*J. Phys. Chem. A* **2001,** *105,* 7085−7090

# Theoretical Study on Structures and Stability of $HCCNN^+$ Isomers

**Yi-Hong Ding,* Ze-Sheng Li, Xu-Ri Huang, and Chia-Chung Sun**

*State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China*

*Received: January 25, 2001; In Final Form: May 3, 2001*

The detailed potential energy surface of $[HC_2N_2]^+$ is theoretically investigated at the B3LYP/6-311G(d,p) and CCSD(T)/6-311G(3df,2p) (single-point) levels. The linear isomer $HCCNN^+$ **5** is predicted to lie just 28.4 kcal/mol higher than the lowest-lying isomer $HNCCN^+$ **1** [the neutral species CCNN lies 82.7 kcal/mol above the lowest-energy NCCN (Ding et al., *J. Chem. Phys.* **2000**, *113*, 1745)]. Moreover, $HCCNN^+$ **5** resides in a very deep potential well stabilized by the barrier of 55.4 kcal/mol either toward dissociation or isomerization (the smallest barrier for CCNN is 42.1 kcal/mol). The calculated C-proton affinity of CCNN is very large as 211.2 kcal/mol. Therefore, CCNN may be significantly stabilized upon protonation at the terminal carbon both thermodynamically and kinetically, a phenomenon characteristic of carbene protonation. In addition, the nitrogen-protonated isomer $HNNCC^+$ **6** at 107.3 kcal/mol also possesses high kinetic stability of 51.9 kcal/mol. Our calculations indicate that while the neutral CCNN, the last kinetically stable isomer of the dicyanogen family, has not been characterized yet, its protonated form **5** and even **6** may be promising targets for future laboratory and interstellar detection. The possible formation of the two isomers is briefly discussed.

## 1. Introduction

The molecule $C_2N_2$ has received considerable attention due to its interest in several aspects such as in photochemistry and in space. NCCN (dicyanogen), the lowest-lying isomer of $C_2N_2$, was early synthesized in 1815.[1] The second and third isomers CNCN[2] (isocyanogen) and CNNC[3] (diisocyanoen) were not experimentally known until more than 170 years later. NCCN was also detected within Titan's upper atomosphere.[4] A number of theoretical investigations have been devoted to the structures, spectroscopies, and interconversion of the three linear species (see refs 5−7 and references cited in).

Compared with other $C_2N_2$ isomers, the fourth linear isomer CCNN has been paid much less attention to.[5−9] Recently, detailed theoretical analyses[6] have shown that CCNN might well be considered as a charge-transfer species with a HOMO-LUMO interaction between neutral $N_2$ (which donates charge with its $3\sigma_g$ HOMO) and $C_2$ (which in its valence state accepts charge with its $3\sigma_g$ LUMO). Moreover, the detailed potential energy surface surveys[5,7] have indicated that CCNN might be kinetically stable either toward dissociation or isomerizaton. Then, CCNN was termed as "the last kinetically stable isomer of dicyanogen".[7] However, any experimental information of CCNN is still not available despite an unsuccessful attempt.[9] In view of the low thermodynamical stability (CCNN lies 82.7 kcal/mol above NCCN[7]), the experimental condition for CCNN to be observed may be very severe.

Protonation is a very important process in ionic environments and in interstellar space. Up to now, many protonated species such as $HCO^+$, $HOC^+$, $H_3O^+$, $N_2H^+$, $HCS^+$, $H_3^+$, $HCNH^+$, and $HC_3NH^+$ have been detected in space.[10] Note that $HC_3NH^+$ is isoelectronic to the protonated cyanogen, $HNCCN^+$, which has been the subject of many experimental[11−19] and theoretical[13,20−22] studies. Very recently, the protonation of CNCN and CNNC has been called into theoretical attention.[22] Both the terminal carbon and terminal nitrogen sites of CNCN were notably found to have almost the same high proton affinity. The protonated forms $HNCCN^+$, $HCNCN^+$, $HNCNC^+$, and $HCNNC^+$ were all predicted to possess considerable kinetic stability and are expected to be observable.[22] Yet, the protonation of CCNN has not been subjected to both theoretical and experimental investigations.

