

Formation of E-cyanomethamine in a nitrile rich environment

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Abstract Recently a new molecule, cyanomethamine, has been detected towards Sagittarius B2(N) (Sgr B2(N)). Studying the formation mechanisms of complex interstellar molecules is difficult. Hence, a theoretical quantum chemical approach for analyzing the reaction mechanism describing the formation of interstellar cyanomethamine through detected interstellar molecules and radicals (NCCN+H) is discussed in the present work. Calculations are performed by using quantum chemical techniques, such as Density Functional Theory (DFT) and Møller-Plesset perturbation (MP2) theory with a 6-311G(d,p) basis set, both in the gas phase and in icy grains. The proposed reaction path (NCCN+H+H) has exothermicity with no barrier which indicates the possibility of cyanomethamine formation in the interstellar medium.

Key words: interstellar medium: abundances, general — general: extraterrestrial intelligence — meteorites — individual: Sgr B2(N) region

1 INTRODUCTION

The development of chemistry related to the interstellar medium (ISM) and planetary surfaces can be studied through the associated chemical evolution and composition. This provides essential information about the composition of organic matter, which is found to be important for understanding prebiotic chemistry. In the ISM, chemical reactions occur in the gas phase and solid phase from different organic, inorganic and prebiotic molecules. The analysis of these chemical routes under different physical and chemical conditions of interstellar space and planetary surfaces is a challenge in the field of astrobiology. Mechanisms can be conceived to describe the evolution of planets with related constituents transported by assemblages close to the planetary system, viz., comets and meteorites (Chyba 1990). Among all the detected interstellar gas-phase organic molecules, nitriles are the most reported. The CN group containing molecules (or nitriles) are of unique importance because they are the key intermediates for the formation of amino acids, nucleobases, etc. These nitrile containing molecules are very important for understanding processes leading to the origin of life, including Michael addition and Strecker synthesis (Kaiser & Balucani 2001; Ehrenfreund et al. 2001; Bernstein et al. 2004).

Nitriles are very important intermediates through which prebiotic organic molecules like amino acids, nucleobases, nucleic acids, peptides, etc are suggested to be formed, thus they have considerable astrobiological relevance. Most of these complex molecules have been detected in Sagittarius B2(N) (Sgr B2(N)). Due to the abundance of complex molecules in Sgr B2(N), it has been identified as a place for young star formation in comparison with Sagittarius B(M) (Snyder et al. 1994; Miao et al. 1995). Roughly half of the known interstellar molecules were first observed in the Sgr B2(N) molecular cloud (Jones et al. 2008). Various nitrile molecules have been already detected in Sgr B2(N) such as HCN, CH₂CN, CH₃CN, NH₂CN, etc (Nummelin et al. 1998). The observed column densities of H₂ and the CN radical in Sgr B2(N) are found to be $\geq 10^{24} \text{ cm}^{-2}$ and $5.5 \times 10^{14} \text{ cm}^{-2}$ respectively (Lis & Goldsmith 1990; Gerin et al. 1984), that are essential for nitrile containing compounds. Krasnopolsky (2009) reported that CN is essential in the formation of several biologically important nitriles, such as cyanoacetylene HC₃N, cyanogen NC₂N and dicyanoacetylene NC₄N in nitrile rich environments. Hence, the presence of NCCN in Sgr B2(N) can be highly expected. Cyanogen (NCCN) has been detected in Titan's environment in the infrared band. Nitriles pro-

duced in Titan's atmosphere are supposed to change into other nitrogen containing molecules through the bombardment of cosmic radiations (Flasar 1998; Hudson & Moore 2004; Petrie et al. 2003).

Recently, a new molecule, cyanomethamine, has been detected towards Sgr B2(N) by using the reaction product screening method with a spectral survey of Sgr B2(N) by the Green Bank Telescope (GBT) (Zaleski et al. 2013; Hollis et al. 2011). The above mentioned method is conceptually the same as the Miller-Urey-experiments through which all chemical products in the reaction of highly abundant interstellar molecules can be identified after applying an electric discharge (Miller 1953; Miller & Urey 1959). Zaleski et al. (2013) suggested a reaction path for E- and Z-cyanomethamine formation with the molecules CH_2CN and NH_2 and both isomers of cyanomethamine were produced in the laboratory in equal abundances. However, not enough work has been done in studying the formation of E-cyanomethanimine and Z-cyanomethanimine in Sgr B2(N).

