디시아노아세틸렌 및 그 이성체들의 분광학적 성질에 대한 이론 연구

전인선 · 박성우 · 이성렬*
경희대학교 환경응용화학대학
(2004. 10. 1 접수)

Structures and Spectroscopic Properties of Dicyanoacetylene and Isomers: Density Functional Theory Study

In-Sun Jeon, Sung-Woo Park, and Sungyul Lee*

School of Environmental Science and Applied Chemistry, Kyunghee University, Kyungki-do 449-701, Korea

(Received October 1, 2004)

요   약. 디시아노아세틸렌 및 그 이성체들에 대하여 밀도함수이론을 적용하였다. 구조 및 조화진동수를 계산하여 여러 가지의 이성체 구조를 예측하였고, 그 상대에너지를 비교하여 열역학적 안정성을 추정하였다.

주제어: 디시아노아세틸렌

ABSTRACT. Density functional theory calculations are presented for dicyanoacetylene $N \equiv C-C \equiv C-C \equiv N$ and its geometrical isomers. The structures and harmonic frequencies are computed by the BLYP theory employing the 6-311G* basis set. A variety of isomers are predicted, and the relative energies are compared to estimate their thermodynamic stability.

Keywords: Dicyanoacetylene

INTRODUCTION

Carbon clusters containing cyano groups received considerable attention recently because of their interesting spectroscopic properties and astrophysical importance. Cyanopolyacetylenes, $H(C \equiv C)_n C \equiv N$, are quite interesting due to their unusual abundance in interstellar medium. Smaller cyanopolyacetylenes[1,2] were first observed in interstellar space quite long ago, and recently long chain cyanopolyacetylenes such as $HC_{11}N$[3,4] were also detected. In contrast, studies on dicyanopolyacetylenes have been relatively rare. Since the lack of permanent dipole moments of the dicyanopolyacetylenes precludes their detection by radiospectroscopy, studies on these clusters have been focused on the infrared spectra. Cyanogen (C_2N_2), the most well-known member of these clusters, have been detected in Titan's atmosphere[5], and good amount of knowl-

edge has been obtained both by experiments[6-8] and by theoretical investigations[9-11]. It has been predicted[10,11] that some isomers of cyanogens, such as CNCN, CNNC and CCNN, are kinetically stable. C_4N_2 is the next molecule of considerable interest both in spectroscopy and astrophysics in the series of dicyanoacetylenes $N \equiv C-(C \equiv C)_n-C \equiv N$. One of the isomers, NC_4N, has been detected[12] in interstellar medium, and others may also be good candidates for astrophysical observation. While NC_4N, which is linear, may be described by canonical structures in terms of alternating single and triple bonds, chemical bonding in other geometrical isomers is not that clear, and most of them are neither single nor triple. Accordingly, these isomers may display a variety of geometries such as linear, bent, nonplanar or cyclic structures.

In this paper, we present theoretical investigations on the dicyanoacetylene NC_4N and its iso-

mers as our continuing effort[13-19] to calculate the spectroscopic properties of carbon clusters containing medium number (2-8) of carbon atoms. We employ the BLYP density functional theory. which proved[13-19] to be very cost-effective for studying medium-sized carbon clusters, employing the 6-311G* basis set. A variety of structures (linear, bent, cyclic and nonplanar) are predicted, and the harmonic frequencies are reported.

COMPUTATIONAL METHODS

In this study all the calculations are carried out using the GAUSSIAN 94 set of programs.[20] The density functional theory with the exchange functional of Becke[21] and correlation functional by Lee et al.[22] (BLYP) is employed with the 6-311G* basis set. The stationary structures of the molecules considered in this work are computed by verifying that all the harmonic frequencies be real. The transition state is obtained by ascertaining that one of the harmonic frequencies be imaginary. Intrinsic coordinate analysis is carried out to follow the reaction pathway involving the transition state. The relative energies of the isomers are compared in order to estimate their thermodynamic stability, with the zero point energies included.

RESULTS AND DISCUSSION

Fig. 1 shows that all the structures of the isomers of NC_4N we computed in the present work are planar with the exception of (r), in which two three-membered rings are in twisted positions. Calculations for NC_3NC and CNC_2NC, have been presented elsewhere,[23] but we include them in this work for completeness. The isomer of the lowest energy is computed to be NC_4N (a) as presented in *Fig.* 1 and *Table* 1. It is a linear molecule of the canonical structure $N\equiv C-C\equiv C-C\equiv N$ with alternating triple and single bonds, although some other resonance structures may also contribute as we discuss below. The isomer (b) NC_3NC is quite stable (that is, low in energy) with ZPE-corrected energy of only 25.5 kcal/mol above (a). The linear isomers (d), (e) and (h) lie moderately higher (45-60 kcal/mol) in energy than (a). The energies of the isomers (f) and (i), in which two nitrogen atoms are bonded inside the chain, are extremely high, being 107.3 and 158.3 kcal/mol, respectively, relative to (a). The two branched isomers (k) and (l) lie 50.2 and 64.7 kcal/mol, respectively, above (a), while those ((m) and (n)) with six-membered ring structures are of very high energy, more than 150 kcal/mol above (a). Therefore, only the azo compound C_4N_2 (c), and the isomers (b) and (h) containing one

