Structure, Spectroscopic Properties and Reactions of Interstellar Molecule HC_2N and Isomers : *Ab initio* Study

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Calculations are presented for the molecule HC_2N and its geometrical isomers. The structures, harmonic frequencies and dipole moments are reported. The potential energy surface of the [H,C,C,N] system is investigated in detail, and the transition states, intermediate complexes, and the energies of barrier for the isomerization and dissociation reactions are computed in order to determine the reaction paths and to estimate the stability of the isomers. The barriers of isomerization among HCCN, HCNC and HNCC are computed to be rather large and dissociations of these molecules are highly endothermic, indicating that these molecules are kinetically stable. The association reactions HC + CN → HCCN, HC + NC → HCNC, and HN + CC → HNCC are barrierless and very exothermic, suggesting that they may be considered as efficient means of producing the HCCN and the isomers in the laboratory and in interstellar space.

Key Words : Interstellar, Structure, Reaction, HC_2N

Introduction

Carbon chain molecules containing heteroatoms have been paid much attention recently due to their astrophysical abundance and interesting spectroscopic properties. Many carbon clusters bonded to heteroatoms such as O,[1,2] S[3-6] and Si[7] were observed in interstellar clouds. Typical example is cyanopolyacetylenes $HC_{2n+1}N$. $HC_{11}N$[8] is one of the largest molecules observed in interstellar medium. The structures and infrared frequencies of these molecules were measured, and numerous *ab initio* computations[9-12] were also carried out.

In contrast to cyanopolyacetylenes $HC_{2n+1}N$, systematic study on the molecules $HC_{2n}N$ containing *even* number of carbon atoms was relatively scarce. Only HC_2N was observed in interstellar space,[13] and very recently, HC_4N was studied in the laboratory,[14,15] but no information on the infrared frequencies has been reported yet. Computations were also carried out by Aoki *et al.*[16-18] and by the Schaefer group[19,20] for the structures and the relative energies of some isomers of this system. While the cyanopolyacetylenes $HC_{2n+1}N$ can readily be assigned canonical structures with alternating single and triple bonds, the bonding structures of the $HC_{2n}N$ molecules are rather complicated, and no simple canonical structures may easily be assumed. Thus, there can exist many isomers with different kind of geometries (linear, bent or cyclic) or different multiplicity (singlet or triplet) having similar energies for the $HC_{2n}N$ molecules. For example, McCarthy *et al.*[14] recently identified singlet bent HC_4N in the laboratory, while Endo and co-workers[15] observed linear triplet HC_4N. Aoki *et al.*[16-18] also predicted that some singlet HC_2N and HC_4N isomers are cyclic, but triplets are either linear or bent. Since the properties of some isomers of the cyanopolyacetylenes, such as HNC_3, were predicted to be very different from the corresponding cyanopolyacetylene (for example, HNC_3 is bent and floppy, while HC_3N is linear),[21] the geometrical isomers of triplet $HC_{2n}N$, which are obtained by the exchange of carbon and nitrogen atoms (such as $HC_{2n-1}NC$ or HNC_{2n}), are also believed to be very different from $HC_{2n}N$. The bonding to the nitrogen atoms may also significantly change the structure and chemical reactivity of the carbon chain. It is well known that the lowest-energy structures of the pure carbon clusters up to C_{10} are linear, and the cyanopolyacetylenes $HC_{2n+1}N$ are also known to be linear up to $HC_{11}N$. Despite these interesting features, very few systematic study on the chemical reactions and the kinetic stability of the geometrical isomers of the [H,C,C,N] system has been carried out yet. To our best knowledge, experimental/theoretical study by Schwartz *et al.*[22] is the only systematic work on the [H,C,C,N] system, in which the potential surface was explored quite extensively. However, no infrared frequencies have been reported in their work, and the dissociation (association) to (from) the diatomic fragments such as HC, C_2, and CN, which may be very important as possible formation mechanism of the [H,C,C,N] system in the interstellar medium, has not been studied yet.

The $HC_{2n}N$ molecules and their geometrical isomers are also good candidates for astrophysical observation by microwave and infrared spectroscopy due to the rather large dipole moments of these molecules. Further theoretical and experimental studies may lead to observation of these molecules and isomers with longer carbon chains. Relative stability of the isomers of molecules is also of interest in relation to their abundance and formation mechanism in interstellar space. Some of the isomers may be quite kinetically stable for laboratory detection, while others may rapidly isomerize to more stable isomers. Computation of the relative energies, transition states and the barriers to

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isomerization will be very helpful to elucidate the reactivity and kinetic stability of these molecules.

