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Theoretical study of the reaction of CN with $C_2H_2^+$

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Abstract. A theoretical study of the reaction of CN with $C_2H_2^+$ has been carried out at three levels of theory, namely G2, B3LYP and CCSD(T). The main conclusion is that this is a feasible process under interstellar conditions, but only linear species may be produced. The most favourable product is $HCCCN^+$, followed by $CCCNH^+$. Production of $HCCNC^+$ is predicted to be slightly endothermic; therefore, the reaction of CN + $C_2H_2^+$ may produce precursors of HC_3N and C_3N in space. Furthermore, the B3LYP level is found to perform rather well compared with G2 and even better than CCSD(T).

Key words: Interstellar chemistry – Cyanoacetylene – Ab initio

1 Introduction

The cyanopolyacetylene (cyanopolyyne) family, $HC_{n+1}N$, is one of the most interesting discovered in interstellar media. So far the list of members of this family observed in space includes n = 1–5. The last member of the family, $HC_{11}N$, is the largest interstellar molecule [1] and, of course, the longest linear species observed in interstellar media. Furthermore two new isomers of the first member of the family, cyanoacetylene (HC_3N), have recently been discovered: HCCNC and CCCNH [2].

One of the main questions concerning the cyanopolyacetylene family is how these molecules can be synthesized in interstellar media. In the case of HC_3N a neutral–neutral reaction, CN + C_2H_2, has been suggested as a possible source [3]. Experimental [4] and theoretical [5] studies on this reaction have shown that it may occur appreciably at cool interstellar temperatures. In addition ion–molecule synthetic pathways have also been proposed [3, 6] for the production of precursors of HC_3N in space. For cyanoacetylene, which is the first member of the cyanopolyyne family, the proposed reactions are as follows:

$$C_2H_2^+ + CN \rightarrow HC_3N^+ + H \quad (1)$$

$$HC_3N^+ + H_2 \rightarrow H_2C_3N^+ + H \quad (2)$$

$$C_2H_2^+ + HCN \rightarrow H_2C_3N^+ + H \quad (3)$$

Dissociative recombination of $H_2C_3N^+$ may finally lead to cyanoacetylene:

$$H_2C_3N^+ + e^- \rightarrow HC_3N + H \quad (4)$$

It must be noted that dissociative recombination of HC_3N^+ could also lead to C_3N, another interstellar molecule with two different isomers, CCCN and CCNC.

The aim of the present work is to provide a theoretical study of reaction (1), determining its energetics as well as the possible energy barriers associated with the different channels.

2 Computational methods

Two different levels of theory were employed in the present work for comparative purposes. Firstly, we applied the so-called G2 method [7], which is an approximation of the QCISD(T)/6-311 + G(3df,2p) ab initio level, assuming additivity of several corrections. It involves single-point QCISD(T)/6-311G(d,p), MP4/6-311G(d,p), MP4/6-311 + G(d,p), MP4/6-311G(2df,p) and MP2/6-311 + G(3df,2p) energy calculations on MP2/6-31G(d) geometries. A small empirical correction is added to include high-level correction effects, and zero-point vibrational energies (ZPVE) are included employing scaled (scaling factor 0.8929) HF/6-31G(d) harmonic vibrational frequencies. Secondly, we carried out CCSD(T) calculations [8] with the 6-311G(d,p) basis set. In this case the geometry is obtained using density functional theory. In particular, we selected the B3LYP exchange–correlation functional [9, 10] with the 6-311G(d,p) basis set. B3LYP/6-311G(d,p) harmonic vibrational frequencies were employed to estimate the ZPVE contribution.

All calculations were carried out with the Gaussian 94 program package [11].