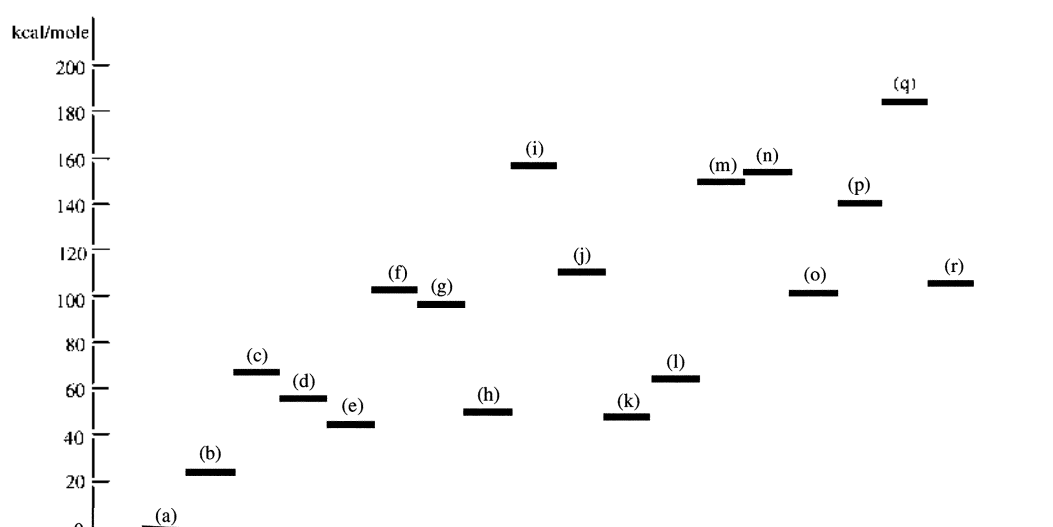*Fig.* 1. Relative energies of the isomers.

　　　　　　　　　진인선 · 박성우 · 이성렬

Table 1. Electronic energies E, zero-point energies (ZPE) and relative energies DE of NC₃N and isomers

	E (a.u.)	ZPE (kcal/mole)	ΔE (kcal/mole)
(a)	-261.83824	16.08	0
(b)	-261.79696	15.70	25.5
(c)	-261.72622	15.23	69.4
(d)	-261.74560	15.16	57.2
(e)	-261.70633	15.21	46.2
(f)	-261.66411	14.19	107.3
(g)	-261.67884	14.35	98.3
(h)	-261.75282	15.18	52.7
(i)	-261.58199	13.61	158.3
(j)	-261.65280	13.64	113.9
(k)	-261.69136	14.04	50.2
(l)	-261.73256	14.53	64.7
(m)	-261.59049	13.01	152.4
(n)	-261.58643	12.82	154.7
(o)	-261.66778	13.92	104.8
(p)	-261.60644	13.19	142.5
(q)	-261.53719	12.46	185.3
(r)	-261.65337	13.05	112.9

and two isocyano groups, respectively, and the branched isomer (k) are moderately higher in energy than the most stable isomer (a), indicting they may be kinetically stable for observation in low temperature laboratory conditions or in interstellar space. In particular, the molecule (b) NC₃NC may be a good candidate for astrophysical observation. Since the energies of other isomers are rather too high, they may be quite amenable to isomerization or dissociation reactions, and thus may be observed only in highly inert conditions such as in rare gas matrix.

Although the lowest energy isomer (a) seems to be described by alternating triple and single bonds, the bond lengths of the molecule indicate that other resonance structures may also contribute. For example, the length (1.360 A) of the two CC bonds adjacent to the terminal CN bonds are much smaller than the typical CC single bond length (~1.50 A), being rather close to typical CC double bond length (~1.34 A). The central CC bond (1.225 A) is also a bit longer than the typical CC triple bond length (~1.20 A). The bonding structures in other isomers are much more complicated, and no simple canonical structures may even be assumed for them. The
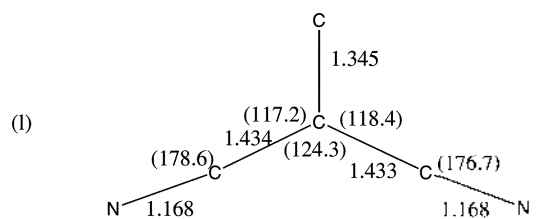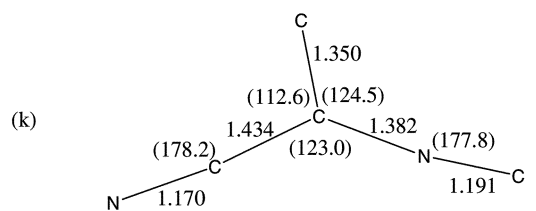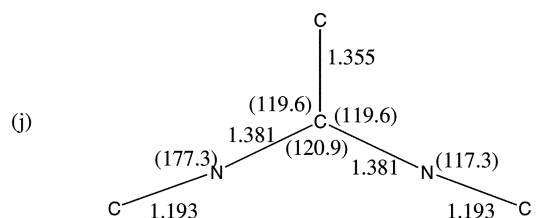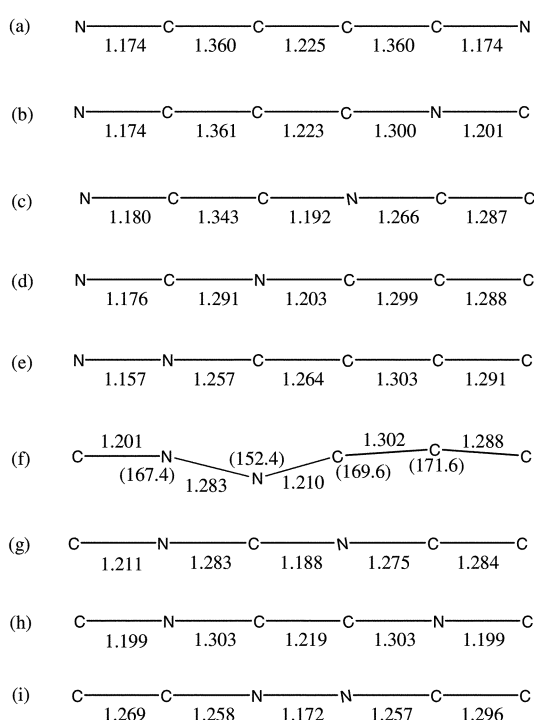