In the present article, we predict the structures and the spectroscopic properties of the smallest member of the $HC_{2n}N$ series of molecules by employing a variety of the computational methods. We employ the MP2 and the CCSD(T) methods with the 6-311G** basis set for the structures and energies of the isomers. The density functional theory (BLYP/6-311G**), which we found very economical and also accurate for calculating the harmonic frequencies of the carbon clusters in a number of works,[23-27] is used to compute the infrared frequencies and to find out the reaction paths by intrinsic reaction coordinate (IRC) analysis. We predict several isomers of the molecule. The potential energy surface of the HC_2N system is studied in detail, and the relative stability and reactivity of the isomers are studied by computing the energies, transition states, reaction pathways and the heights of the barriers to isomerization and dissociation. The barriers of isomerization among HCCN, HCNC and HNCC are computed to be quite large, and the dissociation reactions of these molecules to diatomic fragments are very endothermic, indicating that these molecules are kinetically stable.

Computational Methods

In this study all the calculations were carried out using the GAUSSIAN 94 set of programs.[28] The density functional theory with the exchange functional by Becke[29] and correlation functional by Lee *et al.*[30] (BLYP), and the MP2 methods are employed with the 6-311G** basis set to compute the energies and the structures of the stationary states and the transition states, the harmonic frequencies and to carry out the IRC analysis. Single point energy calculations are also carried out by employing the CCSD(T)/6-311G** method at the MP2 geometries to obtain the relative energies and the barriers to rearrangement between the isomers. The stationary structures are found by ascertaining that all the harmonic frequencies be real, and the structures of the transition states are obtained by verifying that one of the harmonic frequencies be imaginary and by carrying out intrinsic reaction coordinate analysis for the reaction. Barrier heights for the isomerization and the dissociation reactions are computed by subtracting the energies of the reactants and products from those of the transition states, correcting for zero-point energies (ZPE).

Results

The computational strategy we employ in this work is first calculating the structures and the harmonic frequencies of the stationary states by the BLYP/6-311G** method. We then verify the reaction paths by carrying out the IRC analysis by the same method. The structures of the stationary states and the transition states are then computed by MP2/6-311G** theory, based on the structures found by the BLYP/6-311G** method. The IRC analysis is also carried out employing the MP2/6-311G** method to verify the transition states. Single point energy calculations are finally carried out by employing the CCSD(T)/6-311G** method at the MP2 geometries to obtain the relative energies and the barriers to rearrangement between the isomers and dissociation reactions.

There had been uncertainty for a long time concerning whether the HC_2N molecule is linear or not, because it may be described as carbene or allenlike diradical. Earlier experimental studies[31] proposed linear structure for the HC_2N molecule, but more recent microwave spectroscopic experiment by Brown, Saito and Yamamoto[32] suggested quasilinear structure for this molecule. Measurement of the frequency of HC_2N in a series of high-resolution spectroscopy experiments by Curl and co-workers[33] also indicated that HC_2N is indeed

