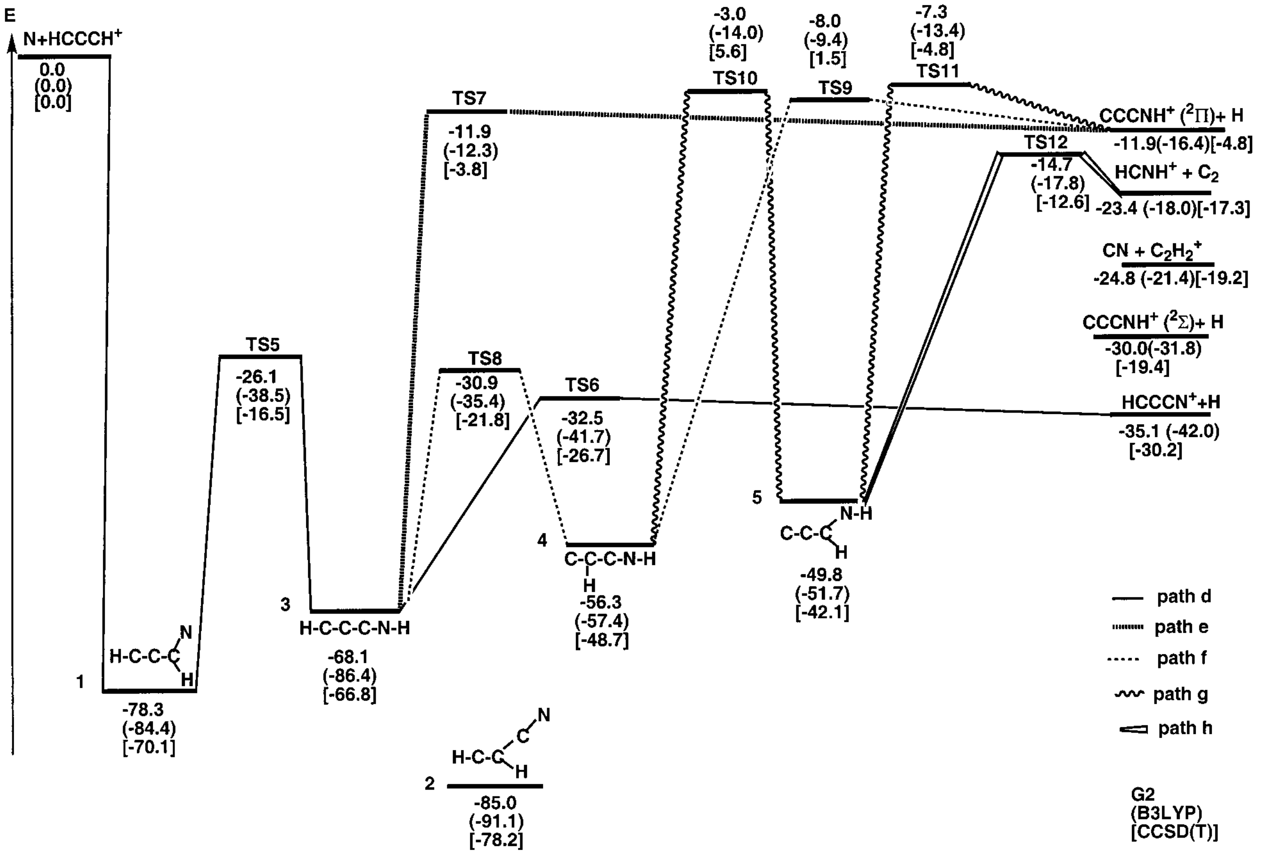

Figure 4. Energy profile (second part), in kcal/mol, for the reaction of N with HCCCH$^+$ at the G2, B3LYP, and CCSD(T) levels (including zero-point vibrational energy differences).

tion into $C_2H_2^+$ + CN:

$$N + CCCH_2^+ \rightarrow \mathbf{6} \xrightarrow{TS14} \mathbf{2} \xrightarrow{TS3} HCCCN^+ + H \qquad (j)$$

$$N + CCCH_2^+ \rightarrow \mathbf{1} \xrightarrow{TS14} \mathbf{2} \xrightarrow{TS4} C_2H_2^+ + CN \qquad (k)$$