Fig. 2. Structures of the isomers.

(m)

```
        1.289      C
   N ──────────    1.389
    (88.2)  (166.1)
                         C
1.473                 (105.7)
    (105.9)                 1.468
   C              (88.5)
        (165.7)  C ────── N
    1.385       1.292
```

(n)

```
        1.284     C   1.290
   N ────────────────────── N
    (90.4)  (172.7)  (99.7)
1.501                      1.518
    (104.8)
   C              (94.7)
        (157.6)  ────── C
    1.331    C   1.366
```

(o)

```
   N
    (70.7)  1.272
          (143.8)
1.575      C ──────── C  1.168
          (145.6) 1.406  (178.3) N
          1.441
          C (157.4)
1.304
   C
```

(p)

```
        C
     (62.8)  1.323
            (153.7)
1.514        N ── 1.326 ── C  1.173
            (141.4)  (179.8)  N
    (160.7) C  1.487
            (147.0)
          C  1.308
```

(q)

```
        C
     (59.2)  1.306
            (148.7)
1.583        N ── 1.312 ── N  1.199
     1.446  (142.3)  (177.3)  C
    (157.9) C
            (151.2)
          C  1.305
```

(r)

```
   N₁          1.412            N₂
    (69.5)            (152.9)    (69.5)
1.283      C₂ ── 1.280 ── C₃  1.412    1.283
           (155.5)    ........
    (59.2) 1.539         1.539    (59.2)
   C₁                            C₄
```

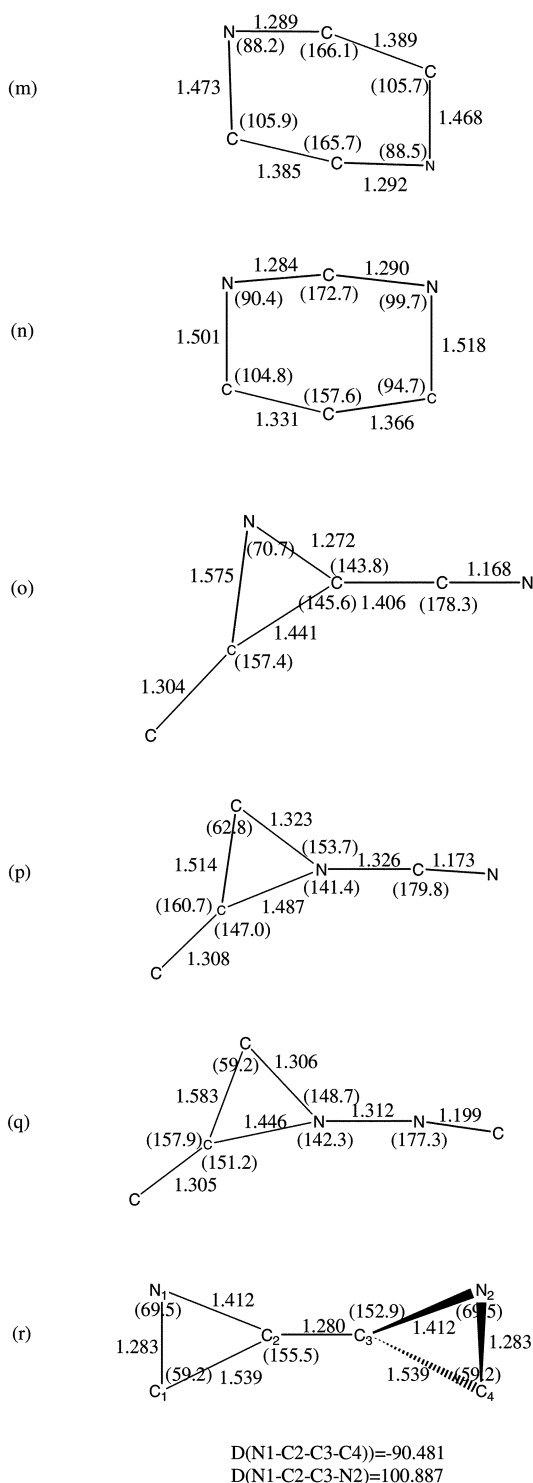D(N1-C2-C3-C4))=-90.481
D(N1-C2-C3-N2)=100.887