3 Results and discussion

The reaction of CN with $C_2H_2^+$ may be initiated by a σ or a π attack, depending on the relative orientation of

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the reactants. The σ attack proceeds through C_s symmetry, whereas the π attack starts along C_{2v} symmetry. In both cases the interaction can take place through the carbon or the nitrogen atom of CN. The energy profiles for the reaction at the G2, B3LYP and CCSD(T) levels are shown in Fig. 1 (σ attack) and Fig. 2 (π attack). The optimized geometries for the relevant transition states (TS) involved in the reaction of CN with $C_2H_2^+$ are shown in Fig. 3. The optimized geometries for the intermediates ($H_2C_3N^+$ isomers) are not shown to save space, but are available upon request. In all cases we checked the nature of the stationary points through computation of the vibrational frequencies. All minima have only real frequencies, whereas in the case of TS one imaginary frequency associated with the reaction coordinate was found. Vibrational frequencies at both the MP2 and B3LYP levels for all species reported in this work are also available from the authors upon request.

When CN approaches $C_2H_2^+$ along the C_s surface, a displacement of a hydrogen atom takes place simultaneously. When the interaction takes place through the nitrogen atom, migration to the terminal carbon takes place resulting in structure **3**. On the other hand, when CN interacts through the carbon atom a nonclassical structure (**1**) is reached, where the hydrogen atom is bonded to the C—C multiple bond. This structure is the

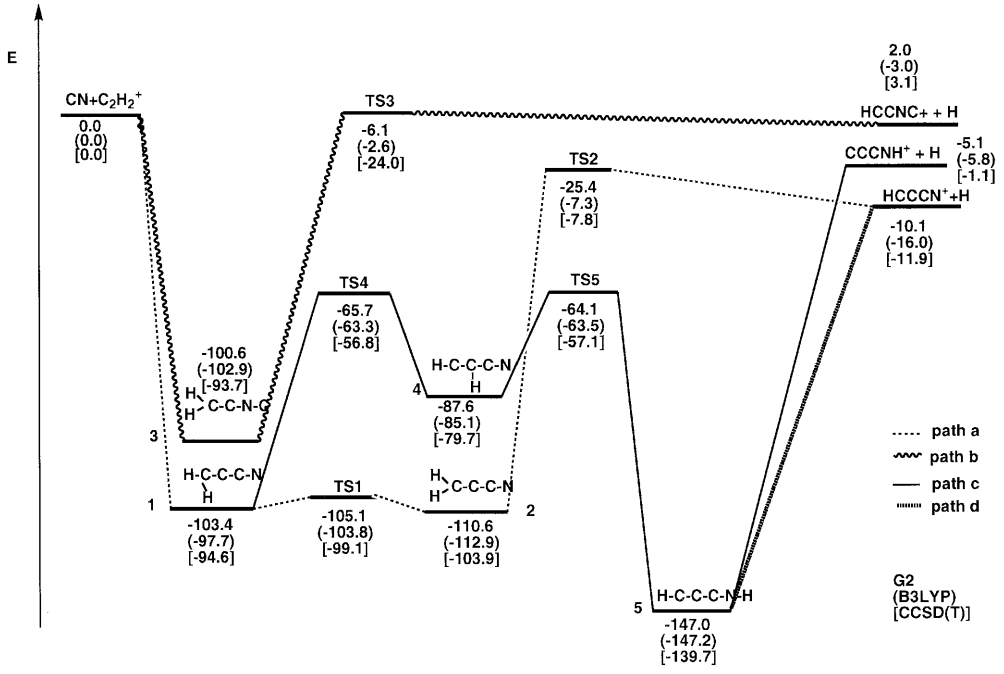

Fig. 1. Energy profile (kcal/mol) at the G2, B3LYP and CCSD(T) levels for the reaction of CN with $C_2H_2^+$ following σ interaction