From our results the most favorable channel should be path i, because, although TS14 lies below TS13 (by some 8 kcal/mol at all levels of theory), the subsequent transition states, TS3 and TS4, respectively for paths j and k, lie higher in energy. Nevertheless, there is even a more favorable isomerization process for structure **6**, namely nitrogen insertion into the C−C bond leading to structure **7**, which implies a transition state, TS15, which clearly lies below TS14. However, the subsequent hydrogen elimination resulting in HCCNC$^+$ + H implies a rather high energy barrier (see the relative energy of TS16). Therefore path l, which can be schematically represented as follows

$$N + CCCH_2^+ \rightarrow \mathbf{6} \xrightarrow{TS15} \mathbf{7} \xrightarrow{TS16} HCCNC^+ + H \qquad (l)$$

should be the less favorable one for this reaction. This means that reaction of N with $CCCH_2^+$ does not seem a feasible process to obtain precursors of CCNC in space, because other channels, particularly those leading to precursors of CCCN, are predominant.

Finally we will discuss the reaction of N atoms with the cyclic $C_3H_2^+$ isomer. It is expected that in the SIFT experiments a mixture of the linear and cyclic isomers is initially formed, and therefore this analysis is relevant in interpreting those experiments, as well as in astrochemistry. The energy profile for this reaction is shown in Figure 6.

The most favorable interaction between nitrogen and c-$C_3H_2^+$ takes place through the apex of the C_3 unit, leading to **8**, the most stable triplet $(NC_3H_2)^+$ species. However, the two channels leading to cyclic structures are clearly endothermic:

$$N + c\text{-}C_3H_2^+ \rightarrow \mathbf{8} \rightarrow NC_3H^+ + H \qquad (m)$$

$$N + c\text{-}C_3H_2^+ \rightarrow \mathbf{8} \xrightarrow{TS17} \mathbf{9} \xrightarrow{TS18} NC_3H^+ + H \qquad (n)$$

Path m, which produces a cyclic isomer with a three-member ring, proceeds through direct hydrogen elimination and does not seem to involve any transition state. All our attempts to obtain a transition state for this process led to very large C−H distances without reaching any stationary point. On the other hand, the product in path n is a four-member ring. Although isomerization into structure **9** involves a transition state, TS17, which lies well below the reactants and other transition states, hydrogen elimination seems to proceed through a significant barrier, as suggested by the relative energy of TS18. It seems that the energy barrier associated with this process should be even slightly higher than its endothermicity. The fact that both paths, m and n, are clearly endothermic and that path n (with the lowest endothermicity) seems to proceed with a certain energy barrier suggest that the interstellar synthesis of precursors of cyclic C_3N should be precluded.

Of course, there are other possible channels that imply ring opening in structure **8** through transition state TS19:

$$N + c\text{-}C_3H_2^+ \rightarrow \mathbf{8} \xrightarrow{TS19} \mathbf{2} \xrightarrow{TS3} HCCCN^+ + H \qquad (o)$$

$$N + c\text{-}C_3H_2^+ \rightarrow \mathbf{8} \xrightarrow{TS19} \mathbf{2} \xrightarrow{TS4} C_2H_2^+ + CN \qquad (p)$$

