Computational Study on the Isomers of Cyanopolyacetylenes H(C≡C)$_n$C≡N (n=1-3)

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Density functional theory calculations are presented for the geometrical isomers of the cyanopolyacetylenes H(C≡C)$_n$C≡N (n = 1-3). The structures, harmonic frequencies and dipole moments are computed, employing the 6-311G** basis set. The energies of barrier to isomerization (exchange of carbon and nitrogen atoms) are also computed in order to estimate the stability of the isomers in interstellar space.

Introduction

Carbon clusters with bonds to the nitrogen atoms have been paid much attention recently due to their astrophysical abundance. A variety of nitrogen-containing carbon clusters were observed in interstellar clouds along with those mixed with other heteroatoms such as O,[1,2] S[3-6] and Si.[7] Among these carbon clusters, cyanopolyacetylenes, H(C≡C)$_n$C≡N with long carbon chains, up to HC$_{11}$N,[8] were observed in interstellar medium. The structures and vibrational frequencies were measured, and numerous *ab initio* computations[9-12] were also carried out.

In contrast to the cyanopolyacetylenes, studies on their geometrical isomers were relatively scarce. It is well known that the cyanopolyacetylenes are the lowest-energy structures, and the abundance of the geometrical isomers of cyanopolyacetylenes is considered to be smaller than the cyanopolyacetylenes in interstellar medium. The relative abundance of HCN and HNC is a good example, and the ratio [HCN]/[HNC] was estimated[13] to be 1.55. However, HC$_2$NC[14] and HNC$_3$,[15] which are the isomers of HC$_3$N, do exist in interstellar medium. Further experimental studies may lead to observation of other isomers with longer carbon chains, and computational studies on them will surely help elucidate their structures and spectroscopic properties.

Another motivation to study the geometrical isomers of cyanopolyacetylenes is the fact that the bonding to the nitrogen atoms may change the structure and chemical reactivity of the carbon clusters. It was found that lowest-energy structures of the pure carbon clusters up to C$_{10}$ are linear. The cyanopolyacetylenes, with alternating single and triple bonds, are also known to be linear up to HC$_{11}$N. The chemical bonds of the geometrical isomers of H(C≡C)$_n$C≡N are, however, much more complicated, and no simple canonical structures may be assigned for these molecules. Presumably, several resonance structures due to the unpaired electrons of the nitrogen atom may contribute to the overall bonding character, as is the case for H$_2$C$_n$O [Ref. 16] (n = 2-6). In the present article, we predict the structures and the spectroscopic properties of the geometrical isomers of H(C≡C)$_n$C≡N (n = 1-3) employing the density functional theory (BLYP/6-311G**) method, which we found very economical and also accurate compared with other correlated methods for the carbon clusters in a number of previous works.[16-20] The rela-

tive stability of some isomers is also studied by computing the energies of the barriers to isomerization.

Computational Methods

In this study all the calculations were carried out using the GAUSSIAN 94 set of programs[21] on DEC alpha work stations. The density functional theory with the exchange functional by Becke[22] and correlation functional by Lee et al.[23] (BLYP) were employed with the 6-311G** basis sets. All the molecules studied in this work are *planar*, except for a transition state. Dipole moments and rotational constants were computed along with the harmonic frequencies. The structures of the transition states were obtained by verifying that one of the harmonic frequencies be imaginary. Energy barriers for the isomerization reactions (exchange of carbon and nitrogen atoms) were computed by subtracting the energies of the stationary structures from those of the transition states, including the zero-point energies.

Results

Table 1 presents the relative energies of the cyanopolyacetylenes H(C≡C)$_n$C≡N (n = 1-3) and their geometrical isomers. The cyanopolyacetylenes H(C≡C)$_n$C≡N are the most stable, and other isomers are 20-80 kcal/mol higher in energies. The HC$_{2n}$NC (n = 1-3) molecules, which are formed by the exchange of the terminal carbon and the nitrogen atoms, are the second most stable structures, lying about 27 kcal/mol above the corresponding cyanopolyacetylenes. On the other hand, HCNC$_{2n}$ (n = 1-3) molecules are found to be the least stable, 70-80 kcal/mol higher in energies than the corresponding cyanopolyacetylenes. Isomers with the H-N bonding, HNC$_{2n+1}$, are predicted to be the third most stable structures in each series. Those with the generic structures of HCNC$_{2n}$ are found to be the least stable, when the zero point energies are considered. These differences in energies between the isomers would, of course, determine their relative abundance in interstellar space. The dipole moments of the molecules given in Table 2 are rather large, up to more than 11 Debye for HNC$_7$ and HCNC$_6$, indicating that they may be studied by microwave and infrared spectroscopy. The computed rotational constants are presented in Table 3. It can be seen that the computed values compare very well with the

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Table 1. Relative energies of $H(C \equiv C)_n C \equiv N$ (n = 1-3) and their isomers