We have proposed a new barrierless reaction path $\text{NCCN} + \text{H} + \text{H}$ for the formation of cyanomethamine and calculated some more parameters in support of this proposed reaction path. The global and local descriptors, thermodynamical parameters, and anharmonic calculations have shown that the proposed reaction path is highly feasible in Sgr B2(N). The $\text{CH}_2\text{CN} + \text{NH}_2$ model possesses a significant potential barrier (TS) while the discussed model $\text{NCCN} + \text{H} + \text{H}$ is barrierless which shows that the $\text{NCCN} + \text{H} + \text{H}$ model is highly feasible and more favorable when compared to the $\text{CH}_2\text{CN} + \text{NH}_2$ model. Although reactions which have a potential barrier are also feasible in Sgr B2(N) or the ISM if a sufficient amount of energy is acquired to cross the potential barrier, barrierless reactions are favorable in the ISM or any star forming regions such as Sgr B2(N).

Various reactions in an ice bound system have been studied and analyzed in finding feasible and key reactions, which are applicable to astrobiology and astrochemistry (Woon 2002; Gupta et al. 2012). Gupta et al. (2012) predicted the formation of cis-diaminomaleonitrile (DAMN) and trans-diaminofumaronitrile (DAFN) molecules in a nitrile rich environment. These also perform a key role in formation of adenine, which is one of the four nucleobases that form the "rungs" seen on the double-helix, ladder-like structure of DNA.

Cyanomethanimine (HNCHCN) is a slightly unsaturated sibling of aminoacetonitrile ($\text{H}_2\text{NCH}_2\text{CN}$). In view of the significance of cyanomethamine ($\text{C}_2\text{N}_2\text{H}_2$) in re-

actions that lead to the formation of adenine, an attempt has been made to understand the reaction mechanism involving a hydrogen radical and the NCCN molecule which plays an important role in the formation of cyanomethamine in nitrile abundant atmospheres. The radical-molecule and radical-radical interaction schemes have been adopted in the gas phase and in icy grains. Both cyanogen and hydrogen are easily detected and abundant in interstellar space.

In the chemistry that occurs on the surface of icy grains (on cold grains (10 K)), the formation of simple molecules takes place by the addition of single atoms as heavier molecules may not be mobile. When increasing the temperature, heavier molecules get ionized and addition-addition reactions take place to form large molecules. Radicals are formed through the photodissociation of simple molecules in grains (Shivani et al. 2014; Laas et al. 2011). A totally exothermic, barrierless reaction path with good estimation of rate coefficients increases the probability of occurrence.

The quantum theory of atoms in molecules (QTAIM, Matta & Boyd 2007) is a suitable method to analyze H-bonding and other interactions of atoms in any molecular system at a bond critical point in expressions of topological parameters. Global and local descriptors, e.g., molecular hardness and softness, electrophilicity and condensed Fukui functions (FFs), have been calculated to identify the chemical reactivity and region-selectivity of the NCCN molecule and H radical additions. A full vibrational analysis of E-cyanomethamine has been attempted in the harmonic and anharmonic approximations. The observed vibrational-rotational spectroscopic constants provide very similar expressions for most of the spectroscopic parameters that are necessary for the investigation of observed frequencies. This approach also appears to be very effective for the study of polyatomic molecules (Barone 2004; Boese & Martin 2004).

2 COMPUTATIONAL DETAILS

All of the computations required to analyze the proposed reaction path of cyanomethamine formation were implemented with Density Functional Theory (DFT) and Møller-Plesset perturbation MP2 theory with the 6-311G(d,p) basis set. DFT results in high accuracy with efficient computational calculations that are accessible to study the ground state properties of any strongly bound molecular system. Generally, the highly reliable hybrid DFT methods with the B3LYP functional are extensively used in the various hybrid DFT methods (Scott & Radom 1996). MP2/6-311G(d,p) is also frequently used in the method because it reproduces results that are

Table 1 Energies of Involved Geometries in Cyanomethamine Formation from DFT

Molecules/Radicals	In gas phase (a.u.)			In icy grains (a.u.)		
	E.E.	ZPVE	Total energy	E.E.	ZPVE	Total energy
NCCN	-185.7046	0.0165	-185.6881	-185.7088	0.0165	-185.6923
H	0.0000	0.0000	0.0000	-0.1645	0.0000	-0.1645
NCCN+H	-185.7046	0.0165	-185.6881	-185.8734	0.0165	-185.8569
HNCCN	-186.2552	0.0246	-186.2306	-186.2624	0.0246	-186.2378
HNCCN+H	-186.2552	0.0246	-186.2306	-186.4270	0.0246	-186.4024
E-HNCHCN	-186.9181	0.0394	-186.8787	-186.9276	0.0395	-186.8881
Z-HNCHCN	-186.9192	0.0395	-186.8797	-186.9269	0.0396	-186.8873
TS(E-Z)	-186.8755	0.0366	-186.8389	-186.8831	0.0364	-186.8467