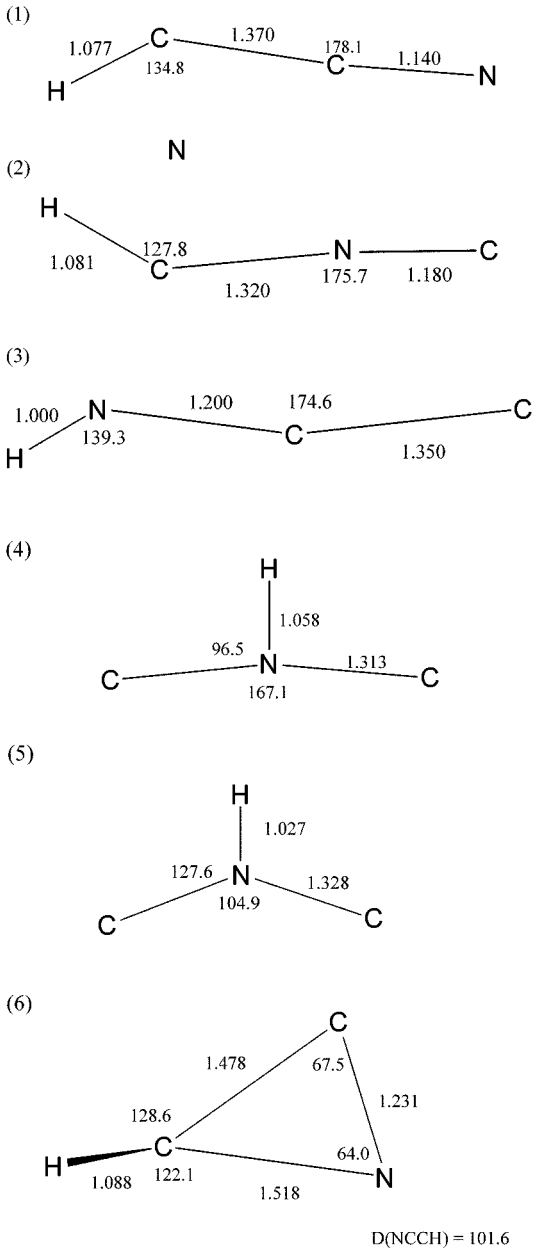

Figure 1. Stationary structures of triplet HC_2N and its conformers. Bond lengths in A and bond angles in degree.

Table 1. Spectroscopic properties of triplet HC_2N, HCNC and HNC_2. Energies[(1)] (Hartee), bond lengths[(1)] (A), bond angles[(1)] (degree) and harmonic frequencies[(2)] (cm^{-1})

HC_2N (1)		HCNC (2)		HNC_2 (3)	
H-C_1	1.077 1.082[(4)] 1.078[(5)]	H-C_1	1. 081	H-N	1.005
C_1-C_2	1.380 1.357[(4)] 1.353[(5)]	C_1-N	1. 328	N-C_1	1.203
C_2-N	1.144 1.208[(4)] 1.210[(5)]	N-C_2	1. 184	C_1-C_2	1.357
∠ H C_1 C_2	134.8° 139.8°[(4)] 140.5°[(5)]	∠ H C_1 N	127.8°	∠ H N C_1	139.3
∠C_1 C_2 N	178.1° 174.6°[(4)] 174.7°[(5)]	∠C_1 N C_2	175.7°	∠N C_1 C_2	174.6
E	-131.09221	E	-131.05580	E	-131.03467
ΔE[(3)]	0	ΔE[(3)]	22.8	ΔE[(3)]	36.1
μ(D)	3.099	μ(D)	2.897	μ(D)	4.559
Rot. Const.	1017.5230	Rot. Const.	828.3466	Rot. Const.	1439.2222
(GHz)	11.0571	(GHz)	12.1100	(GHz)	10.9576
	10.9382		11.9355		10.8748
ZPE	12.22	ZPE	11.85	ZPE	12.00
(kcal/mol)		(kcal/mol)		(kcal/mol)	
ν_1(A')	3333(46)[(6)] 3333[(5)]	ν_1(A')	3157 (12)	ν_1(A')	3522 (119)
ν_2(A')	1758 (20) 1818[(5)]	ν_2(A')	1684 (1)	ν_2(A')	1862 (24)
ν_3(A')	1223 (3) 1123[(5)]	ν_3(A')	1227 (8)	ν_3(A')	1100 (31)
ν_4(A')	442(4) 689[(5)]	ν_4(A')	827 (76)	ν_4(A')	694 (247)
ν_5(A')	281 (52) 376[(5)]	ν_5(A')	337 (3)	ν_5(A')	272 (17)
ν_6(A")	444 (1) 408[(5)]	ν_6(A")	384 (0)	ν_6(A")	352 (8)

(1) CCSD(T)/6-311G**//MP2/6-311**. (2) BLYP/6-311G**. (3) kcal/mol. (4) Ref. 20 (CCSD(T)/DZP). (5) Ref. 16 (QCISD(T)/D95**)). (6) Intensities in km/mole.

