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Theoretical study of the reaction of CN with C$_2$H$_2$$^+$

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Abstract. A theoretical study of the reaction of CN with C$_2$H$_2$$^+$ has been carried out at three levels of theory, namely G2, B3LYP and CCSD(T). The main conclusion is that this is a feasible process under interstellar conditions, but only linear species may be produced. The most favourable product is HCCCN$^+$, followed by CCCNH$^+$. Production of HCCNC$^+$ is predicted to be slightly endothermic; therefore, the reaction of CN + C$_2$H$_2$$^+$ may produce precursors of HC$_3$N and C$_2$N 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 – Cyanocetylene – 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$_4$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, cyanocetylene (HC$_3$N), have recently been discovered: HCCCN and CCCCNH [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$_3$N a neutral–neutral reaction, CN + C$_2$H$_2$, 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$_3$N in space. For cyanocetylene, which is the first member of the cyanopolyacetylene family, the proposed reactions are as follows:

1. C$_2$H$_2$$^+$ + CN → HC$_3$N$^+$ + H
2. HC$_3$N$^+$ + H$_2$ → H$_2$C$_3$N$^+$ + H
3. C$_2$H$_2$ + HCN → H$_2$C$_3$N$^+$ + H

Dissociative recombination of H$_2$C$_3$N$^+$ may finally lead to cyanocetylene:

4. H$_2$C$_3$N$^+$ + e$^-$ → HC$_3$N + H

It must be noted that dissociative recombination of HC$_3$N$^+$ could also lead to C$_2$N, 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(df,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/6-31G(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$_2$H$_2$$^+$ may be initiated by a σ or a π attack, depending on the relative orientation of
the reactants. The σ attack proceeds through $C_2$ 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$_2$H$_2$ are shown in Fig. 3. The optimized geometries for the intermediates (H$_2$C$_3$N$^+$ 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$_2$H$_2$* along the C, 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

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**Fig. 1.** Energy profile (kcal/mol) at the G2, B3LYP and CCSD(T) levels for the reaction of CN with C$_2$H$_2$ following σ interaction.

**Fig. 2.** Energy profile (kcal/mol) at the G2, B3LYP and CCSD(T) levels for the reaction of CN with C$_2$H$_2$ following π interaction.