	ΔE (kcal/mol)
HC_7N	0.0^a
HC_6NC	27.8 (26.7)^b
HC_5NC_2	66.4 (64.5)
HC_4NC_3	59.2 (57.3)
HC_3NC_4	74.0 (71.7)
HC_2NC_5	62.6 (60.7)
$HCNC_6$	73.4 (75.7)
HNC_7	49.6 (48.4)
HC_5N	0.0^a
HC_4NC	27.7 (26.9)
HC_3NC_2	68.1 (71.8)
HC_2NC_3	58.7 (57.4)
$HCNC_4$	77.2 (74.8)
HNC_5	48.3 (47.0)
HC_3N	0.0^a
HC_2NC	27.1 (26.6)
$HCNC_2$	70.7 (68.8)
HNC_3	44.9 (43.6)

^{a}The energies of HC_3N, HC_5N, and HC_7N are -169.58410 (-169.55788), -245.74126 (-245.70494), and -321.90609 (-321.85911) Hartree, respectively. The energies in the parentheses are those including the zero-point energy. ^{b}Zero-point energies included.

experimental observations. the agreement being better than the MP2/4-31G** results by da Silva *et al.*[24] Since the structures of many molecules listed in Table 2 are quasilinear. as described below. their rotational constants comprise two very similar ones with the remaining one very large. Therefore, we list only one of the rotational constants for most molecules in Table 2, with the exception of HNC_3, for which the two rotational constants are somewhat different due to

Table 2. Dipole moments (Debye) of $H(C \equiv C)_n C \equiv N$ (n = 1-3) and their isomers

	MP2/ 4-31G**^{a}	CCSD(T)/ 299 cGTOs^b	BLYP/6-311G**	Exp.
HC_7N	4.93		5.30	
HC_6NC	3.75	3.487	3.81	
HC_5NC_2	7.14		7.77	
HC_4NC_3	6.56		6.08	
HC_3NC_4	8.73		9.25	
HC_2NC_5	8.34		7.45	
$HCNC_6$	11.93		10.06	
HNC_7	11.50		8.25	
HC_5N	4.35		4.53	4.33^c
HC_4NC	3.43	3.253	3.39	
HC_3NC_2			6.97	
HC_2NC_3			5.63	
$HCNC_4$			8.34	
HNC_5	8.35		6.73	
HC_3N	3.70		3.71	3.6^c
HC_2NC	3.08		2.98	
$HCNC_2$			6.52	
HNC_3	5.97		5.14	

^{a}Ref. 24. ^{b}Ref. 27. ^{c}Ref. 25.

Table 3. Rotational constants (MHz) of $H(C \equiv C)_n C \equiv N$ (n = 1-3) and their isomers

	MP2/4-31G**^{a}	BLYP/6-311G**	Exp.
HC_7N	556.8	561.743	564.0^b
HC_6NC	574.8	579.071	582.4^c
HC_5NC_2	590.6	593.840	
HC_4NC_3	599.2	601.449	
HC_3NC_4	601.1	602.520	
HC_2NC_5	597.1	597.200	
$HCNC_6$	583.9	584.320	
HNC_7	567.9	567.540	
HC_5N	1312.9	1325.686	1331.3^d
HC_4NC	1381.3	1390.844	1401^c
HC_3NC_2		1432.570	
HC_2NC_3		1438.823	
$HCNC_4$		1404.060	
HNC_5	1344.4	1342.950	
HC_3N	4491.7	4526.427	4549.1^e
HC_2NC	4885.8	4917.071	4967.8^f
$HCNC_2$		4921.768	
HNC_3	4612.4	4605.690	4668.3^g
		4587.957	
		1191.437^h	

^{a}Ref. 24. ^{b}Ref. 26. ^{c}Ref. 27. ^{d}Ref. 25. ^{e}Ref. 28. ^{f}Ref. 29. ^{g}Ref. 15. The other two rotational constants were not reported. ^{h}in GHz.

the clear nonlinearity of the molecule.

The structures of the geometrical isomers of $H(C \equiv C)_n C \equiv N$ (n = 1-3) are given in Table 4-Table 8 (it should be noted that the two molecules, HC_2NC and HC_4NC, and the cyanopolyacetylenes $H(C \equiv C)_n C \equiv N$ (n = 1-3) were already reported in our previous publication[17]). The isomers of HC_3N are linear. except HNC_3. The latter molecule is predicted to be highly bent but planar (C_s symmetry), with the H-N-C angle of 135.2°. Of the isomers of HC_5N, $HCNC_4$ and HNC_5 are predicted to be bent. Only $HCNC_6$ and HNC_7 are predicted to

Table 4. Bond lengths (Å). bond angles and harmonic frequencies (cm^{-1}) of $HCNC_2$ and HNC_3

$HCNC_2$	BLYP/ 6-311G**	HNC_3	BLYP/ 6-311G**	CEPA-1/ 118 cGTO^a
$H-C_1$	1.068	H N	1.014	1.0038
C_1-N	1.178	$N-C_1$	1.205	1.1928
$N-C_2$	1.281	C_1-C_2	1.307	1.3076
C_2-C_3	1.277	C_2-C_3	1.282	1.2745
		$\angle H N C_1$	135.2°	136.1°
		$\angle N C_1 C_2$	173.6°	173.8°
		$\angle C_1 C_2 C_3$	177.2°	175.0°
$v_1(\sigma)$	3414 (366)^b	$v_1(A')$	3586 (278)	
$v_2(\sigma)$	2172 (617)	$v_2(A')$	2218 (1085)	
$v_3(\sigma)$	1926 (159)	$v_3(A')$	1869 (15)	
$v_4(\sigma)$	954 (1)	$v_4(A')$	932 (3)	
$v_5(\pi)$	505 (0.8)	$v_5(A')$	628 (317)	
$v_6(\pi)$	186 (2)	$v_6(A'')$	557 (0.5)	
$v_7(\pi)$	155 (57)	$v_7(A')$	511 (116)	
		$v_8(A'')$	174 (3)	
		$v_9(A')$	159 (3)	

^{a}Ref. 30. ^{b}Intensities in km/mole.