In this paper, we attempt to establish a detailed potential energy surface of $[HC_2N_2]^+$ to explore the stability of protonated CCNN, i.e., $HCCNN^+$ or $HNNCC^+$, and to compare with other isomers. The calculated results show that protonation at terminal carbon can greatly stabilize CCNN both thermodynamically and kinetically which is usually typified by carbene protonation. The protonated form $HCCNN^+$ and even $HNNCC^+$ (high lying yet kinetically very stable) may represent very promising targets for future laboratory or interstellar detection. Possible formation strategies of $HCCNN^+$ and $HNNCC^+$ are discussed.

## 2. Computational Methods

All calculations are carried out using a Gaussian 98 program package.[23] The geometries of the $HC_2N_2^+$ isomers and interconversion transition states are fully optimized at the B3LYP/6-311G(d,p) level. Harmonic vibration frequencies are calculated at the same level to check whether the obtained structure is a stationary point or a saddle point. To get accurate energies, the CCSD(T)/6-311G(3df,2p) calculations are performed at the B3LYP/6-311G(d,p) geometries. The B3LYP/6-311G(d,p) zero-point vibration energies (ZPVE) are also included. For all transition states, the intrinsic reaction coordinate (IRC) calculations are carried out to test whether they connect the right isomers at the B3LYP/6-311G(d,p) level.

## 3. Results and Discussions

Fourteen isomers are located as minima and twenty-six interconversion transition states are obtained at the B3LYP/6-

---

* Corresponding author.

10.1021/jp0103225 CCC: \$20.00

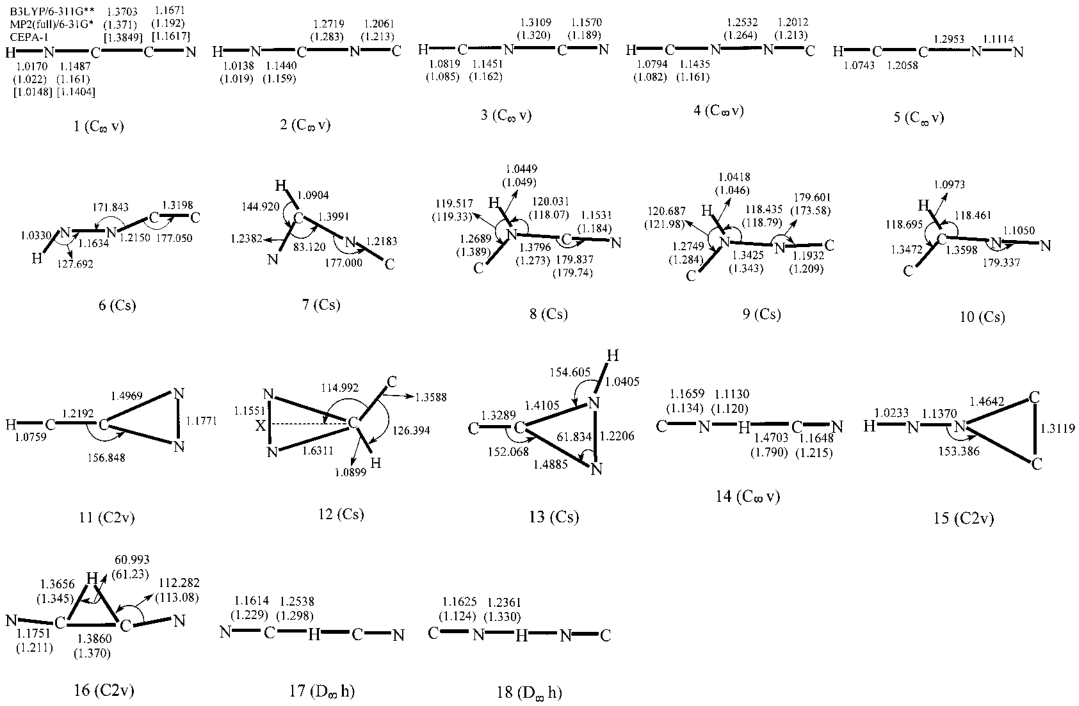

**Figure 1.** Optimized structures of $HC_2N_2^+$ isomers at the B3LYP/6-311G(d,p) level. Bond lengths are in angstroms and angles in degrees. The values at the CEPA-1[20] and MP2(full)/6-31G(d)[22] levels are also given in [] and (), respectively.

