RAA 2014 Vol. **14** No. **3**, 275–284 doi: 10.1088/1674–4527/14/3/002
http://www.raa-journal.org *http://www.iop.org/journals/raa*

Research in
Astronomy and
Astrophysics

Formation of cyanoallene (buta-2, 3-dienenitrile) in the interstellar medium: a quantum chemical and spectroscopic study

Amresh Singh[1], Shivani[1,2], Alka Misra[1] and Poonam Tandon[2]

[1] Department of Mathematics & Astronomy, University of Lucknow, Lucknow 226007, India; *alkamisra99@gmail.com*
[2] Department of Physics, University of Lucknow, Lucknow 226007, India

Received 2013 May 1; accepted 2013 September 24

Abstract The interstellar medium, filling the vast space between stars, is a rich reservoir of molecular material ranging from simple diatomic molecules to more complex, astrobiologically important molecules such as vinylcyanide, methylcyanodiaccetylene, cyanoallene, etc. Interstellar molecular cyanoallene is one of the most stable isomers of methylcynoacetylene. An attempt has been made to explore the possibility of forming cyanoallene in interstellar space by radical-radical and radical-molecule interaction schemes in the gaseous phase. The formation of cyanoallene starting from some simple, neutral interstellar molecules and radicals has been studied using density functional theory. The reaction energies and structures of the reactants and products show that the formation of cyanoallene is possible in the gaseous phase. Both of the considered reaction paths are totally exothermic and barrierless, thus giving rise to a high probability of occurrence. Rate constants for each step in the formation process of cyanoallene in both the reaction paths are estimated. A full vibrational analysis has been attempted for cyanoallene in the harmonic and anharmonic approximations. Anharmonic spectroscopic parameters such as rotational constants, rotation-vibration coupling constants and centrifugal distortion constants have been calculated.

Key words: astrochemistry — techniques: spectroscopic — ISM: abundances — ISM: molecules

1 INTRODUCTION

Interstellar cyanoallene ($\mathrm{CH_2CCHCN}$) has been detected with the 100 m Green Bank Telescope in the dark Taurus molecular cloud (TMC-1) (Lovas et al. 2006a). Chin et al. (2006) have also identified the existence of cyanoallene $(\mathrm{CH_2CCHCN})$ and methylcyanoacetylene $(\mathrm{CH_3CCCN})$, with the use of the 100 m Effelsberg telescope. However, cyanoallene was found to be a more abundant species than methylcyanoacetylene (Lovas et al. 2006b). Cyanoallene is an eight atom molecule, composed of some of the most abundant interstellar atoms, hydrogen, carbon and nitrogen. It is a larger member of the vinyl type molecular series, and is obtained by adding one carbon atom to vinylcyanide $(\mathrm{CH_2CHCN})$, which has been detected in Sgr B2 (Schwahn et al. 1986a).

Schwahn et al. (1986b) reported highly precise frequency predictions for cyanoallene in the 80 GHz region based on microwave and suggested an ion-molecule synthesis starting with the formation of protonated methylcyanoacetylene via the radiative association of (CH_3^+) and cyanoacetylene (HCCCN), and the subsequent formation of methylcyanoacetylene $(\mathrm{CH_3CCCN})$ and cyanoallene $(\mathrm{CH_2CCHCN})$ by dissociative recombination with electrons. Balucani et al. (2002) showed that the neutral-radical reactions between $(\mathrm{C_3H_4})$, in its isomeric forms of allene $(\mathrm{H_2CCCH_2})$ and methylacetylene $(\mathrm{CH_3CCH})$, and the CN radical react to produce all three isomers of cyanopropyne $(\mathrm{C_4H_3N})$, which are methylcyanoacetylene $(\mathrm{CH_3CCCN})$, cyanoallene $(\mathrm{CH_2CCHCN})$, and 3-cyanomethylacetylene $(\mathrm{HCCCH_3CN})$ using a crossed molecular beam as well as ab initio methods. Quan & Herbst (2007) studied the formation mechanism of methylcyanoacetylene and cyanoallene by the neutral-radical reactions involving the radical CN, hydrocarbons methylacetylene $(\mathrm{CH_3CCH})$ and allene using a gas phase chemical reaction network.