Table 2 Energies of Involved Geometries in Cyanomethamine Formation from MP2 Theory

Molecules/Radicals	In gas phase (a.u.)			In icy grains (a.u.)		
	E.E.	ZPVE	Total energy	E.E.	ZPVE	Total energy
NCCN	-185.2192	0.0148	-185.2044	-185.2236	0.0149	-185.2087
H	0.0000	0.0000	0.0000	-0.1646	0.0000	-0.1646
NCCN+H	-185.2192	0.0148	-185.2044	-185.3881	0.0148	-185.3733
HNCCN	-185.6965	0.0255	-185.6710	-185.7047	0.0255	-185.6792
HNCCN+H	-185.6965	0.0255	-185.6710	-185.8693	0.0255	-185.8438
E-HNCHCN	-186.4036	0.0389	-186.3647	-186.4128	0.0392	-186.3736
Z-HNCHCN	-186.4044	0.0389	-186.3655	-186.4180	0.0382	-186.3798
TS(E-Z)	-186.3560	0.0361	-186.3199	-186.3632	0.0360	-186.3272

highly consistent with experimental data (Cramer 2013; Glaser et al. 2007). The energies (electronic (E.E.), zero point vibrational (ZPVE) and total) of all the involved geometries formed during the proposed reaction were computed.

The calculations of vibrational wavenumbers specify all of the stationary points as minima. Geometrical parameters of the optimized structures are used in these calculations and result in positive values of minima and their harmonic vibrational wavenumbers. Frequency calculations give the value of standard enthalpies ΔH^0 and Gibbs free energies ΔG^0 of the compound under study. The thermodynamic equation $\Delta S^0 = \Delta(H^0 - \Delta G^0)/T$ is used to evaluate the entropy of the reaction ΔS^0 . The equilibrium constant K was calculated using the equation $\Delta G^0 = -RT \ln K$ at 298.15 K and 1 atm. All of these thermochemistry parameters are calculated and discussed.

All the ground state energies of optimized geometries involved in the reaction pathway were calculated and are shown in Tables 1 and 2. The self-consistent reaction field calculations with an isodensity-surface polarizable continuum model were performed, to investigate the effect of water icy grains on reactions, including the bulk solvation effect through the Gaussian 03 program. All of the optimized stable geometries that have no imaginary frequency are verified by vibrational analysis. The pro-

posed reaction of the present theoretical study is found to be exothermic and has no barrier, so it does not obey the temperature dependent Arrhenius expression (Bates 1983). Hence in this case, the Langevin expression is used to evaluate the rate coefficient of the proposed ion-molecule reaction

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

where α is the polarizability in \AA^3 and μ is the reduced mass of the reactants on the ^{12}C amu scale, as suggested by Bates (1983).

The isotropic polarizability α of radicals is used in the present work because the molecule is considered to have an evenly distributed charge.

The rate constants of all the reactions were calculated and are shown in Table 3. The values of reaction energies of the reaction steps are shown in Table 4 and the energy diagram of the reaction pathway is shown in Figure 1. The numbering system of atoms discussed in the paper is the same as what is displayed in this figure.

Standard methods were used for calculating local and global electronic descriptors derived from B3LYP with 6-311G(d,p) and are shown in Table 5 (Parr et al. 1999; Chattaraj et al. 2006; Parr & Yang 1989; Berkowitz et al. 1985; Nalewajski et al. 1988). Global reactivity descriptors such as electronegativity χ , chemical potential μ , global hardness η , global softness (S) and electrophilicity index ω are highly successful in analyzing

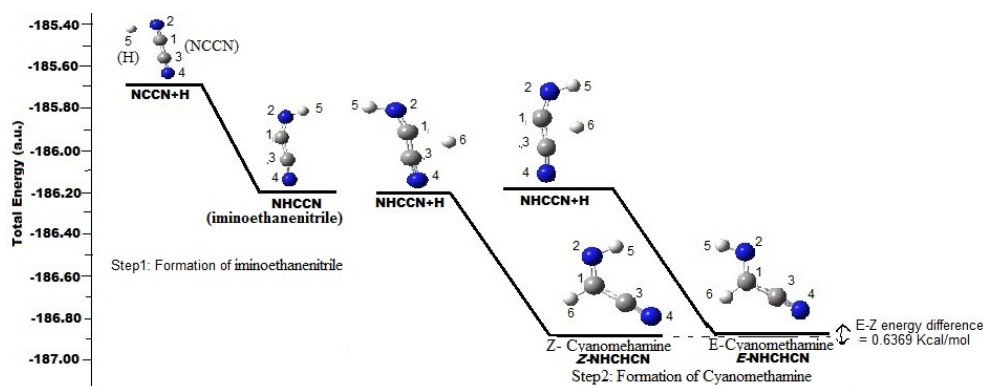


Fig. 1 Steps of cyanomethamine formation by B3LYP/6-311G(d,p).