311G(d,p) level. For later discussions easier, the Arabic number **m** is used to denote various isomers, and the symbol **TSm/n** to denote the transition state between the isomers **m** and **n**. The optimized structures of the isomers and transition states are given in Figure 1 and Figure 2, respectively. The schematic potential energy surface of $[HC_2N_2]^+$ is presented in Figure 3. The harmonic vibration frequencies and infrared intensities of the isomers are listed in Table 1. In Table 2, the total and relative energies with inclusion of zero-point vibration energies (ZPVE) of the isomers and dissociation products are summarized, while those of the transition states are given in Table 3.

**3.1. Isomers.** The fourteen $HC_2N_2^+$ isomers can be classified into five groups as chainlike ($HNCCN^+$ **1**, $HNCNC^+$ **2**, $HCNCN^+$ **3**, $HCNNC^+$ **4**, $HCCNN^+$ **5**, and $HNNCC^+$ **6**), branched chainlike [$NC(H)NC^+$ **7**, $CN(H)CN^+$ **8**, $CN(H)NC^+$ **9,** and $CC(H)NN^+$ **10**], three-membered ring [$HC{-}cCN_2^+$ **11**, $C{-}cC(H)N_2^+$ **12,** and $C{-}cCN_2H^+$ **13**], and proton-bound dimer $CNHCN^+$ **14**. All the isomers except **14** can be considered as protonated forms of NCCN, CNCN, CNNC, CCNN, and $C{-}cCN_2$ at different sites. As shown in Figure 1, the B3LYP/6-311G(d,p) bond lengths of the isomer $HNCCN^+$ **1** are in excellent agreement with the recommended values by Botschwina and Sebald from their high-level CEPA-1 calculations.[20] The isomers **1**, **2**, **3**, **4**, **8**, **9,** and **14** have been calculated by Petrie.[22] Petrie also located several proton-bound isomers $NC(H)CN^+$ **16**, $NCHCN^+$ **17,** and $CNHNC^+$ **18** as minima at the MP2/6-31G(d) level, which are not minima at our B3LYP/6-311G(d,p) level. In fact, isomer **16** is a transition state **TS1/1**, which is associated with the H-shift between the two terminal N-atoms within isomer **1**. Another three-membered ring isomer $HN{-}cNC_2^+$ **15** is also unstable at the B3LYP/6-311G(d,p) level.

The relative energetic ordering (referred to as thermodynamical stability) of these isomers can be written as **1** (0.0) > **3** (14.8, *14.9*, *14.9*, *16.2*, *15.1*) > **2** (15.5, *15.5*, *15.2*, *15.8*, *16.0*) > **5** (28.4) > **4** (56.0, *56.2*, *56.0*, *56.0*, *56.0*) >**8** (73.5, *73.9*, *73.6*, *75.9*, *76.2*) > **10** (77.3) > **11** (79.0) > **7** (95.9) > **6** (107.3) > **9** (114.2) > **12** (119.9) > **13** (150.8) > **14** (179.9). Notice that the values in parentheses are relative energies (in kcal/mol) with reference to isomer **1** at the CCSD(T)/6-311G(3df,2p)//B3LYP/6-311G(d,p) + ΔZPVE level except isomer **14** [its relative energy is at the B3LYP/6-311G(d,p) level] and taken from Petrie's calculations (in italics).[22] The first, second, third, and fourth italic values are at the G2, G2(QCI), CBS, and CBS-APNO levels, respectively. Clearly, the agreement between our calculated energies and Petrie's values is excellent. Generally, protonation at internal sites is much less favorable than that at terminal sites. One exception is that isomer $CC(H)NN^+$ **10** is 30 kcal/mol lower than $HNNCC^+$ **6**. An interesting point is that both the isomers **2** and **3** have very close energies as predicted by Petrie.[22]