In the present work, two totally new exothermic and barrierless reaction paths are considered for the formation of cyanoallene in the interstellar medium (ISM) starting from some simple molecules, ethyne radical, cyanocarbene, propyne carbene and a cyanide radical, all of which have been detected in interstellar space. These precursors may also lead to the formation of organic macromolecules in the ISM. The general problem is finding a viable, thermodynamically feasible mechanism that can account for the formation of such molecules in the ISM. Quantum chemical calculations provide a direct tool for the understanding of systems that are too complex to be observed experimentally and it gives a detailed view of all geometries essential for predicting the mechanisms of organic chemical reactions. Radical-radical and radical-molecule interaction schemes are involved in both of the proposed pathways. A full vibrational analysis is also attempted for cyanoallene in the harmonic and anharmonic approximations and vibro-rotational spectroscopic constants are calculated using B3LYP/aug-cc-pVTZ theory. The value of rate constants and exothermicity of these barrierless reactions raise the possibility of forming cyanoallene in the ISM, a step towards carbon and nitrogen based extraterrestrial life.

In the present paper Section 2 provides detailed information about the methodology used in calculations. Section 3 gives a detailed discussion of reaction mechanisms for both reaction paths and reactions involved in the formation of cyanoalllene in the ISM while Section 4 is about the structural study of cyanoallene. In Sections 5 and 6 we discuss the full vibrational analysis and spectroscopic constants respectively. The conclusion is given in Section 7.

2 COMPUTATIONAL DETAILS

Computations were performed using B3LYP density functional theory with the 6-31G** basis set. The 6-31G** basis set is widely used in chemistry because it succeeds in reproducing experimental data with high reliability (Cramer 2005). All calculations were carried out with the Gaussian 03W program. Total energies, zero point vibrational energy (ZPVE) and electronic energies (EE) of all the molecules/radicals formed during the reaction path towards the formation of cyanoallene were calculated at 10 K. All the energies of molecules/ions involved in reactions are given in Table 1. For a theoretical study of cyanoallene formation in the ISM we use the Gaussian 03W program (Frisch et al. 2003). However, rate constants were calculated by using a semiempirical formula developed by Bates (1983) for values of rate constants at very low temperatures (at approximately 10–30 K temp). These values of the rate constants at temperatures closer to actual physical conditions are calculated in the manuscript. Hence, results obtained under these calculations are favorable in conditions of a cold cloud like temperature of 10–30 K and pressure of 1 atmosphere. Rate constants calculated in this paper demonstrate that the reactions are feasible in conditions of a cold cloud (Bates 1983). In our earlier work, these equations were also used for estimation of rate constants at lower temperatures (Gupta et al. 2011).

Table 1 EE, ZPVE and total energies of molecules and radicals in the gas phase based on B3LYP/6-31G (d, p) calculations (energies in a.u.) at 10 K.

Reaction Path 1				Reaction Path 2			
Molecules/Radicals	EE	ZPVE	Total Energies	Molecules/Radicals	EE	ZPVE	Total Energies
H	–0.500273	0.000000	–0.500273	H	–0.500273	0.000000	–0.500273
C_2H	–76.6060893	0.012661	–76.593428	C_3H	–114.6789148	0.017266	–114.661649
HCCN	–131.3969726	0.018159	–131.378813	C_3H+H	–115.1791878	0.017266	–115.161922
HCCN+C_2H	–208.003062	0.030820	–207.972241	HCCCH	–115.3187889	0.028295	–115.290493
CHCCHCN	–208.2510061	0.041493	–208.209513	CN	–92.71174734	0.004922	–92.706825
CHCCHCN+H	–208.7512791	0.041493	–208.709786	HCCCH+CN	–208.0305362	0.032470	–207.997318
CH_2CCHCN	–208.9030108	0.054984	–208.848026	HCCCHCN	–208.2510060	0.041493	–208.209513
				HCCCHCN+H	–208.7512790	0.041493	–208.709786
				CH_2CCHCN	–208.9030106	0.054983	–208.848027