Fig. 2. Continued

length (1.201 A) of the CN bond in the isomer (b), for example, is considerably longer than that (1.174 A) in (a), indicating that the bond is weaker than the canonical CN triple bond. The terminal CC bond lengths in the isomer (c) and (d) are 1.287-1.288 A, lying between the typical double and triple CC bond lengths. The terminal NC bond lengthens from the triple bond (1.174 A) in (a) to 1.180 A in (c). All the CC bond lengths (1.264-1.303 A) in (e) are intermediate between the double and triple CC bond lengths. Since their lengths are quite different, these CC bonds cannot be simply described as cumulated double bonds, and several resonance structures must be envisaged as contributing to the overall structure of the isomer (e). It should also be noted that the length (1.283 A) of the NN bond in the bent isomer (f) is much larger than that (1.157 A) in the azo compound (e). The bonding structures in the branched isomers (j)-(l) are also peculiar. While the terminal CN bond lengths (1.193 A) in the isomer (j) is larger than the C≡N bond length (1.174 A) in (a), the lengths (1.168 A) of the terminal NC bonds in (l) are smaller, indicating that they are stronger than the C≡N triple bond. Although quite high in energy above (a), the structures of the six-membered ring structures (m) and (n) are interesting. Some CC bonds in these two isomers are about 1.39 A, similar to typical CC double bond distance (~1.34 A). Moreover, some of the distances between the carbon and nitrogen atoms in these isomers are quite long, being 1.47-1.52 A. These molecules may be studied in inert environment such as in rare gas matrix. The isomers (p) and (q) containing a three-membered ring may be intermediate complexes in the isomerization reaction involving the exchange of carbon and nitrogen atoms, as we have shown for simpler systems[25]. The only nonplanar isomer (r) contains two triangular ring structures twisted from each other. The structure with the two coplanar triangular rings is computed to be a transition state, lying 31.7 kcal/mol above (r). The dipole moments of all the computed structures are rather small (mostly below 2 Debye) with the exception of the linear molecules (e) and (g) (3.88 and 3.41 Debye, respectively).

Table 2. Dipole moments μ (Debye), rotational constants B_e (GHz) and harmonic frequencies (cm^{-1}) of the isomers (a)-(f)

(a)		(b)		(c)	
μ	-	μ	1.10	μ	1.99
B_e	1.330956	B_e	1.398654	B_e	1.440341
$v_1(\sigma_g)$	2269 (0.0)	$v_1(\sigma)$	2278 (53)	$v_1(\sigma)$	2259 (518)
$v_2(\sigma_g)$	2113 (0.0)	$v_2(\sigma)$	2193 (28)	$v_2(\sigma)$	2155 (208)
$v_3(\sigma_g)$	608 (0.0)	$v_3(\sigma)$	2003 (166)	$v_3(\sigma)$	1930 (489)
$v_4(\sigma_u)$	2236 (5.2)	$v_4(\sigma)$	1220 (0.16)	$v_4(\sigma)$	1194 (1.3)
$v_5(\sigma_u)$	1175 (0.07)	$v_5(\sigma)$	627 (0.1)	$v_5(\sigma)$	653 (0.008)
$v_6(\pi_g)$	527 (0.0)	$v_6(\pi)$	524 (3.7)	$v_6(\pi)$	468 (1.6)
$v_7(\pi_g)$	279 (0.0)	$v_7(\pi)$	436 (0.009)	$v_7(\pi)$	450 (1.6)
$v_8(\pi_u)$	506 (5.6)	$v_8(\pi)$	254 (0.003)	$v_8(\pi)$	215 (0.001)
$v_9(\pi_u)$	112 (9)	$v_9(\pi)$	116 (7.5)	$v_9(\pi)$	98 (13)

(d)		(e)		(f)	
μ	0.95	μ	3.88	μ	1.69
B_e	1.447803	B_e	1.409506	B_e	445.78986 1.53254 1.53254
$v_1(\sigma)$	2294 (1386)	$v_1(\sigma)$	2246 (1959)	$v_1(A')$	2233 (1148)
$v_2(\sigma)$	2216 (255)	$v_2(\sigma)$	2124 (60)	$v_2(A')$	2048 (468)
$v_3(\sigma)$	1911 (157)	$v_3(\sigma)$	1857 (387)	$v_3(A')$	1869 (18)
$v_4(\sigma)$	1220 (9.6)	$v_4(\sigma)$	1287 (1.8)	$v_4(A')$	1197 (9)
$v_5(\sigma)$	665 (0.02)	$v_5(\sigma)$	654 (0.2)	$v_5(A')$	659 (5)
$v_6(\sigma)$	497 (5)	$v_6(\sigma)$	499 (0.2)	$v_6(A')$	486 (14)
$v_7(\pi)$	434 (13)	$v_7(\pi)$	469 (9)	$v_7(A')$	296 (13)
$v_8(\pi)$	167 (4.6)	$v_8(\pi)$	193 (5)	$v_8(A')$	172 (19)
$v_9(\pi)$	52 (6.8)	$v_9(\pi)$	77 (3.4)	$v_9(A')$	82 (11.7)
				$v_{10}(A'')$	473 (8)
				$v_{11}(A'')$	259 (1)
				$v_{12}(A'')$	126 (10)