The former five low-lying isomers are $HNCCN^+$ **1** (0.0), $HCNCN^+$ **3** (14.8), $HNCNC^+$ **2** (15.5), $HCCNN^+$ **5** (28.4), and $HCNNC^+$ **4** (56.0). Comparing with the deprotoned isomers NCCN (0.0), CNCN (23.6), CNNC (70.8), and CCNN (82.7),[7] we can easily find that the relative thermodynamical stability of the NCCN, CNCN, CNNC, and CCNN can be more or less improved upon protonation. Most noticeably, protonation brings the largest stabilization for CCNN (the relative thermodynamical stability from CCNN to $HCCNN^+$ is lowered by 54.3 kcal/mol).

**3.2. Kinetic Stability.** In addition to the thermodynamical stability, a discussion of the kinetic stability of various $HC_2N_2^+$ isomers may be of more interest. The smallest isomerization or dissociation barrier may usually govern the kinetic stability of an isomer. A high kinetic stability may make it difficult for an isomer (once it is formed) to take further conversion to other isomers or to fragments and may thus enhance the probability of its experimental observation. For simplicity, the details of the conversion between various $HC_2N_2^+$ isomers, as shown in Figure 3, will not be presented. Since no transition state can be located for the proton-bound isomer **14**, it is not depicted in Figure 3. Note that **TS1/2**, **TS2/8***, **TS3/4**, **TS3/8**, **TS4/9,** and **TS9/9** have been obtained by Petrie.[22]

From Figure 3, we can readily find that six isomers **1**, **2**, **3**, **4**, **5,** and **6** lie in considerably deep potential wells either against isomerization or dissociation. The corresponding smallest conversion barriers are 51.3 (**1** → **2**), 35.8 (**2** → **1**), 66.1 (**3** →