Harmonic frequency calculations were conducted at the same level for the molecule to test the stability of its molecular structure. Positive wavenumbers confirmed the stability of the molecular structure at minimum energy. We have also estimated the rate constant of every step for both the reaction paths. A complete vibrational assignment was also conducted for the title compound. Potential energy distributions (PEDs) along internal coordinates were calculated by the software Gar2ped. By combining the results of the GaussView program with symmetry considerations, vibrational wavenumber assignments were made with a high degree of accuracy. There is always some ambiguity in defining internal coordinates. The normal mode analysis was performed and the PED was calculated along the internal coordinates using localized symmetry. A full vibrational analysis was also attempted for cyanoallene in the harmonic and anharmonic approximations and vibro-rotational spectroscopic constants were calculated using B3LYP/aug-cc-pVTZ theory.

The chemical analysis calculates the energy requirement for two paths. The results also showed that the proposed reactions, which are feasible and exothermic at this temperature and pressure, can also have a high probability of occurrence in interstellar space, i.e. in the regions of a cold cloud. Although the results depend on the conditions of the environment such as radiation field, temperature and pressure, our study gives qualitative indicators about the formation of cyanoallene in the ISM. The most suitable reaction pathway is exothermic. All the reactions involved in the present study are exothermic and barrierless, and as such do not follow the temperature dependent Arrhenius expression (Bates 1983). Hence, an estimation of the rate constant at 10–30 K can be made on the basis of the semiempirical relationship developed by Bates (1983)

$$K = 1 \times 10^{-21} A_r (6E_0 + N - 2)^{3N-7}/(3N-7)! \quad \mathrm{cm}^3\ \mathrm{s}^{-1}. \tag{1}$$

Here E_0 is the association energy in eV, N is the number of nuclei in the complex and A_r is the transition probability in s^{-1}, which is taken as 100 as suggested by Bates (1983). In our case the values calculated using Equation (1) exceed the limit set by the following equation and so Equation (2) is used to calculate the values of the rate constant in the range of temperature 10–30 K

$$K = 7.41 \times 10^{-10} \alpha^{1/2} (10/\mu)^{1/2} \quad \mathrm{cm}^3\ \mathrm{s}^{-1}, \tag{2}$$

where α is the polarizability in $\mathrm{\AA}^3$ and μ is the reduced mass of the reactants on the ^{12}C amu scale, as suggested by Bates (1983). In our earlier work, these equations are also used for estimation of the rate constants at lower temperatures (Gupta et al. 2011). The methods that are used for the calculation of rate constants are mainly based on the theory of Bates (1983) and capture theory

(Su & Chesnavich 1982). These theories were used earlier by several authors for calculating the temperature dependence of rate constants (Majumdar et al. 2012; Woon & Herbst 2009; Herbst & Leung 1986; Su & Chesnavich 1982; Herbst 2013; Das et al. 2013). The "Multiwell program" was also used for calculating the temperature and pressure dependence of reaction rates (Woon & Park 2009; Woon 2006). Their results also indicate that the magnitude of the rate constant is not affected much by temperature variations in the range 10–300 K. However, in the present study we have calculated rate constants using Equation (2), i.e. the "Langevin Equation" which is independent of temperature (Herbst 2001; Su & Chesnavich 1982). Herbst (2001) demonstrated that the results obtained from this equation agree well with the experimental results from room temperature and above, down to temperatures below 10 K. It was also reported by several researchers (Bates 1983; Majumdar et al. 2012; Gupta et al. 2011) that if Equation (1) leads to the result exceeding the limits set by Equation (2), then the limit should be adopted. Equation (2) should be used for calculating rate constants in our case. The results obtained by using Equation (2) are given in Table 2 at 10 K. The estimated rate constants are calculated for gas phase reactions. No studies related to radical-radical or radical-molecule interactions have been reported so far for the formation of cyanoallene.

Table 2 Computed reaction energies and estimated rate constants for the formation of Cyanoallene.