The computed harmonic frequencies of the molecules are given in *Table* 2-*Table* 4, and *Fig.* 3 depicts the v_1 modes of the isomers. Considering that the calculated harmonic frequencies of the lowest-energy isomer NC_3N compare very well (mostly to within 30 cm^{-1}) with experimental observations (see *Table* 8 in [Ref. 23]), the harmonic frequencies given in *Table* 2-*Table* 4 could provide useful guide for assigning the experimentally observed infrared spectra to specific isomer(s). The v_1 frequencies of all the linear isomers are those of stretching of the central bond of the molecule and the concomitant contraction of the two adjacent bonds. The magnitude of the harmonic frequencies of the isomers listed in *Table* 2 *Table* 4 may be considered as good measures to scrutinize the difference in chemical bonding among the isomers. For example, the v_1

modes of (a) and (b) depicted in *Fig.* 3 are very similar, consisting of stretching motions of the central four atoms. The only difference is that in (a) the v_1 mode is the stretching of the three CC bonds, while in (b) one of the bond is CN, whose length (1.300 A) is a bit shorter than the CC bond (1.360 A) in (a). Consequently, the n_1 frequency (2278 cm^{-1}) of (b) is a bit larger than that (2269 cm^{-1}) of (a). With the exception of (j), (m), (n), (q) and (r), the harmonic frequencies of the n_1 modes are 2200-2300 cm^{-1}. The v_1 frequencies of (j) and (q) are 2071 and 2016 cm^{-1}, respectively, while that of (r) is 1861 cm^{-1}. The six-membered ring isomers (m) and (n) are characterized by extremely low-frequency (1519 and 1587 cm^{-1}, respectively) v_1 modes of strong intensity. Out-of-plane bending modes of some linear isomers display quite small frequencies (52, 77

Table 3. Dipole moments μ (Debye), rotational constants B_e (GHz) and harmonic frequencies (cm^{-1}) of the isomers (g)-(l)

	(g)		(h)		(i)
μ	3.41	μ	-	μ	-
B_e	1.513401	B_e	1.470297	B_e	1.543058
$v_1(\sigma)$	2300 (304)	$v_1(\sigma_g)$	2295 (0.0)	$v_1(\sigma_g)$	2287 (0.0)
$v_2(\sigma)$	2011 (891)	$v_2(\sigma_g)$	1980 (0.0)	$v_2(\sigma_g)$	1803 (0.0)
$v_3(\sigma)$	1881 (34)	$v_3(\sigma_g)$	647 (0.0)	$v_3(\sigma_g)$	659 (0.0)
$v_4(\sigma)$	1219 (0.02)	$v_4(\sigma_u)$	2073 (388)	$v_4(\sigma_u)$	1974 (1560)
$v_5(\sigma)$	674 (0.05)	$v_5(\sigma_u)$	1251 (0.6)	$v_5(\sigma_u)$	1180 (7.5)
$v_6(\pi)$	421 (0.7)	$v_6(\pi_g)$	424 (0.0)	$v_6(\pi_g)$	332 (0.09)
$v_7(\pi)$	292 (0.2)	$v_7(\pi_g)$	240 (0.0)	$v_7(\pi_g)$	144 (0.0)
$v_8(\pi)$	185 (0.5)	$v_8(\pi_u)$	400 (0.0004)	$v_8(\pi_u)$	225 (0.0)
$v_9(\pi)$	78 (12)	$v_9(\pi_u)$	121 (6.8)	$v_9(\sigma_u)$	97 (18)

	(j)		(k)		(l)
μ	0.58	μ	0.87	μ	1.10
	8.83076		8.89792		8.77750
B_e	3.09217	B_e	2.86186	B_e	2.68219
	2.29022		2.16540		2.05441
$v_1(A')$	2071 (54)	$v_1(A')$	2208 (2.3)	$v_1(A')$	2237 (0.4)
$v_2(A')$	2040 (288)	$v_2(A')$	2076 (128)	$v_2(A')$	2229 (0.3)
$v_3(A')$	1536 (16)	$v_3(A')$	1536 (29)	$v_3(A')$	1533 (46)
$v_4(A')$	1104 (17)	$v_4(A')$	1101 (6.5)	$v_4(A')$	1113 (0.1)
$v_5(A')$	755 (6.8)	$v_5(A')$	731 (5.6)	$v_5(A')$	712 (2)
$v_6(A')$	500 (5.7)	$v_6(A')$	526 (2.7)	$v_6(A')$	546 (0.3)
$v_7(A')$	265 (1.3)	$v_7(A')$	293 (1)	$v_7(A')$	364 (1)
$v_8(A')$	145 (4.9)	$v_8(A')$	127 (3.5)	$v_8(A')$	128 (7)
$v_9(A')$	114 (2.7)	$v_9(A')$	119 (5.4)	$v_9(A')$	100 (2)
$v_{10}(A'')$	551 (6.6)	$v_{10}(A'')$	573 (0.3)	$v_{10}(A'')$	592 (1)
$v_{11}(A'')$	272 (0.0)	$v_{11}(A'')$	333 (4.8)	$v_{11}(A'')$	395 (0.0001)
$v_{12}(A'')$	190 (6.7)	$v_{12}(A'')$	196 (8.5)	$v_{12}(A'')$	215 (15)