Table 5. Bond lengths (A), bond angles and harmonic frequencies (cm^{-1}) of HC$_2$NC$_3$, HCNC$_4$, HNC$_5$ and HC$_3$NC$_2$

HC$_2$NC$_3$	BLYP/6-311G**	HCNC$_4$	BLYP/6-311G**	HNC$_5$	BLYP/6-311G**	HC$_3$NC$_2$	BLYP/6-311G**
H-C$_1$	1.068	H-C$_1$	1.075	H-N	1.017	H-C$_1$	1.069
C$_1$-C$_2$	1.218	C$_1$-N	1.196	N-C$_1$	1.215	C$_1$-C$_2$	1.225
C$_2$-N	1.291	N-C$_2$	1.261	C$_1$-C$_2$	1.296	C$_2$-C$_3$	1.337
N-C$_3$	1.201	C$_2$-C$_3$	1.260	C$_2$-C$_3$	1.270	C$_3$-N	1.192
C$_3$-C$_4$	1.304	C$_3$-C$_4$	1.310	C$_3$-C$_4$	1.303	N-C$_4$	1.273
C$_4$-C$_5$	1.285	C$_4$-C$_5$	1.288	C$_4$-C$_5$	1.290	C$_4$-C$_5$	1.283
		∠HC$_1$N	151.1°	∠HNC$_1$	131.0°		
		∠C$_1$NC$_2$	174.3°	∠NC$_1$C$_2$	172.3°		
		∠NC$_2$C$_3$	179.8°	∠C$_1$C$_2$C$_3$	176.4°		
		∠C$_2$C$_3$C$_4$	179.6°	∠C$_2$C$_3$C$_4$	179.6°		
		∠C$_3$C$_4$C$_5$	179.8°	∠C$_3$C$_4$C$_5$	179.3°		
$v_1(\sigma)$	3409 (145)	$v_1(A')$	3312 (314)	$v_1(A')$	3536 (288)	$v_1(\sigma)$	3395 (174)
$v_2(\sigma)$	2268 (1263)^a	$v_2(A')$	2225 (1959)	$v_2(A')$	2238 (3537)	$v_2(\sigma)$	2238 (374)
$v_3(\sigma)$	2162 (146)	$v_3(A')$	2101 (60)	$v_3(A')$	2122 (134)	$v_3(\sigma)$	2098 (275)
$v_4(\sigma)$	1908 (190)	$v_4(A')$	1857 (404)	$v_4(A')$	1825 (370)	$v_4(\sigma)$	1917 (464)
$v_5(\sigma)$	1221 (0.8)	$v_5(A')$	1284 (0.4)	$v_5(A')$	1250 (2)	$v_5(\sigma)$	1197 (1)
$v_6(\sigma)$	672 (0.6)	$v_6(A')$	659 (0.1)	$v_6(A')$	689 (605)	$v_6(\sigma)$	663 (0.5)
$v_7(\pi)$	575 (41)	$v_7(A')$	491 (3)	$v_7(A')$	643 (39)	$v_7(\pi)$	589 (41)
$v_8(\pi)$	485 (9)	$v_8(A'')$	487 (5)	$v_8(A'')$	553 (3)	$v_8(\pi)$	454 (1)
$v_9(\pi)$	392 (0.8)	$v_9(A')$	444 (2)	$v_9(A')$	546 (4)	$v_9(\pi)$	403 (1)
$v_{10}(\pi)$	188 (7)	$v_{10}(A'')$	444 (1)	$v_{10}(A'')$	513 (1)	$v_{10}(\pi)$	224 (4)
$v_{11}(\pi)$	80 (0.9)	$v_{11}(A')$	359 (479)	$v_{11}(A')$	473 (46)	$v_{11}(\pi)$	103 (2)
		$v_{12}(A')$	208 (11)	$v_{12}(A'')$	222 (6)		
		$v_{13}(A'')$	207 (12)	$v_{13}(A')$	216 (9)		
		$v_{14}(A')$	89 (0.2)	$v_{14}(A'')$	97 (6)		
		$v_{15}(A'')$	88 (1)	$v_{15}(A')$	93 (2)		

^{a}Intensities in km/mole.