Reaction steps	Reaction Energies with ZPVE (kcal mol^{-1}) (Gas phase)	Rate Constant (cm^3 s^{-1})
Reaction Path 1		
HCCN+C_2H→Molecule1	–148.89	1.5×10^{-9}
Molecule1+H→Cyanoallene	–86.74	6.2×10^{-9}
Reaction Path 2		
C_3H+H→Molecule1	–76.10	5.0×10^{-9}
Molecule1+CN→Molecule2	–133.15	1.5×10^{-9}
Molecule1+H→Cyanoallene	–86.75	6.1×10^{-9}

3 RESULTS AND DISCUSSION

3.1 Reaction Pathways

Our study examined two reaction pathways. Both pathways involved radical-neutral molecule interactions and are barrierless. These proposed reactions leading to the formation of cyanoallene in interstellar space involve several simple neutral interstellar molecules and radicals such as HCC, HCCN, HCCC and CN (Fuente et al. 2005; Ziurys 2006; Guelin & Cernicharo 1991; Mangum & Wootten 1990; Saito et al. 1984). The mechanism of formation of cyanoallene will be considered under the following headings.

3.1.1 Reaction Path 1

a. Formation of But-3-ynenitrile

The cyanoallene may be formed in interstellar space through a barrierless exothermic reaction between the ethyne radical (HCC) (Fig. 1(a)) and cyanocarbene (HCCN) (Fig. 1(b)). Hyanocarbene is known to exist in high concentrations in space (Guelin & Cernicharo 1991). The HCCN molecule can have two possible geometries, a linear equilibrium geometry for the triplet electronic ground state and a bent structure consistent with the accepted name 'cyanocarbene.' While initial studies on this molecule show the linear geometry to be the most plausible structure (Saito et al. 1984), theoretical studies by Kim et al. (1983) have suggested that the bent equilibrium geometry is more stable than the linear geometry by about 2.5 kcal mol^{-1}. Finally it has been confirmed by Rice and Schaefer on the basis of MCSCF studies using DZP and TZ2P basis sets that the bent structure lies below the linear conformation by 6.2 and 5.7 kcal mol^{-1}, respectively. Our study involves a bent shaped structure (Rice & Schaefer 1987). The highly reactive carbene structure reacts with HCC to give rise to But-3-ynenitrile having an optimized geometry as shown in Figure 1(c) with a reaction energy of about $-148.89\ \mathrm{kcal\ mol}^{-1}$ with ZPVE. The rate constant for this step is estimated to be $1.5 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ in the gas phase (Table 2).

b. Formation of cyanoallene

In an exothermic addition reaction, atom C5 of Buta-3-ynenitrile gets an attached hydrogen atom, leading to the formation of cyanoallene as shown in Figure 1(d). Hydrogen atoms are known to exist in high concentrations in space. The reaction energy for this process is –86.74 kcal mol^{-1} with ZPVE in the gas phase. The rate constant is estimated to be $6.2 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ in the gas phase (Table 2).

3.1.2 Reaction Path 2

a. Formation of propa-1, 2-diene

Cyanoallene may be formed in interstellar space through a barrierless exothermic reaction between propyne carbene (HCCC) and a hydrogen atom (H), both of which are known to exist in high concentrations in space. The highly reactive carbene structure (propyne carbene) has an optimized geometry as shown in Figure 2(a). In this process, the carbon atom C4 (charge –0.121) of HCCC (Fig. 2(a)) gets attached to the hydrogen atom to give rise to a propa-1, 2-diene radical as shown in Figure 2(b). This process has a reaction energy of about –76.10 kcal mol^{-1}. For this step, the rate constant is estimated to be $5.0 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ in the gas phase (Table 2).

b. Formation of buta-2, 3-dienenitrile radical

In this process, the carbon atom C2 (charge –0.261) of HCCCH (Fig. 2(b)) gets attached to the carbon atom C2 (charge +0.226) of the CN radical having two free electrons on the carbon atom (Fig. 2(c)) and giving rise to the formation of the buta-2, 3-dienenitrile radical. The rate constant of the reaction for this step may be estimated as $1.5 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ (Table 2) while the reaction energy for this process is –133.15 kcal mol^{-1} in the gas phase.

c. Formation of cyanoallene

In the last step of this reaction path, the buta-2, 3-dienenitrile radical picks up a hydrogen atom which leads to the formation of cyanoallene (Fig. 2(e)) with reaction energy of about –86.75 kcal mol^{-1}. The addition of a hydrogen atom in this step has a rate constant of about $6.1 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ in the gas phase (Table 2).