quasilinear and floppy. Several recent theoretical studies on this molecule by the Schaefer group,[19,20] Malmqvist *et al*.,[34] and by Aoki *et al*.[16-18] have also predicted that it is triplet bent (quasilinear). We find here that the most stable structure of HC_2N is predicted to be triplet bent (the structure (1)), as presented in Figure 1 and Table 1. Comparisons are made with the computed structures of HC_2N in (Ref. 16) and (Ref. 20). The agreement with these previous calculations is good, although we obtain a bit less bent structure. The H-C-C and C-C-N bond angles are 134.8° and 178.1°, respectively. The other triplet conformers ((2) and (3)), HCNC and HNC_2, also given in Table 1, are also bent, lying 22.5 and 35.9 kcal/mol (ZPE-corrected), respectively, above the structure (1). These energy differences are very close to those reported by Aoki, Ikuta and Nomura.[16] (25.0 and 35.8 kcal/mol), obtained by the (SDCI+Q) single point energy calculations at the QCISD(T)/D95** optimized geometry. In all of these molecules, the bonds including the terminal hydrogen atom are highly bent, while the two carbon atoms and the nitrogen atom lie almost along a line. The triplet structures obtained here agree well with those given by Aoki *et al*.[16] We also find cyclic and branched triplet isomers as also shown in Figure 1 and Table 2. Two of them ((4) and (5)) are planar with C_{2v} symmetry, while the other one (6) is nonplanar. The nonplanar isomer (6) lies 49.9 kcal above HC_2N. The two C_{2v} isomers lie 59.0 and 75.7 kcal/mol above HNCC and HCNC, respectively. These latter three stationary states play important role as intermediate complexes in the rearrangement reactions between HC_2N, HCNC, and HNC_2, as discussed below. For the singlet molecules, several cyclic stationary structures were proposed along with the bent ones. Figure 2 and Table 3 present the two singlet structures ((7) and (8)) whose energies are higher than the most stable triplet structure (1) by 17.4 and 49.5 kcal/mol, respectively. The structure (7) is cyclic, while (8) is branched. The energy difference between the structure (7) and (8) is 32.3 kcal/mol (ZPE-corrected), in close agreement with the results (30.8 kcal/mol) by Aoki *et al*.[16] The other stationary singlet structures we find are bent ones, but we do not report them here since they were already given in Ref. 16.

Table 1-3 give the harmonic frequencies of the isomers (1)-(8). Except the intense ν_1 modes, the harmonic frequencies of these molecules are rather low, below 1900 cm^{-1}. The harmonic frequencies of the in-plane (A) bending modes of the triplet structures are smaller than the out-of-plane (A) mode frequencies, being 270-340 cm^{-1}. The out-of-plane bending modes of the singlet cyclic isomers are quite stiff, with harmonic frequencies being larger than 770 cm^{-1}. It would be important to recall that our previous experience[23-27] with the BLYP/6-311G** theory as applied to similar carbon clusters suggests that the harmonic frequencies computed here would agree with experimental values mostly to within 30 cm^{-1} without invoking the empirical scaling factors. Therefore, although there exists no experimental information to compare with for the computed harmonic frequencies of the molecules, the harmonic frequencies for the HC_2N, HCNC and HNC_2 listed in Table 1 will be very useful for identifying these isomers synthesized in the laboratory. For example, the frequencies for HC_2N, HCNC and HNC_2 for the intense ν_1 modes are 3333, 3157 and 3522 cm^{-1}, respectively. Since the frequencies for these ν_1 modes are very different from each other, they may serve as signatures of these isomers in the laboratory condition. As depicted in Figure 3, the first two modes are the C-H stretching, and the

Table 2. Spectroscopic properties of triplet intermediate complexes. Energies[(1)] (Hartee), bond lengths[(1)] (A), bond angles[(1)] (degree) and harmonic frequencies[(2)] (cm^{-1})

(4)		(5)		(6)	
H N	1.058	H N	1.027	H C	1.088
C_1 N	1.313	C_1 N	1.328	C1C2	1.478
N -C_2	1.313	N -C_2	1.328	C2- N	1.231
∠ H N C_1	96.5°	∠ H N C_1	127.6	∠HC1C2	128.6
∠H N C_2	96.5°	∠H N C_2	127.6	∠C1C2N	67.5
E	-130.92421	E	-130.93874	D(HCCN)	101.6
$\Delta E^{(3)}$	105.4	$\Delta E^{(3)}$	96.3	E	-131.01316
μ(D)	1.662	μ(D)	3.965	$\Delta E^{(3)}$	49.6
Rot. Const.	338.1380	Rot. Const.	62.2514	μ (D)	1.650
(GHz)	12.3744	(GHz)	19.0120	Rot Const	48.9889
	11.9375		14.5640	(GHz)	27.0155
ZPE	10.82	ZPE	14.13	ZPE	18.1354
(kcal/mol)		(kcal/mol)		(Kcal/mol)	12.54
ν_1(A')	3133(171)[(4)]	ν_1(A')	3085(0)	ν_1	3088(2)
ν_2(A')	992 (4)	ν_2(A')	1216(3)	ν_2	1656(5)
ν_3(A')	955 (85)	ν_3(A')	1165(23)	ν_3	1005(22)
ν_4(A')	446 (120)	ν_4(A')	645(52)	ν_4	829(19)
ν_5(A')	439 (27)	ν_5(A')	524(39)	ν_5	748(13)
ν_6(A")	460 (5)	ν_6(A")	444(25)	ν_6	434(27)

(1) CCSD(T)/6-311G**//MP2/6-311**. (2) BLYP/6-311G**. (3) kcal/mol. (4) Intensities in km/mole.