and 78 cm^{-1} for (d), (e) and (g), respectively) indicating the molecules are floppy with respect to the mode, while those for branched or six-membered ring isomers (j) (n) are of much higher (200-300 cm^{-1}) harmonic frequencies. It seems that the v_1 modes of the linear isomers ((d), (g), (h) and (i)) displaying (antisymmetric) movements of more than two CN bonds are of higher frequencies near at 2300 cm^{-1}. The v_1 mode (2233 cm^{-1}) of the bent isomer (f) involves the antisymmetric movements of the central NC bond and the neighboring CC bond. Although the v_1 frequencies of the two lowest-energy isomers (a) and (b) are rather similar, the computed infrared spectrum of the isomer (b) is characterized by very strong absorption at 2003 cm^{-1}. This latter v_2 (s) mode involves a symmetric stretch-

ing of CN bond as shown in *Fig.* 4, and thus may be quite useful for identifying this potentially kinetically stable molecule either in the laboratory or in interstellar space by infrared spectroscopy. Likewise, the v_3 (s) frequency of the isomer (e) of the third-lowest energy at 1857 cm^{-1} may also be employed to characterize the molecule (see *Fig.* 4). The v_1 modes of the branched isomers (j), (k) and (l) involve the stretching of the terminal CN (or NC) bonds. The v_1 frequency of (j) is much smaller than those of (k) and (l), in line with the observation that the length of the terminal bond (1.193 A) is significantly larger (weaker) than those of (k) and (l). These branched isomers are also characterized by the v_3 (A`) frequencies at 1530-1540 cm^{-1}. The v_1 modes of the six-membered ring isomers (m) and

Table 4. Dipole moments μ (Debye), rotational constants B_e (GHz) and harmonic frequencies (cm^{-1}) of the isomers (m)-(r)

	(m)		(n)		(o)
μ	0.01	μ	0.68	μ	2.01
B_e	11.55135	B_e	10.16863	B_e	12.51683
	2.20694		5.68907		2.47965
	3.58910		3.64807		2.06964
$v_1(A')$	1519 (0.06)	$v_1(A')$	1587 (47)	$v_1(A')$	2236 (6.5)
$v_2(A')$	1474 (34)	$v_2(A')$	1258 (60)	$v_2(A)$	1835 (101)
$v_3(A')$	993 (0.003)	$v_3(A')$	1018 (25)	$v_3(A')$	1581 (119)
$v_4(A')$	890 (0.03)	$v_4(A')$	980 (8)	$v_4(A')$	1014 (33)
$v_5(A')$	791 (12)	$v_5(A')$	879 (6)	$v_5(A')$	701 (0.5)
$v_6(A')$	691 (80)	$v_6(A')$	716 (7.8)	$v_6(A')$	551 (12)
$v_7(A')$	609 (0.08)	$v_7(A')$	623 (37)	$v_7(A')$	400 (10)
$v_8(A')$	530 (0.001)	$v_8(A')$	519 (19)	$v_8(A')$	229 (6)
$v_9(A')$	295 (36)	$v_9(A')$	92 (54)	$v_9(A')$	105 (10)
$v_{10}(A'')$	539 (0.004)	$v_{10}(A'')$	594 (1.5)	$v_{10}(A'')$	560 (1.8)
$v_{11}(A'')$	528 (0.09)	$v_{11}(A'')$	406 (1)	$v_{11}(A'')$	310 (2)
$v_{12}(A'')$	242 (11)	$v_{12}(A'')$	298 (18)	$v_{12}(A'')$	213 (15)