All the calculations related to structural optimization and energy for both reaction paths are performed at different temperatures and no significant change in energies or other parameters has been observed. There is consequently no effective change in rate constant with a change in temperature. Only the values of energies and rate constant at 10 K are reported in Table 1 and Table 2 respectively.

4 STRUCTURAL STUDIES

Cyanoallene exists in isomeric forms in interstellar clouds. Methylcynoacetylene has two isomers, cyanoallene and propargycynide, both of which can be prepared in a pure state, but are equilibrated

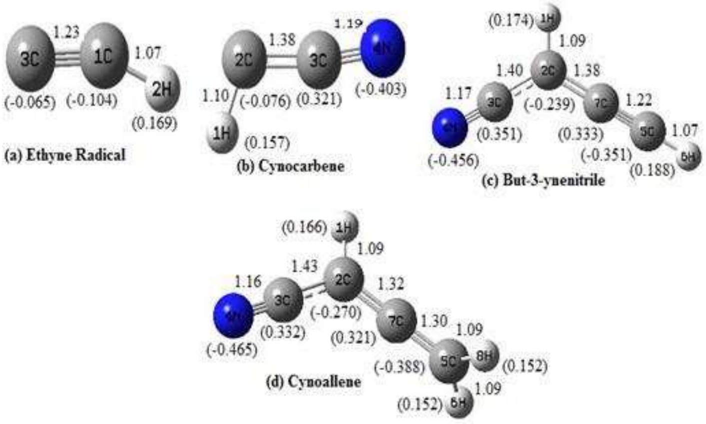

Fig. 1 Geometries of reactants and products in the formation of cyanoallene for path 1. The charge densities are shown in parentheses.

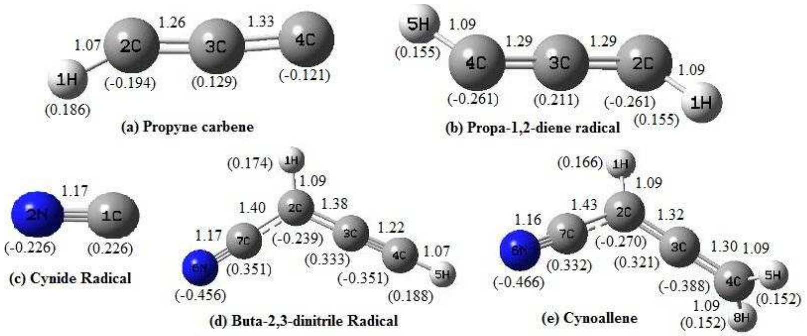

Fig. 2 Geometries of reactants and products in the formation of cyanoallene for path 2. The charge densities are shown in parentheses.

under basic conditions. Landor (1982) has shown that cyanoallene is the most stable isomer in solution. The structure of cyanoallene is given in Figure 1(d) and Figure 2(e) by adopting a numbering scheme. All the bond angles and bond lengths reproduced in the quantum chemical calculation agreed with the bond angles and bond lengths of other well known compounds.

5 HARMONIC AND ANHARMONIC VIBRATIONAL ANALYSIS

Cyanoallene has C1 symmetry and its 18 normal modes can be divided into $14\mathrm{A}' + 4\mathrm{A}''$. A complete vibrational analysis for the molecule has been attempted on the basis of harmonic and anharmonic frequency calculations using the B3LYP/aug-cc-pVTZ theory. No scaling is needed for the anharmonic frequencies. Vibrational frequencies were scaled using the relationship (Yoshida et al. 2002)

$$\nu_{\mathrm{obs}} = \nu_{\mathrm{calc}}(1.0087(9) - 0.0000163(6)\nu_{\mathrm{calc}}) \quad \mathrm{cm}^{-1}. \tag{3}$$

The calculated values have been compared with the experimental frequencies of 3-methyl-2-butenenitrile and 3-methyl-3-butene nitrile (Compton et al. 1981). Assignments of the vibrational

Table 3 ^{a}Proposed assignments and potential energy distribution (PED) for vibrational normal modes of cyanoallene (contribution$\geq$10). Types of vibration: ν, stretching; δ, deformation (bending), scissoring; oop, out-of-plane bending; ω, wagging; γ, twisting; ρ, rocking; τ, torsion.