Table 3 Rate Constants for the Steps Involved in Cyanomethamine Formation

Molecules/Radicals	Rate Constants ($\text{cm}^3 \text{s}^{-1}$)	
	Gas Phase	PCM
NCCN+H	3.6×10^{-9}	4.2×10^{-9}
E-NCCN+H+H	3.9×10^{-9}	3.9×10^{-9}
Z-NCCN+H+H	3.5×10^{-9}	3.9×10^{-9}

Table 4 Reaction Energies (kcal mol^{-1}) of the Steps Involved in Cyanomethamine Formation at 6-311G(d,p)

Steps	DFT		MP2	
	Gas phase	PCM	Gas phase	PCM
NCCN+H	-340.439	-239.051	-292.855	-191.928
E-NCCN+H+H	-406.557	-304.799	-435.243	-332.483
Z-NCCN+H+H	-406.622	-304.339	-435.765	-336.386

global reactivity trends and are calculated using the following equations:

$$\chi = C1/2(\epsilon\text{LUMO} + \epsilon\text{HOMO});$$

$$\mu = 1/2(\epsilon\text{LUMO} + \epsilon\text{HOMO});$$

$$\eta = 1/2(\epsilon\text{LUMO} - \epsilon\text{HOMO});$$

$S = 1/2\eta$; $\omega = \mu^2/2\eta$. The local reactivity descriptors such as FFs $f_k^+(r)$, $f_k^-(r)$, $f_k^0(r)$ are calculated using the following equations:

$$f_k^+(r) = [\rho_{N+1}(r) - \rho_N(r)] = [q_k(N+1) - q_k(N)],$$

for nucleophilic attack;

$$f_k^-(r) = [\rho_N(r) - \rho_{N-1}(r)] = [q_k(N) - q_k(N-1)],$$

for electrophilic attack;

$$\begin{aligned} f_k^0(r) &= 1/2[\rho_{N+1}(r) + \rho_{N-1}(r)] \\ &= 1/2[q_k(N+1) + q_k(N-1)], \end{aligned}$$

for radical attack, where ρ is the electron density of atom k in the molecule, q is the net charge of atom

k in the molecule and N , $N+1$, $N-1$ are electron systems containing the neutral, anion and cation forms of the molecule, respectively (Parr et al. 1999; Parr & Yang 1989; Parr & Pearson 1983; Geerlings et al. 2003; Chattaraj & Giri 2007). FFs are calculated by using Hirshfeld population analyses of the neutral, cation and anion state of the molecule (Table 5).

The optimized geometrical parameters of cyanomethamine were calculated and are shown in Tables 6 and 7. Harmonic and anharmonic frequencies, and spectroscopic constants, viz rotational, vibrational-rotational coupling constants and centrifugal distortion constants, have also been calculated and are shown in Tables 8 and 9.

3 DISCUSSION

The two types of radical reactions which occur between radicals and molecules are unimolecular and bimolecular. The formation of cyanomethamine is discussed with the two step reaction of some interstellar molecules and radicals, both in the gas phase and the water contain-

Table 5 Computed Global and Local Reactivity Descriptors (eV)

Molecules/Radicals	Global Descriptors			Local Descriptors			
	Hardness (η)	Softness (S)	Electrophilicity index (ω)	f_k^0	η_k^0	S_k^0	ω_k^0
NCCN	3.8056	1.9029	5.5483				
1C				0.1999	0.7607	0.3804	1.1091
2N				0.3001	1.1421	0.5711	1.6650
3C				0.1999	0.7607	0.3804	1.1091
4N				0.3001	1.1421	0.5711	1.6650
H	6.8006	3.4004	3.4004				
5H				1.0000	6.8006	3.4004	3.4004
NHCCN	1.6276	0.8139	6.2438				
1C				0.1322	0.2152	0.1076	0.8254
2N				0.2005	0.3263	0.1632	1.2519
3C				0.1031	0.1678	0.0839	0.6437
4N				0.2636	0.4290	0.2145	1.6459
5H				0.1363	0.2218	0.1109	0.8510
E-NHCHCN	3.1278	1.5639	4.8922				
1C				0.1828	0.9355	0.4678	0.8943
2N				0.2991	0.9355	0.4678	1.4633
3C				0.0885	0.2768	0.1384	0.4329
4N				0.2136	0.6681	0.3340	1.0449
5H				0.1305	0.4082	0.2041	0.6384
6H				0.1096	0.3428	0.1714	0.5362
Z-NHCHCN	3.0932	1.5466	5.0603				
1C				0.1783	0.5515	0.2758	0.9023
2N				0.3027	0.9363	0.4682	1.5318
3C				0.1054	0.3260	0.1630	0.5334
4N				0.2245	0.6944	0.3472	1.1360
5H				0.1316	0.4071	0.2036	0.6659
6H				0.0894	0.2765	0.1383	0.4524