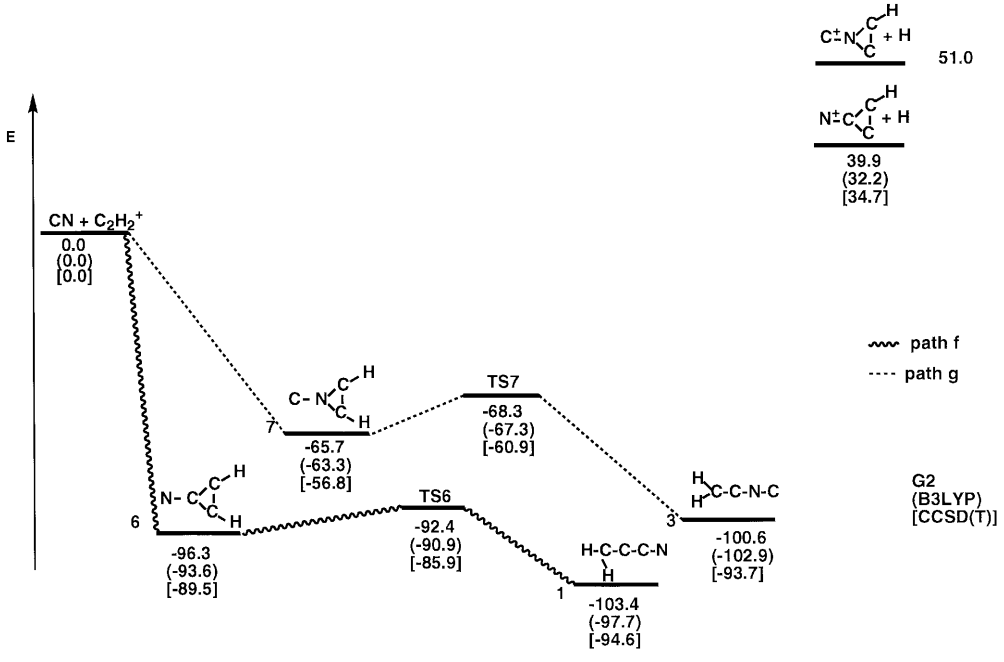

Fig. 2. Energy profile (kcal/mol) at the G2, B3LYP and CCSD(T) levels for the reaction of CN with $C_2H_2^+$ following π interaction