Exp IR	Calculated Freqs. (Scaled)	Anharmonic Freqs.	IR Intensity	^{a}Potential Energy Distribution (%)
	146	144	2.90	δ[(C2H1C3)+(C2H1C7)](72)+LIN1[N4C2C3H1](15)
	317	313	2.10	τ[C7C2](50)+τ[C7C5](50)
	380	377	5.93	τ[C7C5](50)+τ[C7C2](50)
	385	381	5.25	LIN1[N4C2C3H1](93)
	619	613	2.65	δ[(C2H1C3)+(C2H1C7)](58)+LIN1[N4C2C3H1](14)+ν[C2C3](11)
	655	649	3.46	τ[C3H2](51)+τ[C3C6](48)
800	883	875	22.69	τ[C7C2](55)+τ[C7H5](44)
890	906	898	45.43	ω[C6H5C8C7](98)
675	959	950	7.47	δ[(C2H1C3)+(C2H1C7)](46) +ν_a[C2C3](31)
	1008	999	0.01	τ[C7C2](50)+τ[C7H5](50)
1072	1147	1137	0.07	ρ[(C2H1C3)+(C2H1C7)(51)+ν[C2C7](14)+ν[C5C7](14)
	1362	1350	1.03	ρ[(C2H1C3)+(C2H1C7)(57)
	1476	1464	3.90	ρ[(C5H6C7)+(C6H8C7)](43)+ν_a[C2C7](15)+ν_a[C5C7](14)+ρ[(C2H1C3)+(C2H1C7)](11)
2097	2058	2041	92.24	ν[C5C7](50)+ν[C2C7](47)
2255	2354	2334	23.59	ν[C3N4](87)+ν_a[C2C3](12)
2953, 3057	3151	3123	0.96	ν[C6H5](47)+ν[C5H6]1(47)
	3169	3141	2.18	ν[C5H8](84)+ρ[(C2H1C3)+(C2H1C7)(11)
	3226	3197	0.60	τ[C2C3](38)+τ[C5C7](38)+ν[C5H6](11)+ν_a[C5H6](11)

Table 4 Rotational constants (cm^{-1}) including terms due to the quartic centrifugal distortion constant and Nielsen's and Wilson's centrifugal distortion constants (10^{-6} cm^{-1}) of cyanoallene using B3LYP/aug-cc-pVTZ theory.

Rotational constants			Neilson's constant	Wilson's constant
A_e	0.89804	DJ	0.037294	0.205354
B_e	0.08954	DJK	–2.707929	0.026254
C_e	0.08281	DK	65.148436	0.009686
A_0	0.90628	R5	0.190921	–
B_0	0.08927	$\lvert R6\rvert \times 10^{-6}$	0.000605	–
C_0	0.08253	$\Delta J \times 10^{-6}$	0.008984	–

modes have been made on the basis of the PED over internal coordinates for the rb3lyp/aug-cc-pVTZ method. The PED is calculated by using the software GAR2PED (Martin & Van Alsenoy 1995). The results are given in Table 3.

In particular, the strong band in the spectrum of methyl-2-butenenitrile and 3-methyl-3-butene nitrile is observed at 2255 cm^{-1}, which is due to $C \equiv N$ stretching (Compton et al. 1981) modes. In the case of cyanoallene, this mode is calculated at 2354 cm^{-1} and 2334 cm^{-1} by harmonic and anharmonic calculations, respectively. The lowering of anharmonic frequency by 20 cm^{-1} from the harmonic one is due to the uneven spacing of the overtone levels of the different normal modes and the splitting of levels that are degenerate in the harmonic oscillator approximation (Table 3). C5H8 stretching is calculated at 3169 cm^{-1}. A strong band is calculated near 906 cm^{-1} which is due to the out of plane wagging of the double bonded hydrogen. This mode has a well correlated group frequency (Belumy 1954) that normally gives rise to a very strong band in the IR spectrum (890 cm^{-1}).