Table 6 Selected Optimized Geometrical Parameters of E-cyanomethamine at B3LYP

Bond length	(Å)	Bond angle	(°)	Dihedral angles	(°)
R(1,2)	1.2688	A(2,1,3)	120.19764	A(2,1,3,4)	-170.83044
R(1,3)	1.4450	A(1,3,4)	176.95802	A(5,2,1,3)	179.91025
R(3,4)	1.1535	A(6,1,3)	114.20743	A(5,2,1,6)	-0.07525
R(1,6)	1.0941	A(6,1,2)	125.59493	A(6,1,3,4)	9.15663
R(2,5)	1.0220	A(1,2,5)	110.15107		

Table 7 Selected Optimized Geometrical Parameters of Z-cyanomethamine at B3LYP

Bond length	(Å)	Bond angle	(°)	Dihedral angles	(°)
R(1,2)	1.2695	A(2,1,3)	125.22150	A(2,1,3,4)	22.9713
R(1,3)	1.4468	A(1,3,4)	179.46504	A(5,2,1,3)	0.0458
R(3,4)	1.1543	A(6,1,3)	115.57758	A(5,2,1,6)	-179.9396
R(1,6)	1.0903	A(6,1,2)	119.20092	A(6,1,3,4)	-157.04286
R(2,5)	1.0234	A(1,2,5)	111.29778		

ing icy grains. The computed reaction energies and estimated reaction coefficients of both the involved reaction steps for cyanomethamine formation in the gaseous phase and also in icy grains are given in Tables 1 and

2. The reaction path is found to be barrierless. Figures 1 and 2 show the optimized geometries of the reactants and products at B3LYP/6-311G** and MP2/6-311G** level

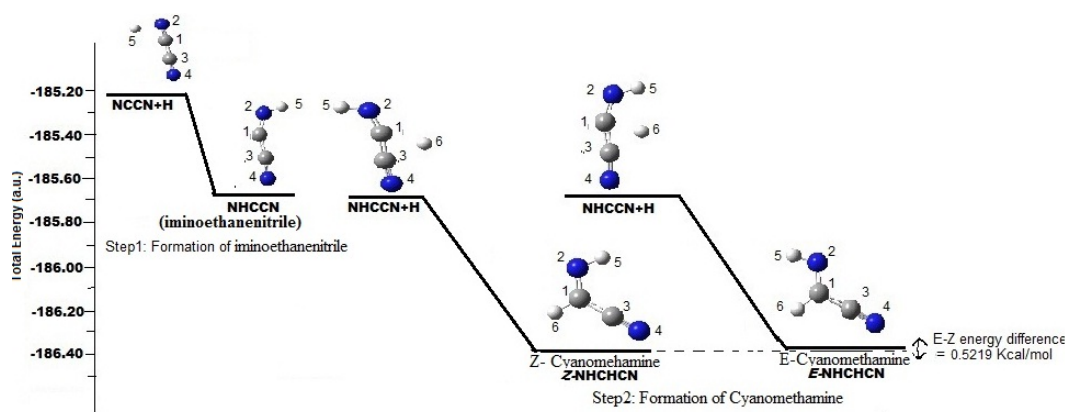


Fig. 2 Steps of cyanomethamine formation by MP2/6-311G(d,p).

respectively. The mechanism of cyanomethamine formation can be discussed under the following steps:

- Step 1 $\text{NCCN} + \text{H} \rightarrow \text{HNCCN}$,
- Step 2 $\text{HNCCN} + \text{H} \rightarrow \text{HNCHCN}$.