	(p)		(q)		(r)
μ	1.58	μ	2.12	μ	0.45
B_e	12.06929	B_e	11.98710	B_e	23.92533
	2.68619		2.84718		2.28434
	2.19178		2.30071		2.28392
$v_1(A')$	2207 (36)	$v_1(A')$	2016 (103)	$v_1(A)$	1861 (13.5)
$v_2(A')$	1745 (139)	$v_2(A')$	1739 (154)	$v_2(A)$	1218 (0.02)
$v_3(A')$	1419 (393)	$v_3(A')$	1454 (256)	$v_3(A)$	744 (0.02)
$v_4(A')$	827 (5)	$v_4(A')$	911 (11)	$v_4(A)$	474 (2)
$v_5(A')$	748 (69)	$v_5(A')$	736 (15.7)	$v_5(A)$	423 (0.6)
$v_6(A')$	533 (13.6)	$v_6(A')$	464 (2)	$v_6(A)$	247 (0.14)
$v_7(A')$	484 (4.6)	$v_7(A')$	416 (32)	$v_7(A)$	161 (3)
$v_8(A')$	255 (6)	$v_8(A')$	188 (5.5)	$v_8(B)$	1580 (34.6)
$v_9(A')$	125 (10)	$v_9(A')$	112 (6.6)	$v_9(B)$	1084 (4.9)
$v_{10}(A'')$	419 (5.5)	$v_{10}(A'')$	314 (0.05)	$v_{10}(B)$	695 (28.5)
$v_{11}(A'')$	300 (0.06)	$v_{11}(A'')$	239 (0.2)	$v_{11}(B)$	471 (2.6)
$v_{12}(A'')$	118 (7)	$v_{12}(A'')$	126 (8)	$v_{12}(B)$	166 (4)

(n) are also depicted in *Fig.* 3. The movements of the atoms in the v_1 modes of these two isomers are not along the bonds, and they may be regarded as combination of stretching and in-plane bonding motions, giving very low characteristic infrared frequencies (1519 and 1587 cm^{-1}). The v_1 modes of (o), (p) and (q) consists of the stretching of the terminal CN (or NC) bonds, and that of the isomer (r) containing two three-membered rings is also of low frequency (1861 cm^{-1}), involving ring-distorting motion.

One of the more interesting questions concerning these molecules is the kinetic stability of the low-energy isomers such as (b). Since the isocyano isomer (b) NC$_3$NC is computed to be only 25.5 kcal/mol above (a), it may be a good candidate for astrophysical molecule. Since the energy difference between the two interstellar molecules HC$_3$N and HC$_2$NC is computed to be 26.6 kcal[24], the ratio of [NC$_4$N]/[NC$_3$NC] in interstellar media may be similar to the estimated interstellar abundance ratio [HC$_3$N]/[HC$_2$NC] of 20-60[25], if the barriers of isomerization of the two systems are comparable. We extensively searched for the dynamic (isomerization) path connecting these two lowest-energy
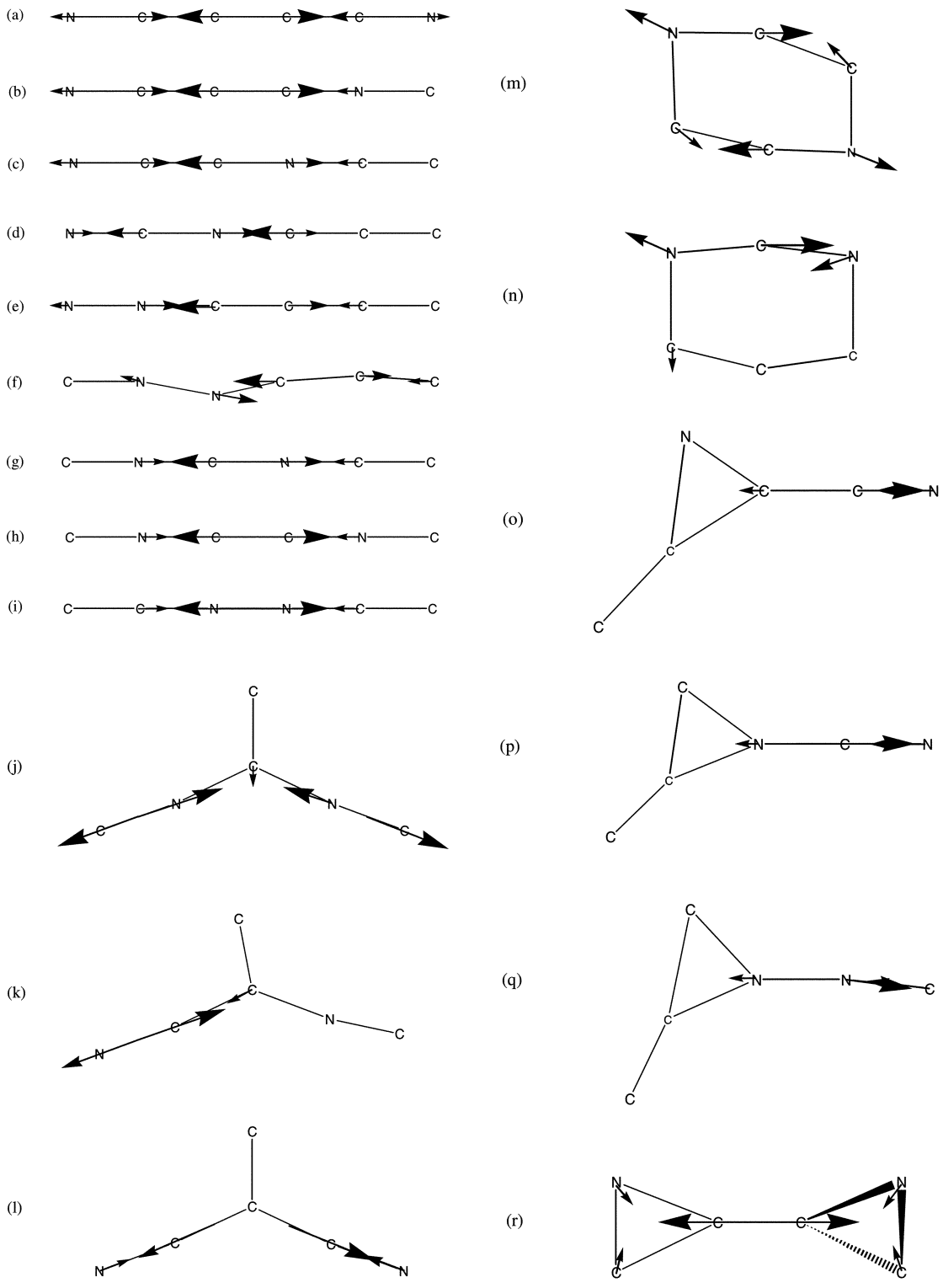
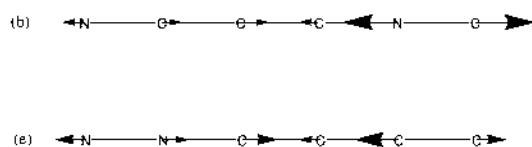Fig. 3. Vector presentation of the v_1 modes.