be completely bent isomers of HC$_7$N, with the H-C-N and H-N-C angles of 144.7° and 129.4°, respectively. Other isomers of HC$_7$N are either linear or quasilinear. For example, the bond angles of HC$_5$NC$_2$, HC$_3$NC$_4$ and HC$_2$NC$_5$ are very close to 180°, as reported in Table 7 and Table 8. Thus, for the series of molecule studied here, those with the nitrogen atom either bonded to the hydrogen atom or to the H-C moiety are bent, while others are linear or essentially linear. The carbon-carbon and the carbon-nitrogen bond lengths for the isomers of H(C≡C)$_n$C≡N (n = 1-3) clearly show the peculiar character of the chemical bonds of these molecules. For example, the distance between the two terminal carbon atoms in HCNC$_2$ given in Table 4 is 1.277 A, considerably larger than the C=C bond length (1.215 A) in HC$_3$N, indicating that the carbon-carbon bonding in the former molecule is not canonically triple. Similarly, the nitrogen-carbon distance in HC$_6$NC (Table 6) is 1.201 A, larger than the C≡N bond length (1.177 A) in HC$_7$N, showing that the N-C bonding in HC$_6$NC is not perfectly triple. Da Silva *et al.*[24] suggested for the bonding structure in HC$_{7-x}$NC$_x$ type of molecules that the nitrogen atom may be regarded as dividing the carbon chain in two parts with different degree of electron delocalization, such as the canonical structure H-C≡C-C≡C-N=C=C=C for HC$_4$NC$_3$. However, this simplification may not work well for other molecules such as HCNC$_6$ reported in Table 8. No canonical structure could be drawn for this molecule, and it seems that several resonance structures may contribute. Since the pure carbon clusters are known to be linear up to C$_{10}$, it can be seen in Table 4 Table 8 that bonding to the nitrogen atom gives substantial changes in the geometry of the carbon chains in the isomers of cyanopolyacetylenes.

The harmonic frequencies are also given in Table 4-Table 8. Most of the frequencies for these molecules are reported for the first time here. The high-frequency modes $v_1(\sigma)$ of the linear isomers are very similar to those of the corresponding cyanopolyacetylenes. For example, the $v_1(\sigma)$ frequency (3414 cm^{-1}) of HC$_2$NC is close to that of HC$_3$N (3398 cm^{-1}), while those of HC$_4$NC, HC$_3$NC$_2$, and HC$_2$NC$_3$ are 3402, 3395 and 3409 cm^{-1}, respectively, similar to that of HC$_5$N (3397 cm^{-1}). Likewise, the $v_1(\sigma)$ modes of the linear or quasilinear HC$_6$NC, HC$_5$NC$_2$, HC$_4$NC$_3$ and HC$_3$NC$_4$ molecules have the similar frequencies of 3401, 3396, 3400, and 3394 cm^{-1}, respectively, while that of HC$_7$N is 3399 cm^{-1}. This observation results from the fact that the $v_1(\sigma)$ modes of these linear isomers are predominantly the stretching of the C-H bond (see Figure 1), that are essentially single bond, well isolated from the movements of other chemical bonds with more complicated characters. Differences in other stretching modes of the linear isomers indicate the complicated changes in the character of the chemical bondings in these molecules. For example, the $v_2(\sigma)$ mode of HCNC$_2$ has the harmonic frequency of 2172 cm^{-1}, smaller than that of HC$_3$N (2267 cm^{-1}). The $v_2(\sigma)$ modes of these two mole-

Table 6. Bond lengths (A), bond angles and harmonic frequencies (cm^{-1}) of HC$_6$NC and HC$_4$NC$_3$

HC$_6$NC	CCSD(T) cc-pVTZ (254 cGTOs)[a]	BLYP/ 6-311G**	HC$_4$NC$_3$	BLYP/ 6-311G**
H-C$_1$	1.0628	1.068	H-C$_1$	1.068
C$_1$-C$_2$	1.2101	1.224	C$_1$-C$_2$	1.222
C$_2$-C$_3$	1.3654	1.350	C$_2$-C$_3$	1.350
C$_3$-C$_4$	1.2164	1.235	C$_3$-C$_4$	1.233
C$_4$-C$_5$	1.3603	1.342	C$_4$-N	1.279
C$_5$-C$_6$	1.2110	1.230	N-C$_5$	1.205
C$_6$-N	1.3067	1.299	C$_5$-C$_6$	1.303
N-C$_7$	1.1822	1.201	C$_6$-C$_7$	1.287
$v_1(\sigma)$	3454[b]	3401 (156)	$v_1(\sigma)$	3400 (156)
$v_2(\sigma)$	2312	2219 (6)	$v_2(\sigma)$	2241 (1519)
$v_3(\sigma)$	2262	2186 (39)	$v_3(\sigma)$	2212 (11)
$v_4(\sigma)$	2122	2073 (35)	$v_4(\sigma)$	2090 (144)
$v_5(\sigma)$	2057	1980 (112)	$v_5(\sigma)$	1908 (251)
$v_6(\sigma)$	1307	1349 (0.1)	$v_6(\sigma)$	1364 (17)
$v_7(\sigma)$	930	948 (8)	$v_7(\sigma)$	938 (4)
$v_8(\pi)$	631	623 (11)	$v_8(\pi)$	595 (41)
$v_9(\pi)$	530	579 (30)	$v_9(\sigma)$	505 (0.4)
$v_{10}(\sigma)$	470	481 (0)	$v_{10}(\pi)$	496 (0.4)
$v_{11}(\pi)$	458	472 (0)	$v_{11}(\pi)$	474 (5)
$v_{12}(\pi)$	403	408 (0.1)	$v_{12}(\pi)$	360 (2)
$v_{13}(\pi)$	262	279 (0)	$v_{13}(\pi)$	214 (0.7)
$v_{14}(\pi)$	163	168 (5)	$v_{14}(\pi)$	152 (8)
$v_{15}(\pi)$	64	66 (0)	$v_{15}(\pi)$	56 (2)

[a]Ref. 27. The bending modes are corrected by the off-diagonal MP2 force constants. [b]Intensities in km/mole.

