



Ab initio studies on cyanoacetylenes of astrochemical interest: [Y(C≡C)CN, Y = C₂H₅, C₃H₇, C₄H₉, F, Cl, Br and CN]



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HIGHLIGHTS

- Structural and spectroscopic data of cyanoacetylenes were computed using theoretical methods.
- Comparisons of these parameters with experiments indicate the good performance of DFT method.
- The large electric dipole moment of the cyanoacetylenes should help towards their detections.
- The theoretical findings of these cyanoacetylenes should be helpful to experimentalists.
- Plausible formation mechanisms of the cyanoacetylenes are also proposed.

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ABSTRACT

Theoretical studies were performed on seven potential interstellar and circumstellar substituted cyanoacetylenes, Y(C≡C)CN [Y = C₂H₅, C₃H₇, C₄H₉, F, Cl, Br and CN]. Geometry optimizations were carried out using the DFT/B3LYP, the CCSD and CCSD(T) levels of theory. The cc-pVTZ basis set was used for all atoms. Frequency computations were also carried out at the same level of theory as for the optimization to check the nature of the stationary points. The molecular and spectroscopic parameters of the cyanoacetylenes were computed. An analysis of these parameters is in line with the satisfactory performance of the B3LYP/cc-pVTZ level compared to the golden standard, the CCSD(T) level. The theoretical data reported in this work should facilitate future identifications of these cyanoacetylenes in extraterrestrial locations. Plausible mechanisms for the formation of these molecules have been proposed.

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1. Introduction

The cyano (C≡N) functional group, found in neutral molecules, radicals and ions, is extremely prevalent in the interstellar medium (ISM) and other extraterrestrial regions (Ehrenfreund and Charnley, 2000; Bernstein et al., 2004; Carles et al., 2013). Cyanoacetylene, H(C≡C)CN, has been a known interstellar molecule for a long time (Turner, 1971) and a precursor to biomolecules found in ISM (Majumdar et al., 2012). The famous experiment by Urey and Miller concluded hydrogen cyanide to be of prime importance in the formation of organic compounds on the Earth and its environment (Miller and Urey, 1959). Biomolecules such as amino acids, nucleotides and carbohydrates have been formed in interstellar medium and molec-

ular clouds starting from hydrogen cyanide and cyano compounds (Abelson, 1996; Orgel, 2004). More recently, larger models of cyano compounds having astrochemical interest have been studied (Misra and Tandon, 2014; Das et al., 2013) and iso-propyl cyanide was detected in ISM (Belloche et al., 2014).

Methyl cyanoacetylene, CH₃(C≡C)CN, was also identified in the ISM (Brotten et al., 1984). Carles et al. (2013) predicted the presence of ethyl cyanoacetylene, C₂H₅(C≡C)CN, in the ISM. They carried out a laboratory investigation of the rotational spectrum of this molecule, followed by quantum-chemical computations at the B3LYP/cc-pVTZ and CCSD/cc-pVTZ levels of theory to obtain the structural and spectroscopic parameters. The experimentally determined rotational constants and dipole moment were found to be in close agreement with the theoretical values computed using the CCSD level of theory.

The infrared (IR) spectra of three halogeno-derivatives of cyanoacetylene, Y(C≡C)CN [Y=F, Cl, Br], were experimentally