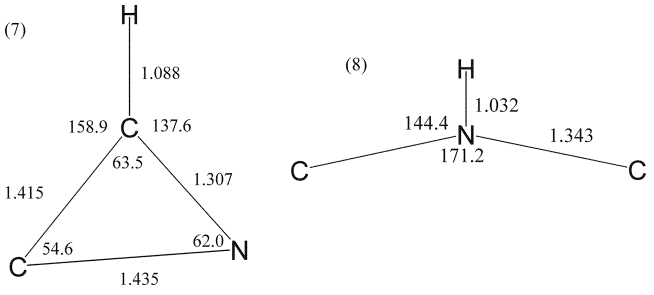

Figure 2. Stationary structures of singlet HC_2N. Bond lengths in A and bond angles in degree.

last mode is N-H stretching. Similarly, the intense modes of HC_2N, HCNC and HNC_2 at 442, 827 and 694 cm^{-1}, respectively, are also characteristic of each isomer, and thereby may be useful for identifying them by the infrared spectroscopy. These normal modes are also shown in Figure 3.

The relative stability of cyano- and isocyanocarbon clusters has been of much interest (primary example is HC_3N *vs*. HC_2NC: the interstellar ratio [HC_3N]/[HC_2NC] was estimated[35] to be 20-60). Although HC_2NC is of higher energy than HC_3N, the rather high barrier for the isomerization reaction $HC_2NC \leftrightarrow HC_3N$ renders it to be quite kinetically stable at low temperature environments, especially in interstellar space. In this regard, it will be quite interesting to examine the isomerization reactions $HC_2N \leftrightarrow$ HCNC and $HC_2N \leftrightarrow$ HNCC in detail. The thermodynamic and kinetic stability[36,37] of the isomers are determined, respectively, by the relative energies and the barriers to isomerization, and therefore, these quantities will be important to compute. As we have also mentioned above, we find many stationary structures for the [H,C,C,N] system with various geometrical structures. It seems that there can exist many isomers of HC_2N due to the peculiar chemical bonding and that the potential surface of this system is quite complicated. Therefore we study the topology of this system in detail, probing the transition states, reaction paths and the barriers to rearrangement and dissociation reactions of HC_2N, HCNC, and HNC_2. The structures of the computed

Table 3. Spectroscopic properties[(1)] of singlet isomers of HC_2N. Bond lengths (A), bond angles (degree) and harmonic frequencies (cm^{-1})

(7)	BLYP/ 6-311G**	(8)	BLYP/ 6-311G**
H-C_1	1.088	H-N	1.032
C_1-C_2	1.451	N-C_1	1.032
C_1-N	1. 307	N-C_2	1. 343
C_2-N	1.435	C_1-C_2	1.564
∠ H C_1 C_2	158.9°	∠ H N C_1	144.4°
∠C_1 C_2 N	54.6°	∠C_1 N C_2	171.2°
∠C_2 C_1 N	63.5°		
E	-131.39853	E	-131.38545
μ(D)	3.036	μ(D)	
Rot. Const.	39.6515	Rot. Const.	3.503
	33.8817		37.5420
	18.2701		34.4305
ZPE	12.3	ZPE	17.9591
(kcal/mol)		(kcal/mol)	12.1
ν_1(A')	3135(2) [(3)]	$\nu_1(A_1)$	3264 (11)
ν_2(A')	1558 (3)	$\nu_2(A_1)$	1435 (21)
ν_3(A')	1269 (26)	$\nu_3(A_1)$	768 (1)
ν_4(A')	960 (16)	$\nu_4(B_1)$	805 (37)
ν_5(A')	775 (28)	$\nu_5(B_2)$	1289 (72)
ν_6(A")	882 (3)	$\nu_6(B_2)$	912 (11)

(1) BLYP/6-311G**. (2) Intensities in km/mole.