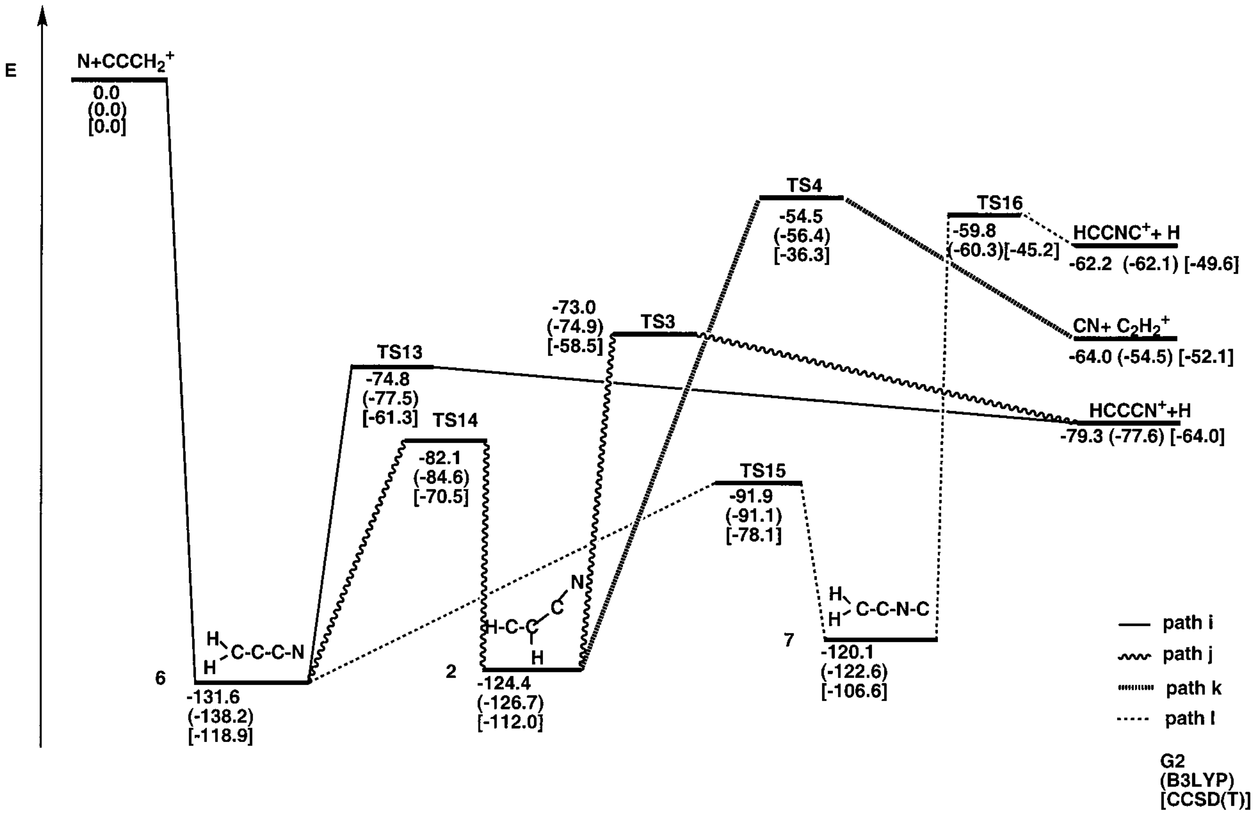

Figure 5. Energy profile, in kcal/mol, for the reaction of N with $CCCH_2^+$ at the G2, B3LYP, and CCSD(T) levels (including zero-point vibrational energy differences).