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investigated (Bjorvatten, 1974; Niedenhoff et al., 1991; Christensen et al., 1969; Klaboe and Kloster-Jensen, 1967). An *ab initio* study of the molecular structure of fluorocyanopolyynes was carried out by La Manna (La Manna, 1998). The first three members in the series (FC_{2n+1}N), i.e., fluorocynoacetylene ($\text{F}(\text{C}\equiv\text{C})\text{CN}$), fluorocyanobutadiyne ($\text{F}(\text{C}\equiv\text{C})_2\text{CN}$) and fluorocyanohexatriyne ($\text{F}(\text{C}\equiv\text{C})_3\text{CN}$), were optimized at the HF/6-31G(d) and MP2/6-31G(d) levels of theory, followed by a vibrational analysis. Comparison with available experimental data shows that there is only qualitative agreement between the theoretical and experimental results. Varadwaj, (2006) performed a Density Functional Theory (DFT) study on chlorocynoacetylene, $\text{Cl}(\text{C}\equiv\text{C})\text{CN}$, using the B3LYP and B3PW91 functionals and different basis sets, to obtain the molecular parameters. The bond lengths and rotational constants display satisfactory agreement with their experimental counterparts using the B3LYP/6-311++G(d,p) method. Varadwaj and Bangal, (2005) used the restricted HF level of theory and B3LYP functional to investigate bromocynoacetylene, $\text{Br}(\text{C}\equiv\text{C})\text{CN}$. The bond lengths, rotational constants and harmonic vibrational frequencies computed at the B3LYP level with either 6-311G(d) or 6-311++G(d,p) basis sets show satisfactory agreement with available experimental literature data.

Experimental data on the IR spectrum of $\text{NC}(\text{C}\equiv\text{C})\text{CN}$ is available from literature (Miller and Hannan, 1953; Miller et al., 1955). The vibrational frequencies and structural parameters of $\text{NC}(\text{C}\equiv\text{C})\text{CN}$ were predicted using quantum-chemical computations by Jensen, (2004). The molecule, maintained in $D_{\infty h}$ symmetry, was optimized using the HF and MP2 levels of theory and the B3LYP functional, using the 6-311G(d,p) basis set. The vibrational frequencies obtained at the three different levels were scaled using different correction factors. The bond lengths and corrected harmonic frequencies were compared with available experimental data from literature with satisfactory agreement. Kołos, (2002) carried out an *ab initio* study of $\text{NC}(\text{C}\equiv\text{C})\text{CN}$ and its isomers. The equilibrium structures, energetics, electric dipole moments and vibrational frequencies of nine non-branched chain isomers and three branched chain isomers were studied. In addition to these studies, larger cyanopolyynes such as HC_5N (Winnewisser and Walmsley, 1978), HC_7N (Winnewisser and Walmsley, 1978; Kroto et al., 1978; Langston and Turner, 2007), HC_9N (Bell et al., 1992; Broten et al., 1978; Graham, 1993) and HC_{11}N (Oka, 1978) have also been reported for their existence in ISM. Recently, Jolly et al. (2015) reported the relevant experimental infrared spectrum of C_4N_2 recorded in the gas phase.

In view of the above, in the present investigation in the gas phase, the theoretical study performed by Carles et al. (2013) on ethyl cyanoacetylene was augmented by computations with the very tight convergence criteria to investigate its effect on the computed parameters. Additional molecular parameters such as polarizability and hyperpolarizability were also computed. The structural and spectroscopic parameters are reported and compared with available experimental data. This investigation was extended to other potential interstellar molecules which include the propyl, butyl and halogeno-derivatives of cyanoacetylene and dicyanoacetylene. The latter was detected by IR in the atmosphere of Titan (Khanna et al., 1987), one of the moons of Saturn. However, it is yet to be found in the ISM and it was also postulated by Woon and Herbst (2009) as an interstellar molecule. Some possible chemical pathways for the formation of these cyanoacetylenes in the ISM are also presented.

2. Computational methods

The quantum-chemical computations were performed using the Gaussian 09 program package (Frisch et al., 2013) by means of the resources provided by GridChem Science Gateway (Dooley et al., 2006; Milfeld et al., 2005; Dooley et al., 2005) Becke's three-parameter hybrid functional (Becke, 1988) employing the Lee et al. (1988) correlation functional (B3LYP) was used in the DFT computations. *Ab initio*

coupled-cluster computations with singlet and doublet excitations (CCSD) (Purvis III and Bartlett, 1982; Scuseria et al., 1988), and perturbative triplet excitations (CCSD(T)) (Scuseria, 1991) were also implemented. The Peterson and Dunning's Correlation-Consistent Polarized Valence Triple Zeta (cc-pVTZ) basis set (Peterson and Dunning, 2002) was employed with all theoretical models.