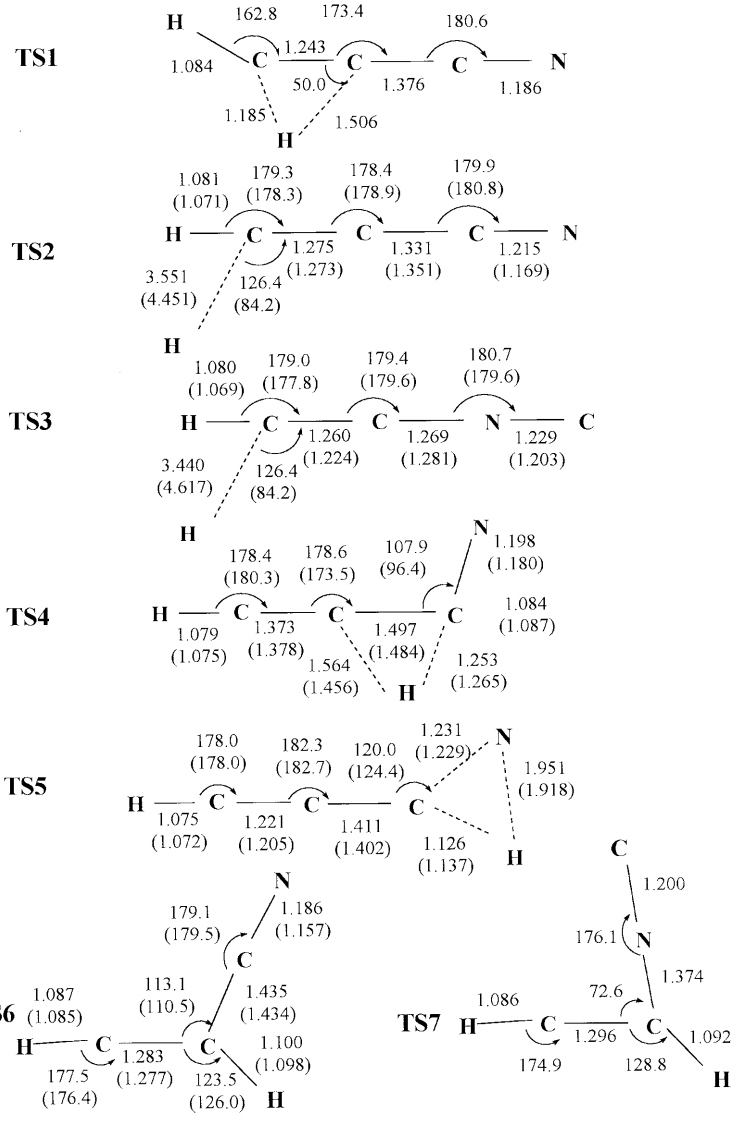

Fig. 3. MP2/6-31G(d) and B3LYP/6-311G(d) optimized geometries for the different transition states found on the $(C_3NH_2)^+$ potential surface. Distances are given in Angstroms and angles in degree

analogue of the nonclassical structure found for $C_2H_3^+$ [12] and is shown to be a true minimum on the MP2 potential surface. At the B3LYP level structure **1** is not found and only structure **2**, with the two hydrogens bonded to the terminal carbon atom is obtained. Consequently the TS connecting structures **1** and **2** is only obtained at the MP2 level [the energy values at the B3LYP and CCSD(T) levels for **1** and TS1 in Fig. 1 were obtained for the MP2 geometries]. Our energy results suggest that the approach through the carbon atom is favoured, since structure **2** lies below **3** by some 10 kcal/mol.

Once structures **2** and **3** are reached, hydrogen elimination can take place, leading to the final products, $HCCCN^+$ and $HCCNC^+$, respectively. These two processes can be represented schematically as follows:

$$CN + C_2H_2^+ \rightarrow \mathbf{1} \xrightarrow{TSI} \mathbf{2} \xrightarrow{TS2} HCCCN^+ + H \qquad (a)$$

$$CN + C_2H_2^+ \rightarrow \mathbf{3} \xrightarrow{TS3} HCCNC^+ + H \qquad (b)$$

TS2 and TS3 are the corresponding TS for hydrogen elimination from H_2CCCN^+ and H_2CCNC^+, respectively. As can be seen in Fig. 3 in both cases the C—H bond is very long. Furthermore the energy results at the G2 and CCSD(T) levels show that these TS are likely to disappear at higher levels of theory, with direct hydrogen elimination to reach the products.

Path a is clearly exothermic at all levels of theory and both TS1 and TS2 lie below the reactants; therefore this seems a feasible process under interstellar conditions (low temperature and low density, which preclude reactions that are endothermic or proceed through significant activation barriers). On the other hand, path b is slightly endothermic at both the G2 and CCSD(T) levels of theory. Although this channel cannot be definitely ruled out, it is clear that path a should be favoured over path b.

There are still other possibilities for the reaction to proceed. Once structure **1** is formed, migration of hydrogen towards the carbon atom bonded to nitrogen can take place, giving structure **4**. Furthermore, isomerization into structure **5**, through migration of hydrogen towards the nitrogen atom, is also possible. Finally hydrogen elimination from structure **5** could lead to two

different products: $HCCCN^+$ and $CCCNH^+$. These processes can be summarized as follows:

$$CN + C_2H_2^+ \rightarrow \mathbf{1} \xrightarrow{TS4} \mathbf{4} \xrightarrow{TS5} \mathbf{5} \rightarrow CCCNH^+ + H \quad (c)$$

$$CN + C_2H_2^+ \rightarrow \mathbf{1} \xrightarrow{TS4} \mathbf{4} \xrightarrow{TS5} \mathbf{5} \rightarrow HCCCN^+ + H \quad (d)$$