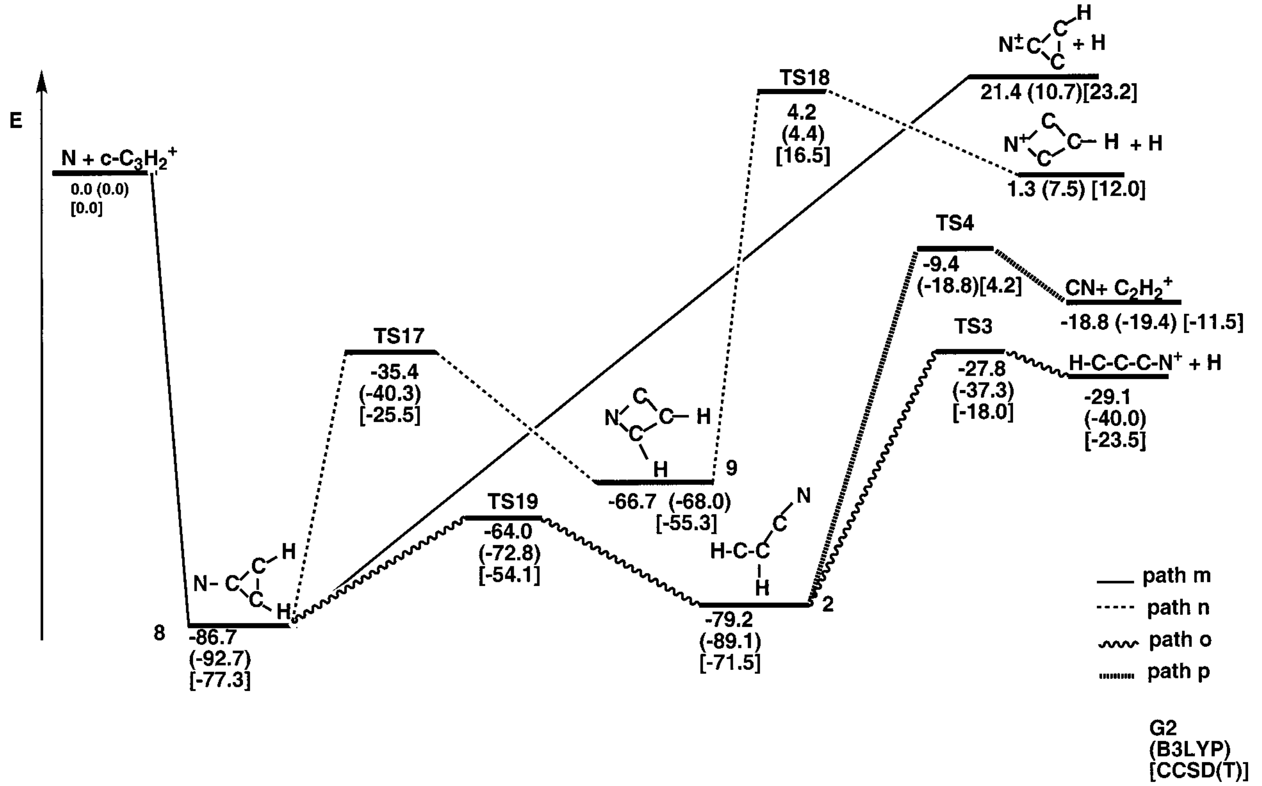

Figure 6. Energy profile, in kcal/mol, for the reaction of N with $c\text{-}C_3H_2^+$ at the G2, B3LYP, and CCSD(T) levels (including zero-point vibrational energy differences).

TS19 has an imaginary frequency whose normal mode is associated with CCC bending, and has very similar geometrical parameters at both MP2 and B3LYP levels. Once the open-chain structure **2** is reached, $HCCCN^+ + H$ or $C_2H_2^+ + CN$ are obtained through transition states TS3 and TS4, respectively. The same previous discussion about paths b and c now applies to paths o and p. Therefore there seems to be only two competitive channels for the reaction with the cyclic cation, production of $HCCCN^+$ and formation of $C_2H_2^+ + CN$, the first one being in principle the most favorable.

Conclusions

A theoretical study of the reaction of atomic nitrogen with the different isomers of $C_3H_2^+$ has been carried out. We have characterized the possible intermediate species, as well as the relevant transition states for this reaction. The lowest-lying triplet species are those directly obtained from the interaction of nitrogen with cyclic $C_3H_2^+$ and $CCCH_2^+$. On the other hand, the result of the interaction with linear $HCCCH^+$ is not very stable. Concerning the reaction of N with linear $HCCCH^+$, our theoretical results suggest that the predominant channel, from both thermodynamic and kinetic arguments, should correspond to production of $HCCCN^+$, followed by production of $C_2H_2^+ + CN$. Other channels that are exothermic but imply higher energy barriers, and therefore should be less favorable, lead to $C_2 + HCNH^+$ and $CCCNH^+$. In the case of the reactions of N with either $CCCH_2^+$ or c-$C_3H_2^+$, it is also observed that the preferred channel is that leading to $HCCCN^+$, followed by production of $C_2H_2^+ + CN$, whereas production of $HCCNC^+$ or cyclic species is much less favorable.

Our results are in partial disagreement with the experimental findings from SIFT experiments, where only two channels, corresponding to $C_2H_2^+ + CN$ and $C_2 + HCNH^+$ (with branching ratios of 0.85 and 0.15, respectively), were observed. Our prediction for the enthalpies of these two channels agrees quite well with the experimental values, and our theoretical results are in agreement with the fact that production of $C_2H_2^+ + CN$ should prevail over formation of $C_2 + HCNH^+$. However, the theoretical results suggest that production of $HCCCN^+$ should be the dominant channel. A possible explanation could be that fragmentation of the most exothermic products takes place. Alternatively, one may propose that the reaction could proceed in a very different way at ~0 K than at thermal energies.

The implications in astrochemistry are also interesting, because our results suggest that the reaction of nitrogen with $C_3H_2^+$ is feasible under interstellar conditions and may lead predominantly to $HCCCN^+$. This species could be a precursor of HCCCN or CCCN upon hydrogenation or dissociative recombination.

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