Table 7. Bond lengths (A), bond angles and harmonic frequencies (cm^{-1}) of HC$_5$NC$_2$ and HC$_3$NC$_4$

HC$_5$NC$_2$	BLYP/ 6-311G**	HC$_3$NC$_4$	BLYP/ 6-311G**
H-C$_1$	1.069	H-C$_1$	1.069
C$_1$-C$_2$	1.225	C$_1$-C$_2$	1.229
C$_2$-C$_3$	1.343	C$_2$-C$_3$	1.331
C$_3$-C$_4$	1.243	C$_3$-N	1.201
C$_4$-C$_5$	1.321	N-C$_4$	1.258
C$_5$-N	1.198	C$_4$-C$_5$	1.261
N-C$_6$	1.271	C$_5$-C$_6$	1.310
C$_6$-C$_7$	1.286	C$_6$-C$_7$	1.289
$\angle$ H C$_1$ C$_2$	179.8°	$\angle$ H C$_1$ C$_2$	179.5°
$\angle$ C$_1$ C$_2$ C$_3$	179.9°	$\angle$ C$_1$ C$_2$ C$_3$	179.6°
$\angle$ C$_2$ C$_3$ C$_4$	179.9°	$\angle$ C$_2$ C$_3$ N	179.5°
$\angle$ C$_3$ C$_4$ C$_5$	179.8°	$\angle$ C$_3$ N C$_4$	179.7°
$\angle$ C$_4$ C$_5$ N	179.7°	$\angle$ N C$_4$ C$_5$	179.5°
$\angle$ C$_5$ N C$_6$	180.0°	$\angle$ C$_4$ C$_5$ C$_6$	179.8°
$\angle$ N C$_6$ C$_7$	179.9°	$\angle$ C$_5$ C$_6$ C$_7$	179.8°
$v_1(A')$	3396 (193)[a]	$v_1(A')$	3394 (260)
$v_2(A')$	2212 (418)	$v_2(A')$	2231 (1481)
$v_3(A')$	2151 (53)	$v_3(A')$	2182 (895)
$v_4(A')$	2058 (342)	$v_4(A')$	2046 (386)
$v_5(A')$	1918 (684)	$v_5(A')$	1892 (291)
$v_6(A')$	1334 (8)	$v_6(A')$	1395 (60)
$v_7(A')$	955 (8)	$v_7(A')$	942 (7)
$v_8(A')$	596 (41)	$v_8(A')$	565 (43)
$v_9(A'')$	594 (43)	$v_9(A'')$	562 (43)
$v_{10}(A')$	541 (0)	$v_{10}(A')$	511 (1)
$v_{11}(A'')$	540 (0)	$v_{11}(A')$	490 (2)
$v_{12}(A')$	497 (0.1)	$v_{12}(A'')$	488 (3)
$v_{13}(A')$	445 (0.1)	$v_{13}(A')$	402 (0)
$v_{14}(A'')$	442 (0.4)	$v_{14}(A'')$	382 (0)
$v_{15}(A')$	394 (0)	$v_{15}(A')$	376 (2)
$v_{16}(A'')$	387 (0.4)	$v_{16}(A'')$	373 (3)
$v_{17}(A')$	256 (0.1)	$v_{17}(A')$	229 (2)
$v_{18}(A'')$	251 (0.1)	$v_{18}(A'')$	229 (2)
$v_{19}(A')$	156 (8)	$v_{19}(A')$	147 (5)
$v_{20}(A'')$	74 (4)	$v_{20}(A'')$	146 (4)
$v_{21}(A')$	64 (2)	$v_{21}(A')$	59 (1)

[a]Intensities in km/mole.

cules are antisymmetric stretching of the terminal C-C-N and N-C-C moiety, respectively. The length of the N-C bond in HCNC$_2$ is 1.281 A, and is larger (that is, the bond is weaker) than the N-C bond length (1.172 A) in HC$_3$N, while the C-C bond length of HCNC$_2$ is 1.277 A, smaller (that is, the bond is stronger) than that (1.369 A) in HC$_3$N. Therefore, complicated balance of the opposing changes in the two chemical bonds gives the overall decrease of the $v_2(\sigma)$ frequency in HCNC$_2$ compared with HC$_3$N. The $v_1(A')$ frequencies of the highly bent isomers are predicted to be much higher that the $v_1(\sigma)$ modes of cyanopolyacetylenes: For example, the v_1 frequencies of HNC$_3$, HNC$_5$, and HNC$_7$ are 3586, 3536, and 3515 cm^{-1}, respectively, more than 100 cm^{-1} higher than those of HC$_3$N, HC$_5$N, and HC$_7$N. Figure 1 shows the origin of these differences in a simple fashion: the v_1 modes of HNC$_{2n+1}$ molecules are the stretching of H-N bond mixed with small motion of N-C bond, while those of other isomers (except HCNC$_{2n}$) are almost pure H-C stretching. Likewise, the v_1 modes of HCNC$_{2n}$ molecules are about 100 cm^{-1} lower than those of HC$_{2n+1}$N, and this difference is due to the fact that the v_1 modes of HCNC$_{2n}$ molecules comprise antisymmetric stretching of the H-C-N bonding. The lowest-frequency bending modes also show interesting behavior as a function of the chain length. The v_7, v_{11} and v_{15} modes of HC$_2$NC, HC$_4$NC [Ref. 17], and HC$_6$NC are 223, 116, 66 cm^{-1}, respectively, while the v_9, v_{15}, and v_{21} modes