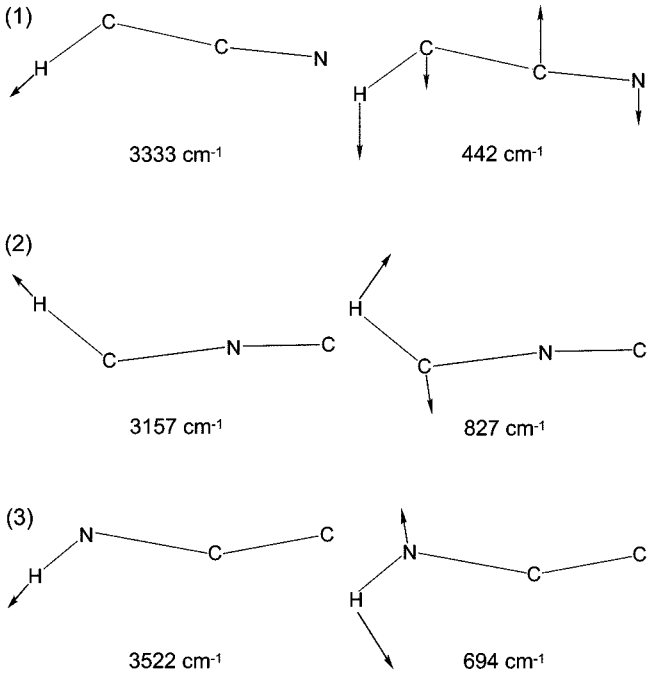

Figure 3. Normal modes of HC_2N (3333, 442 cm^{-1}), HCNC (3157, 827 cm^{-1}), and HNC_2 (3522, 694 cm^{-1}) molecules.

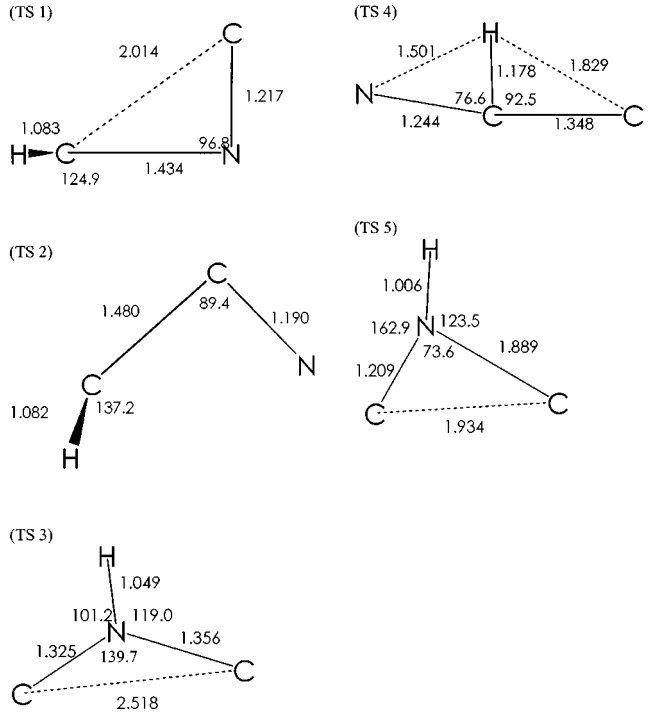

Figure 4. Structures of the transition states along the isomerization reactions among HC_2N, HCNC, and HNC_2. Bond lengths in A and bond angles in degree.

transition states along the isomerization reactions among HC_2N, HCNC, and HNC_2 are depicted in Figure 4, Table 4 and Table 5.

First, we carry out computations on the reaction path for $HC_2N \leftrightarrow$ HCNC, and find that the reaction does not occur by concerted motions of the nuclei, as discussed by Schwartz *et al*.[22] The isomerization reaction rather proceeds in stepwise fashion through a reaction intermediate (6) and the two transition states (TS1 and TS2) connecting the latter structure to the reactant and product, as shown in Figure 5. Detailed motions of the nuclei along the reaction path are obtained by intrinsic reaction coordinate analysis. As expected, the exchanging carbon and nitrogen atoms, and the carbon atom adjacent to the exchanging carbon atom form triangles in the intermediate complex. The intermediate complex (6) is not planar in contrast to HC_2N or HCNC, and the C-H bond makes an angle of 101.6° with the CCN plane. One of the C-N bonds of the intermediate complex is quite long (1.518 A), while the lengths of the C-H and C-C bonds are similar to those of HC_2N or HCNC. Along the reaction path from HC_2N to the intermediate complex (6), the C-N bond highly bends, forming C-C-N angle of 89.4° in the nonplanar transition state (TS2: dihedral angle is 21.7°). The C-C bond also slightly lengthens from 1.380 A to 1.480 A. Going from the transition state (TS2) to the intermediate complex (6), the C-N bond bends more for the nitrogen atom to get closer to the carbon atom bonded to hydrogen, while the C-H bond rotates more out of the C-C-N plane. As the reaction proceeds from the intermediate complex (6) to HCNC, the C-C bond significantly lengthens from 1.478 A in the intermediate molecule to 2.014 A in the transition state (TS1), while the C-H bond remains virtually identical. The C-C bond length still increase along the reaction path, and the C-H bond bends to C-C-N plane, eventually forming HCNC. The HCNC molecule may also undergo another reaction to the stationary structure (4) of C_{2v} symmetry *via* a transition state (TS3). The barrier height from HCNC to (4) is computed to be quite large (81.5 kcal/mol). Along the isomerization reaction $HC_2N \leftrightarrow$ HCNC, the transition states TS1 and TS2 are 52.3 and 55.4 kcal/mol (ZPE-corrected), respectively, above HC_2N. The energy of the intermediate complex (6) is quite high, being 49.9 kcal/mol above HC_2N.