Table 5 Rotational-vibrational coupling constants of cyanoallene using B3LYP/aug-cc-pVTZ theory.

Rotational - vibrational coupling constants (10^{-4} cm^{-1})	a	b	c
α_1	10.2	0.4	0.3
α_2	–86.2	3.3	2.1
α_3	14.3	0.4	0.3
α_4	30.1	2.3	2.2
α_5	46.6	2.6	2.6
α_6	21.2	0.0	–0.1
α_7	39.7	–1.1	–0.2
α_8	122.9	–2.9	–1.4
α_9	–88.4	–0.1	–0.6
α_{10}	–100.0	3.5	3.0
α_{11}	71.4	–0.1	0.2
α_{12}	34.2	–0.1	–0.2
α_{13}	–69.0	–1.0	–0.5
α_{14}	–27.6	3.0	1.7
α_{15}	–4615.1	–2.7	–1.3
α_{16}	4639.0	–1.3	–1.8
α_{17}	–90.5	–2.6	0.8
α_{18}	117.5	–3.7	–1.7

However, the strong band observed at 800 cm^{-1} may arise from the corresponding wagging of a lone hydrogen on a tetrasubstituted double bond. In the case of cyanoallene, the calculated band observed at 883 cm^{-1} may be assigned to torsion around the bond C2C7 mixed with C5C7. Calculated strong absorption bands observed at 2058 cm^{-1} may be assigned to the C5C7 stretching coupled with C5–C4 stretching. The bands at 380 and 619 cm^{-1} may be assigned to the linear bending, LIN1 of the CCN group.

6 ANHARMONIC SPECTROSCOPIC CONSTANTS

The rotational constants of cyanoallene at the same order of the theory are given in Table 4. The constants A_0, B_0 and C_0 for the ground vibrational state include the effects due to zero-point vibrations and centrifugal distortions. The rotational constants at the equilibrium geometry of the molecule were calculated by B3LYP/aug-cc-pVTZ. Wilson's and Nielsen's centrifugal distortion constants for cyanoallene are also given Table 4. The rotation-vibration coupling constants based on the B3LYP/aug-cc-pVTZ vibrational treatment using density functional theory are given in Table 5. Very small magnitudes of the rotation-vibration coupling constants and Wilson's and Nielsen's centrifugal distortion constants show that the molecular vibrations of cyanoallene are almost harmonic in nature.

7 CONCLUSIONS

The possibility of forming cyanoallene from some simpler interstellar molecules like HCCN, HCC, H and CN has been explored using quantum chemical methods via radical-radical and radical-molecule interaction schemes, in the gas phase. Total energies, ZPVEs and EEs of all the molecules/radicals formed during the reaction pathways are calculated. Molecular geometries of the reactants and products have been optimized and harmonic frequencies are calculated to identify the stable states. The study of reaction energies and structures of the reactants and products show that the formation of cyanoallene is possible in the gas phase. After performing the calculations we observe that there is approximately no effect of temperature change on the energy of the molecules, ions involved in the reactions and rate constants. Both the reaction paths in the gaseous phase are totally exothermic and do not involve potential barriers, which give rise to a high probability of occurrence for the reactions under the conditions of interstellar space. Cyanoallene is found to have C_1 symmetry. A complete assignment has been provided to the fundamental vibrational modes of cyanoallene on the basis of harmonic and anharmonic frequency calculations using the B3LYP/aug-cc-pVTZ theory and a comparison made with the experimental values of frequencies. Anharmonic spectroscopic parameters such as rotational constants, rotation-vibration coupling constants and centrifugal distortion constants have been also calculated.