of HNC$_3$, HNC$_5$, and HNC$_7$ have the frequencies of 159, 93, and 60 cm^{-1}, respectively. This indicates that the molecules become floppier as the length of the carbon chain increases. For the quasilinear molecules listed in Table 4-Table 8, the π bending modes are split into two with A' and A" symmetry with very similar frequencies. Although there exists little experimental information to compare with the computed vibrational frequencies of these molecules, our previous experience with the BLYP/6-311G** theory as applied to similar carbon clusters suggests that the frequencies reported here would agree with experimental values to within 30 cm^{-1} without invoking the empirical scaling factors. Since the B3LYP method tends to give inaccurate high-frequency stretching modes for carbon clusters,[16-20] we did not employ the method in this report.
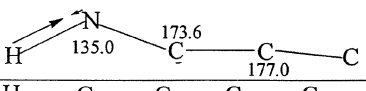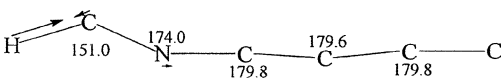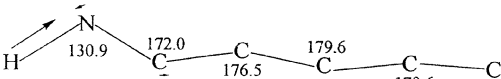
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Table 8. Bond lengths (Å), bond angles and harmonic frequencies (cm^{-1}) of HC_2NC_5, $HCNC_6$ and HNC_7
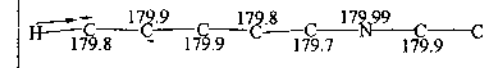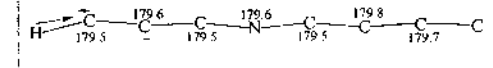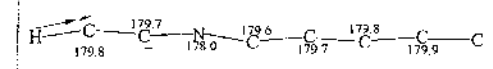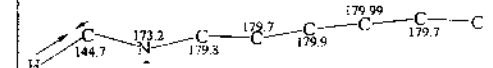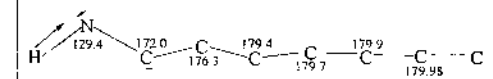
HC_2NC_5	BLYP/6-311G**	$HCNC_6$	BLYP/6-311G**	HNC_7	BLYP/6-311G**
H-C_1	1.067	H-C_1	1.079	H-N	1.018
C_1-C_2	1.221	C_1-N	1.203	N-C_1	1.219
C_2-N	1.287	N-C_2	1.258	C_1-C_2	1.294
N-C_3	1.207	C_2-C_3	1.263	C_2-C_3	1.274
C_3-C_4	1.292	C_3-C_4	1.299	C_3-C_4	1.292
C_4-C_5	1.271	C_4-C_5	1.270	C_4-C_5	1.273
C_5-C_6	1.303	C_5-C_6	1.307	C_5-C_6	1.303
C_6-C_7	1.291	C_6-C_7	1.291	C_6-C_7	1.292
$\angle$ H C_1 C_2	179.8°	$\angle$ H C_1 N	144.7°	$\angle$ H N C_1	129.4°
$\angle$ C_1 C_2 N	179.7°	$\angle$ C_1 N C_2	173.2°	$\angle$ N C_1 C_2	172.0°
$\angle$ C_2 N C_3	178.0°	$\angle$ N C_2 C_3	179.8°	$\angle$ C_1 C_2 C_3	176.3°
$\angle$ N C_3 C_4	179.6°	$\angle$ C_2 C_3 C_4	179.7°	$\angle$ C_2 C_3 C_4	179.4°
$\angle$ C_3 C_4 C_5	179.7°	$\angle$ C_3 C_4 C_5	179.9°	$\angle$ C_3 C_4 C_5	179.7°
$\angle$ C_4 C_5 C_6	179.8°	$\angle$ C_4 C_5 C_6	180.0°	$\angle$ C_4 C_5 C_6	179.9°
$\angle$ C_5 C_6 C_7	179.9°	$\angle$ C_5 C_6 C_7	179.7°	$\angle$ C_5 C_6 C_7	180.0°
$\nu_1(A')$	3408 (195)^a	$\nu_1(A')$	3260 (285)	$\nu_1(A')$	3315 (322)
$\nu_2(A')$	2245 (2141)	$\nu_2(A')$	2204 (1000)	$\nu_2(A')$	2223 (1267)
$\nu_3(A')$	2190 (899)	$\nu_3(A')$	2163 (2147)	$\nu_3(A')$	2175 (2865)
$\nu_4(A')$	2103 (677)	$\nu_4(A')$	2014 (1386)	$\nu_4(A')$	2036 (1561)
$\nu_5(A')$	1867 (318)	$\nu_5(A')$	1846 (35)	$\nu_5(A')$	1821 (32)
$\nu_6(A')$	1388 (18)	$\nu_6(A')$	1422 (79)	$\nu_6(A')$	1398 (88)
$\nu_7(A')$	971 (1)	$\nu_7(A')$	982 (6)	$\nu_7(A')$	960 (13)
$\nu_8(A')$	561 (37)	$\nu_8(A')$	639 (3)	$\nu_8(A'')$	757 (5)
$\nu_9(A'')$	561 (37)	$\nu_9(A'')$	628 (4)	$\nu_9(A')$	720 (333)
$\nu_{10}(A')$	544 (11)	$\nu_{10}(A')$	500 (18)	$\nu_{10}(A')$	704 (616)
$\nu_{11}(A'')$	544 (11)	$\nu_{11}(A')$	461 (9)	$\nu_{11}(A'')$	538 (0.2)
$\nu_{12}(A')$	507 (0.6)	$\nu_{12}(A'')$	460 (2)	$\nu_{12}(A')$	529 (4)
$\nu_{13}(A')$	440 (5)	$\nu_{13}(A'')$	437 (1)	$\nu_{13}(A'')$	495 (0.3)
$\nu_{14}(A'')$	440 (5)	$\nu_{14}(A')$	435 (678)	$\nu_{14}(A')$	492 (7)
$\nu_{15}(A')$	383 (3)	$\nu_{15}(A')$	431 (207)	$\nu_{15}(A')$	458 (39)
$\nu_{16}(A'')$	383 (2)	$\nu_{16}(A')$	244 (1)	$\nu_{16}(A'')$	256 (0.8)
$\nu_{17}(A')$	224 (2)	$\nu_{17}(A'')$	241 (0.6)	$\nu_{17}(A')$	253 (2)
$\nu_{18}(A'')$	224 (2)	$\nu_{18}(A')$	140 (10)	$\nu_{18}(A'')$	148 (4)
$\nu_{19}(A')$	116 (6)	$\nu_{19}(A'')$	137 (15)	$\nu_{19}(A')$	146 (9)
$\nu_{20}(A'')$	114 (6)	$\nu_{20}(A'')$	61 (1)	$\nu_{20}(A'')$	62 (8)
$\nu_{21}(A')$	52 (0.5)	$\nu_{21}(A')$	60 (0.3)	$\nu_{21}(A')$	60 (1)