It is worth noting that processes c and d proceed through structure **5**, $HCCCNH^+$, which is found to be, as expected, the global minimum on the $[NC_3H_2]^+$ surface. The second lowest-lying structure is **2**, which lies about 36 kcal/mol higher at both the G2 and CCSD(T) levels of theory. This seems to be a rather stable structure, since it is a deep minimum on the potential surface (it lies more than 140 kcal/mol below the reactants). This means that it is quite likely that this structure could be a long-lived complex. The very large energy difference with the final products, either $HCCCN^+ + H$ (more than 130 kcal/mol) or $CCCNH^+ + H$ (about 140 kcal/mol), also suggests that this structure could be a long-lived species. In principle, formation of structure **5** should be favoured over paths a and b, since TS4 and TS5 lie well below the corresponding TS2 and TS3. Structure **5**, $HCCCNH^+$, is the result of the protonation of HCCCN and has been studied both theoretically [13, 14] and experimentally [15]. Our optimized geometries are very close to those reported in previous work.

Hydrogen elimination from structure **5** takes place directly. All our attempts, at both the MP2 and B3LYP levels, to obtain the corresponding TS failed. We followed these processes in detail through partial optimizations at different fixed C—H and N—H bond distances (up to 6.0 Å) and found no sign of TS. This is not surprising given the large energy difference between **5** and the final products. In conclusion, paths c and d are both exothermic and the TS involved, TS4 and TS5, lie well below the reactants; therefore, both can occur in interstellar media. Path d should be favoured thermodynamically over c. It is interesting to note that charge transfer (producing $CN^+ + C_2H_2$) is not a competitive process, since the corresponding reaction enthalpy is 53.3 and 53.5 kcal/mol at the G2 and CCSD(T) levels, respectively.

Finally we should comment on the possible reaction paths through π interaction, which are represented in Fig. 2. Two different schemes may be proposed:

$$CN + C_2H_2^+ \rightarrow \mathbf{6} \xrightarrow{TS6} \mathbf{1} \quad (f)$$

$$CN + C_2H_2^+ \rightarrow \mathbf{7} \xrightarrow{TS7} \mathbf{3} \quad (g)$$

Once again, as in the case of σ interaction, the π interaction through the carbon atom is favoured, since structure **6** lies below **7**. Hydrogen elimination from these species to give cyclic products is precluded, since these processes are clearly endothermic (by about 40 and 51 kcal/mol, respectively, at the G2 level). The reaction should then proceed through the opening of the three-membered ring (involving TS6 and TS7), resulting in the open-chain structures **1** and **3**. These species would evolve according to the reaction paths discussed previously and, therefore, linear products are finally obtained.

A final comment on the performance of the different theoretical methods is in order. From the energy results shown in Figs. 1 and 2, it can be concluded that the B3LYP level generally provides values that are rather close to the G2 results, which should be the most reliable ones. The mean absolute errors (taking G2 values as a reference) for intermediates, TS and products are 2.8, 4.1 and 4.8 kcal/mol, respectively, at the B3LYP level and 7.4, 10.2 and 3.0 kcal/mol, respectively, at the CCSD(T) level. The global mean errors are 3.8 kcal/mol (B3LYP) and 7.5 kcal/mol [CCSD(T)]. Consequently, it seems that B3LYP performs even better than CCSD(T), when compared with the G2 method.

4 Conclusions

The main conclusion from this work is that the reaction of CN with $C_2H_2^+$ to produce HC_3N^+ is feasible under interstellar conditions, since it is exothermic and barrier-free. Only linear species can be produced. $HCCCN^+$ should be the most favourable product, followed by $CCCNH^+$. Production of $HCCNC^+$ seems to be slightly endothermic. These species could be precursors of HC_3N and C_3N upon hydrogenation and/or dissociative recombination. The B3LYP level compares rather well with higher levels of theory, such as G2, and performs even better than the more expensive CCSD(T) method in this case. This suggests that the B3LYP functional could be a possible good choice for studying related more complex reactions.

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