3.1 Step 1 Formation of Iminoethanenitrile

Cyanogen is a stable linear molecule having $D_{\infty H}$ symmetry. The isomer of cyanogen, i.e. isonitrile (NCNC), is also found in interstellar space. The presence of cyanogen (NCCN) has been observed in Titan's atmosphere as a solid. Cyanogen is a symmetric molecule having two nitrogens at the terminal end. Nitrogen is more electronegative than carbon. The formation of cyanogen in Sgr B2(N) is expected because of the detection of the cyanide radical in Sgr (B2). The abundance of hydrogen has also been observed in Sgr B2(N). The hydrogen (H) radical attacks the nitrogen atom (N2) of cyanogen and forms iminoethanenitrile. The feasibility of Step 1 in the reaction has been observed with the help of thermochemistry parameters. The calculated values of Gibbs free energy change ΔG^0 , enthalpy change ΔH^0 and entropy change ΔS^0 in Step 1 of the above mentioned reaction are $-342.8133 \text{ kcal mol}^{-1}$, $-339.9788 \text{ kcal mol}^{-1}$ and $9.507 \text{ cal mol}^{-1} \text{ K}^{-1}$ respectively. The negative value of standard enthalpies ΔH^0 and Gibbs free energies ΔG^0 of Step 1 indicates that the reaction is exothermic and spontaneous. The feasibility of the reaction has also been checked with the help of electronic descriptors derived from conceptual DFT (Chattaraj et al. 2006; Parr & Pearson 1983; Geerlings et al. 2003). The chemical behavior of a molecule can be predicted and analyzed through the study of relevant electronic density principles and concepts of conceptual DFT (a subfield

of DFT). Information about the reacting active sites of molecules in a chemical model is important for determining the reaction path as well as products of the reaction. Therefore, chemical potential, molecular hardness and softness, electrophilicity and condensed FFs, and global and local descriptors were calculated. These descriptors are used to study the mechanistic aspects of the chemical reaction and region-selectivity of the NCCN molecule and H radical additions. The higher value of the FF of nitrogen atoms demonstrates that it is the most suitable reaction site for a hydrogen atom in comparison to carbon atoms in NCCN. Frontier molecular orbitals, i.e. the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are used to calculate the global electronic parameters such as electronegativity χ , chemical potential μ , global hardness η , global softness (S) and electrophilicity index ω . These are highly successful in predicting global reactivity trends (given in Table 5). The global electrophilicity index ($\omega = 5.54 \text{ eV}$) for cyanogen (NCCN) shows that it behaves as a stronger electrophile than hydrogen. Calculated electrophilic charge transfer (ECT) is -2.707 eV (Chattaraj et al. 2006; Padmanabhan et al. 2007) for reactant system $[(\text{NCCN}) \leftrightarrow (\text{H})]$, indicating that charge flows from (H) to (NCCN). The selection of a particular reaction site of reactants has been computed with the calculation of local (condensed) FFs, local softness and local philicity (Chattaraj et al. 2006; Parr & Pearson 1983; Geerlings et al. 2003). Selected nucleophilic reactivity descriptors ($f_k^0(r)$, $S_k^0(r)$, ω_k^0) for reactant (NCCN) using Hirshfeld atomic charges are given in Table 5. In reactant (NCCN), the maximum values of the local nucleophilic reactivity descriptors ($f_k^0(r)$, $S_k^0(r)$, ω_k^0) at N2 (0.3001, 0.5711, 1.6650 eV) indicate that this site is prone to electrophilic attack compared to other atoms of cyanogen. Therefore, reactant (H) only attacks

an N atom. Thus, the local reactivity descriptors for reactant (NCCN) confirm the formation of product (NHCCN) by nucleophilic attack at an N atom by an H atom. The nature of the reaction can be understood by the value of equilibrium constant (K_{eq}) as: (i) if $K_{\text{eq}} > 1$, the reaction is favored in the forward direction, (ii) if $K_{\text{eq}} = 0$, the reaction is in the equilibrium state, and (iii) if $K_{\text{eq}} < 1$, the reaction is favored in the backward direction where K_{eq} can be calculated by the thermodynamic relation between equilibrium constant K_{eq} and Gibbs free energy change of reaction ($\Delta G_{\text{reaction}}$) at temperature (T): $K_{\text{eq}} = e^{-\Delta G/RT}$. With the help of the above equation, equilibrium constant (K_{eq}) for Step 1 is calculated as $4.92 \times 10^{246} \text{ cm}^{-2}$ at room temperature. Therefore, the reaction is favored in the forward direction at room temperature. This again confirms that HNCCN forms at room temperature, with CS symmetry and a bent structure.