^{a}Intensities in km/mole.

Since the stability of the isomers would be determined by the relative energies and the barriers to isomerization between the isomers, the latter quantity will be important quantity to compute. In laboratory experiments, these barriers will also affect the rates of isomerization reactions between the geometrical isomers. In order to compute the actual rates of isomerization between the molecules studied here, detailed topology of the potential surfaces near the transition states needs to be known as functions of the reaction coordinates. Since the relative abundance of the isocyanopolyacetylenes H(C≡C)$_n$N≡C with respect to the corresponding cyanopolyacetylenes H(C≡C)$_n$C≡N is of much interest, we examine the structures of the transition states and the energies of the barriers of isomerization. The obtained structures of the transition states for the isomerization (exchange of the terminal nitrogen and carbon atoms) from the cyanopolyacetylenes HC$_3$N and HC$_5$N are shown in Figure 2. As expected, the

exchanging carbon and nitrogen atoms, and the carbon atom adjacent to the exchanging carbon atom form triangles in the transition states. From the structure of the transition state for HC$_3$N → HC$_2$NC isomerization, it can be seen that during the reaction the two adjacent CN and CC bond distances in HC$_3$N slightly lengthen from 1.172 to 1.224 Å, and from 1.389 to 1.522 Å, respectively, while the forming CN bond shortens from 1.643 in the transition state to 1.311 Å in the product HC$_2$NC. It should also be noted that the carbon skeletons in the transition states depicted in Figure 2 are somewhat bent, while both the cyanopolyacetylenes and the isocyanopolyacetylenes are linear. The bond angles of the carbon chain in the transition state for HC$_5$N → HC$_4$NC are 163°-175°. The barriers for HC$_3$N → HC$_2$NC, HC$_5$N → HC$_4$NC isomerization reactions are computed to be 65.8 and 65.9 kcal/mol, respectively, including the zero-point energies. The barrier for the reaction HC$_7$N → HC$_6$NC could not

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Figure 1. The v_1 modes of the geometrical isomers of cyanopoly-acetylenes.