(b)   N————G————G————C————N————G

(e)   N————N————C————C————C————C

Fig. 4 $v_3(\sigma)$ modes of the isomers (b) and (e).

isomers NC_4N and NC_3NC, but failed to find one most probably due to the size of the molecules and the rather drastic movements of the nuclei along the isomerization reaction. This is left as a future work.

In conclusion, we have presented the density functional theory calculations for dicyanoacetylene and its geometrical isomers. Due to the complicated nature of the chemical bonding, a lot of isomers are predicted. We hope that the present calculations would stimulate further investigations on these interesting molecules.

REFERENCES

1. Avery, L. W.; Broten, N. W.; MacLeod, J. M.; Oka, T.; Kroto, H. W., *Astrophys. J.* **1976**, L173.

2. Broten, N. W.; Oka, T.; Avery, L. W.; MacLeod, J. M., *Astrophys. J.* **1978**, *223*, 1.105.

3. Bell, M.; Feldman, P. A.; Kwok, S.; Matthews, H. E., *Nature*, **1982**, *295*, 389.

4. Snyder, L. E.; Dykstra, C. E.; Bernholdt, D. in *Proceedings of a meeting on Masers, Molecules and Mass Outflows in Star Forming Regions*, ed. A. D. Haschick (1985).

5. Khanna, R. K.; Perera-Jarmer, M. A.; Ospina, M. J., *Spectrochim. Acta* **1987**, *43A*, 421.

6. Botschwina, P.; Flügge, J., *Chem. Phys. Lett.* **1991**, *180*,

7. Botschwina, P.; Flügge, J., *Chem. Phys. Lett.* **1993**, *210*, 495.

8. Jones, J. H., *J. Mol. Spectrosc.* **1974**, *49*, 82.

9. Botschwina, P., *J. Chem. Phys.* **1993**, *99*, 6217.

10. Ding, Y. H.; Huang, X. R.; Li, Z. S.; Sun, C. C., *J. Chem. Phys.* **1998**, *108*, 2024.

11. Ding, Y. H.; Li, Z. S.; Huang, X. R.; Sun, C. C., *J. Chem. Phys.* **2000**, *113*, 1745.

12. Kunde, V. G.; Aikin, A. C.; Hanel, R. A.; Jennings, D. E.; Maguire, W. C. Samuelson, R. A., *Nature* **1981**, *292*, 686.

13. Lee, S. *J. Phys. Chem.* **1996**, *100*, 13959.

14. Lee, B.; So, J.; Lee, S. *Bull. Korean Chem. Soc.* **1996**, *17*, 767.

15. Lee, S. *Chem. Phys. Lett.* **1997**, *268*, 69.

16. Lee, B.; Lee, S. *Chem. Phys. Lett.* **1998**, *286*, 171.

17. Kim, K.; Lee, B.; Lee, S. *Chem. Phys. Lett.* **1998**, *297*, 65.

18. Park, S.-W.; Lee, S. *Bull. Korean Chem. Soc.* **2002**, *23*, 1553.

19. Park, S.-W.; Park, K.-T.; Lee, S.; Kim, B. *Chem. Phys. Lett.* **2000**, *326*, 530.

20. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M; Gonzalez, C.; J. A. Pople, J. A. Gaussian, Inc. Pittsburgh, PA, 1995.

21. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

22. Lee, C.; Yang, W.; Parr, R. P. *Phys. Rev. B* **1988**, *37*, 785.

23. Lee, S. *J. Mol. Struct. (Theochem)* **1998**, *427*, 267.

24. Lee, S.-C.; Park, S.-W.; Lee, S. *Bull. Korean Chem. Soc.* **2000**, *21*, 734.

25. Kawaguchi, K.; Ohishi, M.; Ishikawa, S.-I.; Kaifu, N. *Astrophys. J.* **1992**, *386*, L51.