Acknowledgements Financial support to the authors Alka Misra from the University Grant Commission (UGC), Government of India through a major research project and Shivani under the BSR Fellowship of UGC is gratefully acknowledged. We also acknowledge the facilities provided by the Department of Mathematics & Astronomy, and the Department of Physics, University of Lucknow, Lucknow for the execution of this work.

References

Balucani, N., Asvany, O., Kaiser, R. I., & Osamura, Y. 2002, The Journal of Physical Chemistry A, 106, 4301

Bates, D. R. 1983, ApJ, 270, 564

Belumy, L. J. 1954, The Infrared Spectra of Complex Molecules (London: Methuen)

Chin, Y.-N., Kaiser, R. I., Lemme, C., & Henkel, C. 2006, in ASPC 855, Astrochemistry - From Laboratory Studies to Astronomical Observations, eds. R. I. Kaiser, P. Bernath, Y. Osamura, S. Petrie, & A. M. Mebel, 149

Compton, D. A. C., Murphy, W. F., & Mantsch, H. H. 1981, Spectrochimica Acta Part A: Molecular Spectroscopy, 37, 453

Cramer, C. J. 2005, Essentials of Computational Chemistry: Theories and Models (New York: John Willey & Sons)

Das, A., Majumdar, L., Chakrabarti, S. K., Saha, R., & Chakrabarti, S. 2013, MNRAS, 433, 3152

Frisch, M. J., Trucks, G. W., Schlegel, H. B., et al. 2003, Gaussian 03 Software Package

Fuente, A., García-Burillo, S., Gerin, M., et al. 2005, ApJ, 619, L155

Guelin, M., & Cernicharo, J. 1991, A&A, 244, L21

Gupta, V. P., Tandon, P., Rawat, P., Singh, R. N., & Singh, A. 2011, A&A, 528, A129

Herbst, E. 2001, Chemical Society Reviews, 30, 168

Herbst, E. 2013, in American Institute of Physics Conference Series, 1543, eds. S. K. Chakrabarti, K. Acharyya, & A. Das, 15

Herbst, E., & Leung, C. M. 1986, ApJ, 310, 378

Kim, K. S., Schaefer III, H. F., Radom, L., Pople, J. A., & Binkley, J. S. 1983, Journal of the American Chemical Society, 105, 4148

Landor, S. R. 1982, The Chemistry of the Allenes, 1 (New York: Academic)

Lovas, F. J., Remijan, A. J., Hollis, J. M., Jewell, P. R., & Snyder, L. E. 2006a, ApJ, 637, L37

Lovas, F. J., Hollis, J. M., Remijan, A. J., & Jewell, P. R. 2006b, ApJ, 645, L137

Majumdar, L., Das, A., Chakrabarti, S. K., & Chakrabarti, S. 2012, RAA (Research in Astronomy and Astrophysics), 12, 1613

Mangum, J. G., & Wootten, A. 1990, A&A, 239, 319

Martin, J. M. L., & Van Alsenoy, C. 1995, Computer Program GAR2PED (University of Antwerp)

Quan, D., & Herbst, E. 2007, A&A, 474, 521

Rice, J. E., & Schaefer, H. F., III 1987, J. Chem. Phys., 86, 7051
Saito, S., Endo, Y., & Hirota, E. 1984, J. Chem. Phys., 80, 1427
Schwahn, G., Winnewisser, G., Joentgen, W., Altenbach, H.-J., & Vogel, E. 1986a, A&A, 161, 327
Schwahn, G., Schieder, R., Bester, M., & Winnewisser, G. 1986b, Journal of Molecular Spectroscopy, 116, 263
Su, T., & Chesnavich, W. J. 1982, The Journal of Chemical Physics, 76, 5183
Woon, D. E. 2006, Chemical Physics, 331, 67
Woon, D. E., & Herbst, E. 2009, ApJS, 185, 273
Woon, D. E., & Park, J.-Y. 2009, Icarus, 202, 642
Yoshida, H., Takeda, K., Okamura, J., Ehara, A., & Matsuura, H. 2002, The Journal of Physical Chemistry A, 106, 3580
Ziurys, L. M. 2006, Proceedings of the National Academy of Science, 103, 12274