▶ v_1 means the highest vibrational frequency(cm^{-1})

be determined due to the size of the molecules, but it seems to be similar to the barriers given above for smaller systems. Since these transition states are about 40 kcal above the energy of the corresponding isocyanopolyacetylene, and about 66 kcal above the energy of the corresponding cyanopolyacetylene, the isomerization $HC_{2n}NC \rightarrow HC_{2n}CN$ may not take place readily in interstellar space, and the $HC_{2n}NC$ molecules may be formed by other mechanism. Considering the fact that HC_2NC was already detected in interstellar
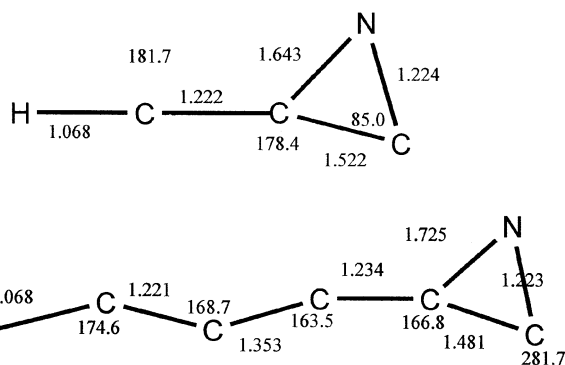
Figure 2. The structures of the transition states for the $HC_3N \rightarrow HC_2NC$ and $HC_3N \rightarrow HC_4NC$. Bond lengths in angstrom and bond angles in degrees.
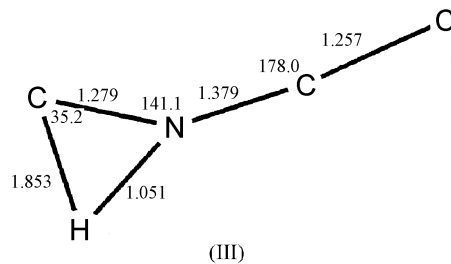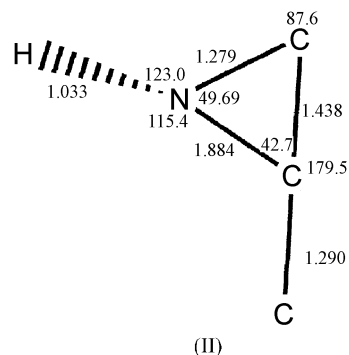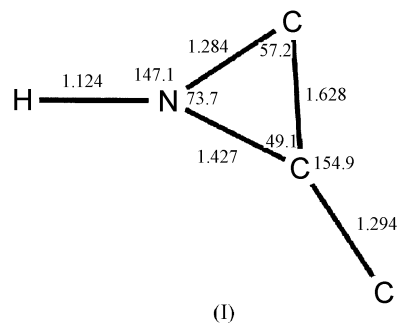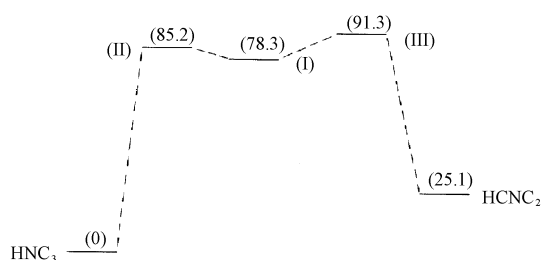

Figure 3. The structures of the stationary states and the transition states for the $HC_3N \rightarrow HC_2NC$ isomerization reactions. Energies in kcal/mol. bond lengths in angstrom and bond angles in degrees.

space (the ratio [HC$_3$N]/[HC$_2$NC] was estimated[14] to be 20-60), the molecules HC$_4$NC and HC$_6$NC may also be quite stable in interstellar space, and they may be good candidates for astrophysical observation, as their isomers HC$_5$N [Ref. 25] and HC$_7$N [Ref. 26].

We also studied possible routes for the isomerization HNC$_3$ ↔ HCNC$_2$. We carried out extensive search for the direct pathway for this reaction, but it seems that a stationary cyclic structure (I) shown in Figure 3 may be involved. This cyclic isomer lies 78.3 kcal/mol above HNC$_3$ (zero-point energies included). The transition state (II) between HNC$_3$ and the cyclic isomer is also given in Figure 3. This transition state is nonplanar (the angle between the N-H bond and the triangular plane is 97°), and lies 6.9 kcal/mol above the cyclic isomer (II). Since the energy of the cyclic isomer is quite higher than that of HNC$_3$, and since the barrier height is small, the cyclic isomer (II) would readily isomerize to HNC$_3$ in normal conditions. The other half of the pathway, that is, (II) → HCNC$_2$ was also studied. The resulting transition state, which lies 13 kcal/mol above the cyclic structure (I), is given in Figure 3. Since the barrier of isomerization is also rather small for this path, it can be concluded that the cyclic structure (I) is prone to isomerization either to HNC$_3$ or HCNC$_2$, and would exist only as an intermediate state. Thus, the overall barrier for HCNC$_2$ → HNC$_3$ isomerization is estimated to be 66.2 kcal/mol, suggesting that the HNC$_3$ molecule may be formed in interstellar space by other mechanism, such as the recombination of HC$_3$NH$^+$ (HC$_3$NH$^+$ + e → HNC$_3$+H).[15]

Conclusions

In the present work, we have reported the DFT computations on the geometrical isomers of cyanopolyacetylenes. Hopefully our results will help elucidate the structures and the spectroscopic properties of these molecules both in the laboratory and in interstellar space. We are currently planning to carry out the intrinsic reaction coordinate analysis of the isomerization reactions in order to compute the rate constants by employing the variational transition state theory.

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