Table 4. Spectroscopic properties of the transition states for the isomerization reaction $HC_2N \leftrightarrow$ HCNC. Energies[(1)] (Hartee), bond lengths[(1)] (A), bond angles[(1)] (degree) and harmonic frequencies[(2)] (cm^{-1})

TS 1		TS 2	
E	-131.00745	E	-131.00199
$\Delta E^{(3)}$	53.2	$\Delta E^{(3)}$	56.6
μ (D)	1.456	μ (D)	1.272
Rot Const	66.8494	Rot Const	59.2062
(GHz)	18.4883	(GHz)	19.8770
	15.0537		14.9304
ZPE	11.30	ZPE	11.03
(Kcal/mol)		(Kcal/mol)	
ν_1	3088 (2)[(3)]	ν_1	3185(11)
ν_2	1621(20)	ν_2	1621(19)
ν_3	1047(24)	ν_3	1070(1)
ν_4	928(20)	ν_4	693(76)
ν_5	367(9)	ν_5	328(32)
ν_6	-491(24)	ν_6	-495(35)

(1) CCSD(T)/6-311G**//MP2/6-311**. (2) BLYP/6-311G**. (3) kcal/mol. (4) Intensities in km/mole.

Table 5. Spectroscopic properties of the transition states TS 3, TS 4 and TS 5 for the isomerization reactions HCNC ↔ (4), HCCN ↔ HNCC, and HCNC ↔ (5). Energies[(1)] (Hartee), bond lengths[(1)] (A), bond angles[(1)] (degree) and harmonic frequencies[(2)] (cm^{-1})

TS 3		TS 4		TS 5	
E	-130.92309	E	-130.95323	E	-130.93521
$\Delta E^{(3)}$	106.1	$\Delta E^{(3)}$	87.2	$\Delta E^{(3)}$	98.5
μ (D)	2. 930	μ (D)	1.134	μ (D)	3. 570
Rot Const	140.0251	Rot Const	396.5215	Rot Const	43.4183
(GHz)	13.2767	(GHz)	11.7383	(GHz)	18.2033
	12.1268		11.4008		12.8260
ZPE	9.66	ZPE	8.92	ZPE	9.95
(Kcal/mol)		(Kcal/mol)		(Kcal/mol	
ν_1(A')	2290(77)[(3)]	ν_1(A')	2514(109)	ν_1(A')	3402(62)
ν_2(A')	1103(40)	ν_2(A')	1516(11)	ν_2(A')	1682(26)
ν_3(A')	1002(21)	ν_3(A')	1020(15)	ν_3(A')	791(38)
ν_4(A')	475(21)	ν_4(A')	380(22)	ν_4(A")	468(106)
ν_5(A")	412(1)	ν_5(A")	374(3)	ν_5(A')	439(35)
ν_6(A')	-609(35)	ν_6(A')	-1250(226)	ν_6(A')	-418(10)

(1) CCSD(T)/6-311G**//MP2/6-311**. (2) BLYP/6-311G**. (3) kcal/mol. (4) Intensities in km/mole.

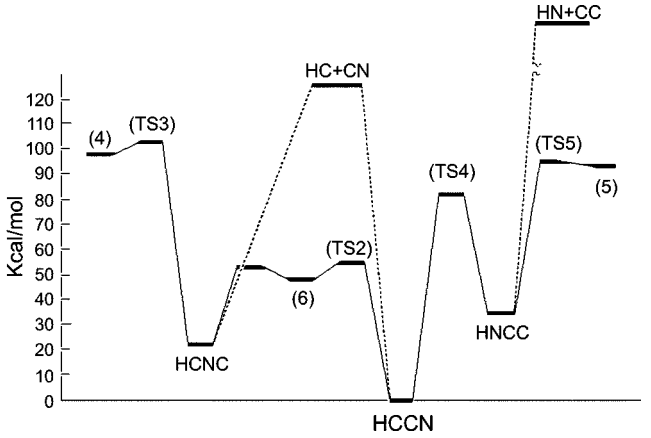

Figure 5. Energy profile and reaction path for the isomerization HC_2N ↔ HCNC, HC_2N ↔ HNC_2 and dissociation reactions.