3.2 Step 2 Formation of Cyanomethamine

The hydrogen radical (H6) attacks the carbon atom (C1) of iminoethanenitrile and leads to the formation of E-cyanomethamine. The calculated thermochemistry parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) of Step 2 are $-407.5318 \text{ kcal mol}^{-1}$, $-406.9745 \text{ kcal mol}^{-1}$ and $-1.868 \text{ cal mol}^{-1} \text{ K}^{-1}$ respectively. The negative value of standard enthalpies (ΔH^0) and Gibbs free energies (ΔG^0) of Step 2 indicates that the reaction is exothermic and spontaneous. The negative values of enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) show that energy is favorable, whereas entropy is unfavorable. The net spontaneity of the chemical reaction depends upon the change in Gibbs free energy of the reaction (ΔG). The global electrophilicity index ($\omega = 6.24 \text{ eV}$) for HNCCN shows that it behaves as a strong electrophile. ECT value -3.769 eV for reactant system [(HNCCN) \leftrightarrow (H)] indicates charge flows from (H) to (HNCCN). The calculated local (condensed) FFs (Nalewajski et al. 1988) for selected nucleophilic reactivity descriptors (f_k^0 , S_k^0 , ω_k^0) for one carbon atom (0.1322, 0.1076, 0.8254 eV) indicate that this site is more prone to electrophilic attack than the other carbon atom (Table 5). In this case, again local reactivity descriptors for reactant HNCCN confirm the formation of product (NH = CHCN) by nucleophilic attack at the C atom by an H atom. The value of equilibrium constant (K_{eq}) for Step 2 is 5.30×10^{293} at room temperature. Therefore, the reaction is favored in the forward direction at room temperature. This confirms the formation of

HN = CHCN (cyanomethamine) having C1 symmetry at room temperature.

The potential energy curves of Steps 1 and 2 are shown in Figures 1 and 2 by B3LYP and MP2 theories respectively. The rate constants (Table 3) of the reaction steps involved in formation of E- and Z-cyanomethamine demonstrate the feasibility of the proposed reaction pathway. The reaction energies (Table 4) of both steps in the formation of E- and Z-cyanomethamine indicate that the reaction is more favorable in ice compared to the gas phase. The final products (E- and Z-cyanomethamine) that formed under the IPCM model or in icy grains were more stable than what formed in the gas phase.

4 CONFORMATIONAL STUDY

Zaleski et al. (2013) have reported the detection of interstellar E-cyanomethanimine in Sgr B2(N) through GBT PRIMOS observations by using astronomical data and laboratory reaction screening measurements. Results of these studies indicate that ground state energy of the Z-configuration of cyanomethanimine is more stable than its E-configuration which agrees with results from Zaleski et al. (2013) in their reaction mechanism applied to the formation of E- and Z-cyanomethamine. The total energy of cyanomethamine with ground state geometry is calculated as -186.878676 a.u. (E) and -186.879691 a.u. (Z) with DFT. The different forms have an energy difference of $-0.6369 \text{ kcal mol}^{-1}$ which is greater than kT . The rotational barrier between the Z- and E-conformers is found to be $25.558 \text{ kcal mol}^{-1}$ which indicates that rotation is not possible at room temperature. The geometrical parameters of Z- and E-cyanomethamine are calculated at B3LYP (listed in Tables 6 and 7) which agree with the data given at <http://turbo.kean.edu/~wbailey/HNCHCN.html>. Both conformers possess C1 symmetry. The molecule exists in E-configuration about the N = C bond. The Z-configuration is more stable than the E-configuration due to steric hindrance but it was experimentally shown by Zaleski et al. (2013) that Z-cyanomethanimine has considerably weaker intensities of rotational transitions because of the difference in dipole moments. Hence, this may be the reason why the lower polar Z-isomer is not detected in the ISM. The conversion of E conformer into Z conformer of cyanomethamine is not possible at room temperature because of the high potential barrier, as shown in Figure 3. At room temperature, the Boltzmann occupation ratio of the two forms is 71 : 29, showing that the E- form will be the most populated one.

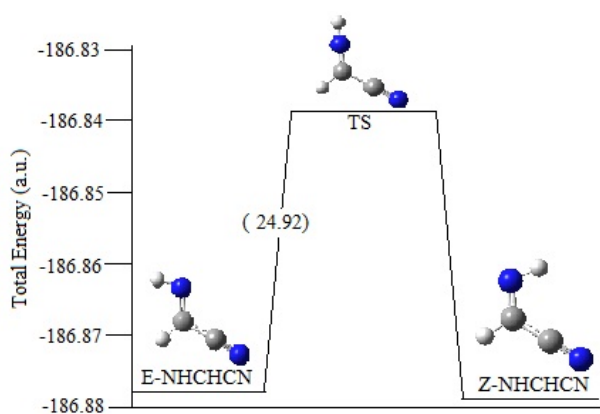


Fig. 3 Transition State between *E* and *Z* Conformers of Cyanomethamine.