The seven substituted cyanoacetylenes studied were first optimized using the B3LYP/cc-pVTZ method, and the default convergence criteria, yielding the structural parameters of their respective optimized geometries. The Berny optimization algorithm (Schlegel, 1982) was used. Frequency computations (both harmonic and anharmonic) were performed on these optimized structures to identify the nature of the stationary points.

For the $\text{Y}(\text{C}\equiv\text{C})\text{CN}$ [$\text{Y}=\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$] molecules, the optimizations were carried out at the CCSD/cc-pVTZ level of theory using the very tight convergence criteria. However, frequency computations were not possible at this level of theory with our present computational resources. For the $\text{Y}(\text{C}\equiv\text{C})\text{CN}$ [$\text{Y}=\text{F}, \text{Cl}, \text{Br}$ and CN] molecules, optimized geometries at the CCSD(T)/cc-pVTZ level of theory were obtained using the tight convergence criteria. The harmonic frequencies for these four linear molecules were also computed.

3. Results and discussion

3.1. Molecular structures

The optimized geometry of $\text{C}_2\text{H}_5(\text{C}\equiv\text{C})\text{CN}$ computed using the B3LYP/cc-pVTZ and CCSD/cc-pVTZ methods was reported by Carles et al. (2013). The use of more stringent (very tight) convergence criteria did not have any significant effect (up to 3 d.p. for bond length and 1 d.p. for bond angle) on the molecular parameters computed and hence, results obtained for $\text{C}_2\text{H}_5(\text{C}\equiv\text{C})\text{CN}$ from this work are not reported.

The selected optimized bond lengths and bond angles of $\text{Y}(\text{C}\equiv\text{C})\text{CN}$ [$\text{Y}=\text{C}_3\text{H}_7, \text{C}_4\text{H}_9$] are illustrated in Figs. 1 and 2, generated using CYLview (Legault, 2009). These two molecules are in C_s symmetry with six and eight out of plane hydrogen atoms, respectively. Experimental structural data is not available from literature for these two compounds. The bond lengths and bond angles computed using the B3LYP functional and those obtained using the CCSD level of theory agree within $\pm 0.017 \text{ \AA}$ and $\pm 0.9^\circ$, respectively.

The three halogeno-derivatives of cyanoacetylene, $\text{Y}(\text{C}\equiv\text{C})\text{CN}$ [$\text{Y}=\text{F}, \text{Cl}, \text{Br}$], have a linear structure maintained in $C_{\infty v}$ symmetry. For these three molecules, the bond lengths obtained at the B3LYP/cc-pVTZ level are in excellent agreement with their experimental counterparts, with the largest deviation being an underestimation of approximately 0.4% for the C–C bond in the chloro and bromo derivatives (Figs. 3–5). However, for the bond lengths predicted using the CCSD(T) level of theory, the largest deviation is about 1% for the C≡C bond in the $\text{Br}(\text{C}\equiv\text{C})\text{CN}$ molecule. Detailed structural information for all the molecules is provided as Supplementary Information (SI) (Tables S1, S7, S13, S18, S23, S28).

The centrosymmetric linear structure of dicyanoacetylene, $\text{NC}(\text{C}\equiv\text{C})\text{CN}$, maintained in $D_{\infty h}$ symmetry, is illustrated in Fig. 6. The structure optimized at the B3LYP/cc-pVTZ level of theory displays good agreement with experimental data with the largest deviation being an overestimation of about 0.8% for the C≡C bond. The CCSD(T)/cc-pVTZ level, however, overestimates the C≡C bond by approximately 1.5%.

3.2. Dipole moment and rotational constants

Molecules with larger dipole moments possess rotational spectral lines of larger intensities and can therefore be more easily detected by means of radioastronomy. Most astromolecules are detected through

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