The ZPE-corrected energy barrier from HCNC to the intermediate structure (6) is 29.8 kcal/mol. Therefore, the isomerization between HC_2N and HCNC may not readily occur at low temperatures. The energy barrier for HC_2N → HCNC is lower that that for HC_3N → HC_2NC reaction (65.8 kcal/mol) by about 16 kcal/mol. We extensively searched for the direct (that is, involving only a single transition state) route for HC_2N ↔ HCNC reaction, but failed to find one. Most probably, the motions of the nuclei for the isomerization reaction are too drastic to allow for concerted motion of the nuclei along a single vibrational mode. The transition state TS2 lies 32.9 kcal above HCNC. Considering that the barrier for the isomerization between the two interstellar molecules, HC_2NC → HC_2CN, is about 40 kcal/mol,[33] the relative ratio [HC_2N]/[HCNC] in interstellar space may be more or less similar to the [HC_3N]/[HC_2NC] ratio of 20-60. The computed barriers for HCNC → HC_2N reaction may indicate that it may not take place readily at low temperatures, and HCNC may be kinetically stable for detection in the laboratory or in interstellar space.

The reaction path between HC_2N and HNC_2 is simpler in that it may occur in one-step mechanism *via* the transition state TS4 as also depicted in Figure 5. The barrier from HC_2N to HNC_2 is computed to be quite high (83.9 kcal/mol), higher than those for the HC_2N↔HCNC reaction. It is worth noting that along the reaction path HCNC ↔ HNC_2, all the structures are planar. Along the reaction path from HNC_2 to HC_2N, the hydrogen atom moves from the nitrogen atom to the adjacent carbon atom in the transition state (TS4), while the C-N and C-C bond lengths remain nearly unchanged. Subsequent transfer of the hydrogen atom between the two carbon atoms produces the HC_2N molecule. The HNC_2 molecule may also undergo reaction to the stationary structure (5) of C_{2v} symmetry *via* a transition state (TS5). The barrier height from HNC_2 to (5) is also computed to be quite large (60.4 kcal/mol). The one-step reaction path between HC_2N and HNC_2 has also been predicted by Schwartz *et al*.,[22] but the transition state obtained by them looks nearly square, and different from that (TS4) depicted in Figure 4. Thus, the reaction path between HC_2N and HNC_2 reported in the present work seems to be different from that predicted by Schwartz *et al.*[22] Compared with the barrier height (100.9 kcal/mol) from HC_2N to HNC_2 reported by Schwartz *et al*., our computed barrier height is about 17.0 kcal/mol lower, indicating that the reaction rate for the isomerization process HC_2N → HNC_2 would be smaller than that predicted by Schwartz *et al.*[22]

Finally, we compute the dissociation reactions of the [H,C,C,N] system, since some of the isomers of higher energies may be amenable to dissociation at low temperature or in interstellar space if the barriers to dissociation are sufficiently small, and since the barriers for the reverse association reactions may give invaluable information for the mechanism of formation of HCCN and the isomers both in laboratory and in interstellar space. Our calculations both at BLYP/6-311G** and MP2/6-311G** level of theory indicate that the reactions HC ($^2\Pi$) + CN ($^2\Sigma^+$) → HCCN, HC ($^2\Pi$) + NC ($^2\Sigma^+$) → HCNC, and HN ($^3\Sigma^-$) + CC ($^1\Sigma^+_g$) → HNCC are barrierless with very large reaction energies of

-126.5, -104.0, and 128.1 kcal/mol, respectively, as depicted in Figure 5. Since these association reactions are highly exothermic without barriers, they may be considered as efficient means of producing the HCCN and the isomers. Noting that the diatomic molecules CH, CN, NH and C_2 are well-known interstellar molecules,[38] these association reactions may be considered as very good sources of the HCCN, HCNC and HNCC molecules, providing efficient mechanisms of formation of these molecules in interstellar space. On the other hand, the reverse reactions are highly endothermic, prohibiting the dissociations of the HCCN molecule and the isomers. Therefore, combined with the barriers of isomerization reactions among HCCN, HCNC and HNCC already given above, we may consider the latter two molecules are kinetically stable at least at low temperatures. Therefore, the two molecules, HCNC and HNCC, seem to be good candidates for astrophysical detection.

Conclusions

In the present work, we have reported computations on the [H,C,C,N] system. Hopefully our results will help elucidate the structures, the spectroscopic properties, and the reactivity of these interesting molecules both in the laboratory and interstellar space.

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