Table 8 Rotational Constants (cm^{-1}) and Nielsen-Wilson's Centrifugal Distortion Constants (10^{-6}cm^{-1}) of Cyanometamine using the DFT Theory

	Rotational constants			Nielsen's constant		Wilson's constant	
	Z-	E-		Z-	E-	Z-	E-
A_e	1.8410925	2.1131361	DJ	0.0767469	0.0597980	0.0486511	0.0400756
B_e	0.1692990	0.1663349	DJK	-3.4662248	-3.22993021	0.0448936	0.0318276
C_e	0.1550420	0.1541973	DK	118.4649899	160.0191394	0.0150638	0.0101564
A_0	1.8493942	2.1128120	R5	0.06178049	0.02779557		
B_0	0.1685229	0.1658842	$ R6 \times 10^{-6}$	-0.0009415	-0.0006348		
C_0	0.1542146	0.1535917	$\Delta J \times 10^{-6}$	0.0149893	0.0104959		

Table 9 Rotational-vibrational Coupling Constants ($\times 10^{-4} \text{cm}^{-1}$) of Cyanomethamine using the DFT Theory

	Z-cyanomethamine			E-cyanomethamine		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
α_1	0.00367	0.00006	0.00008	0.00921	-0.00002	0.00003
α_2	-0.00476	0.00030	0.00021	-0.00190	0.00023	0.00018
α_3	0.00319	0.00072	0.00062	-0.00036	0.00077	0.00065
α_4	0.01583	0.00023	0.00029	0.02137	0.00020	0.00029
α_5	0.00291	-0.00022	0.00005	-0.00490	-0.00014	0.00009
α_6	-0.00543	-0.00073	0.00017	-0.04077	-0.00037	0.00002
α_7	0.01249	0.00081	-0.00001	0.05083	0.00035	0.00001
α_8	-0.03572	0.00072	0.00066	-0.06029	0.00054	0.00052
α_9	0.03112	0.00003	-0.00013	0.05491	0.00000	-0.00012
α_{10}	-0.02249	0.00034	0.00030	-0.01188	0.00017	0.00018
α_{11}	-0.03760	-0.00010	-0.00031	-0.07229	-0.00016	-0.00034
α_{12}	0.02019	-0.00061	-0.00026	0.05674	-0.00067	-0.00030

5 ANHARMONIC SPECTROSCOPIC CONSTANTS

The rotational constants of E- and Z-cyanomethamine at the equilibrium geometry are calculated at the same level as predicted by theories and are shown in Table 8. The constants A_0 , B_0 and C_0 for the ground vibra-

tional state include the effect of zero-point vibrations and distortions. Kivelson-Wilson formalism (Kivelson & Wilson Jr 1952) based quadratic centrifugal distortion constants for E- and Z-cyanomethamine are also given in Table 8. The anharmonic vibrations deform the molecule from its equilibrium configuration. These distortions occur due to centrifugal force which are calculated and de-

veloped by Wilson and Nielsen (Nielsen 1951; Wilson & Howard 1936). The rotation-vibration coupling constants α are calculated by using B3LYP and MP2 theories with the 6-311G(d,p) basis set and are shown in Table 9 where constant α is the difference between rotational constant in the first excited state of a normal vibration and that in the ground state and based on perturbation theory of second order (Barone 2005). The small values of rotation-vibration constants and centrifugal distortion constants give insight into the molecular vibrations of E-cyanomethamine.

6 CONCLUSIONS

The radical-molecule and radical-radical interaction reactions were studied to explore the possibility of formation of E-cyanomethamine in a nitrile rich environment with highly abundant NCCN and H radicals. These reactions are analyzed both in the gas phase and icy grains by using quantum chemical methods. The IPCM model was simulated as a continuum of dielectric constant ϵ ($= 78.5$) and used to study the reactions in the grains. The total energies, ZPVEs and E.E.s of all the involved geometries formed during the reaction path were calculated. E- and Z-cyanomethamine formed by the calculations at the DFT level are more stable than ones formed by the calculations performed at the MP2 level (shown in Tables 1 and 2 respectively). To identify the stable states, the optimized molecular geometries of the reactants, products and harmonic frequencies were calculated. The value of reaction energies and the stable configuration of geometries of reactants and products demonstrate that E-cyanomethamine formation is possible in the gas phase as well as in icy grains. Reaction energy calculations show that the reactions under DFT are more feasible than those of MP2 theory (shown in Table 4). The reaction path is totally exothermic and barrierless in both the gas phase and icy grains. These properties enhance the feasibility of the proposed reactions under the conditions of a nitrile rich environment; the upper limit of the rate constant is $3.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. E-cyanomethamine formation is confirmed by calculated thermochemistry parameters, equilibrium constant, and global and local electronic descriptors derived from conceptual DFT.

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