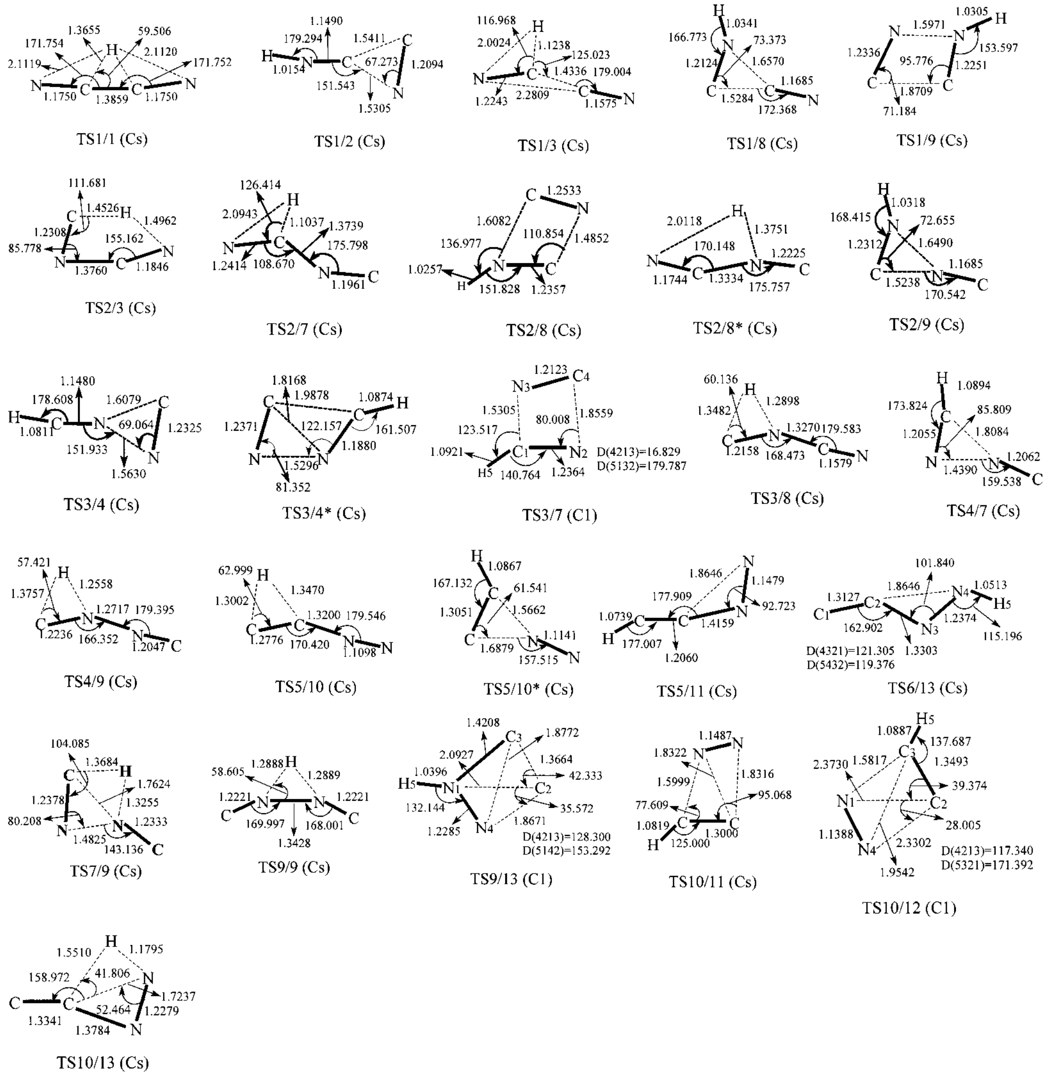

**Figure 2.** Optimized structures of $HC_2N_2^+$ transition states at the B3LYP/6-311G(d,p) level. Bond lengths are in angstroms and angles in degrees.

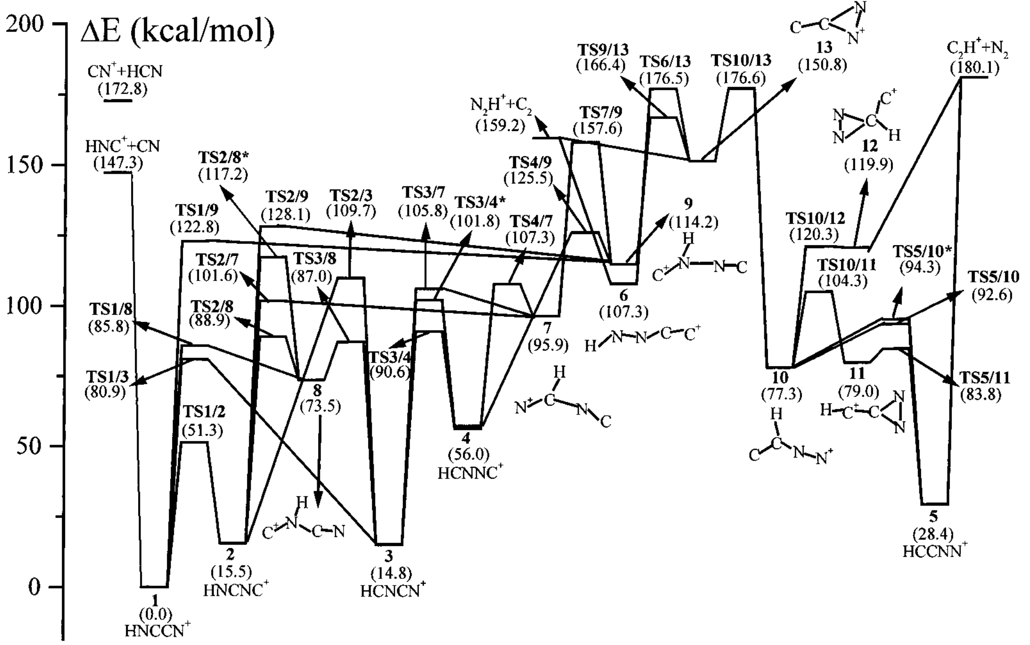

**Figure 3.** Schematic potential energy surface of $[HC_2N_2]^+$ at the CCSD(T)/6-311G(3df,2p)//B3LYP/6-311G(d,p) + ΔZPVE level.

**1**), 34.6 (**4** → **3**), 55.4 (**5** → **11**), and 51.9 (**6** → $N_2H^+ + C_2$) kcal/mol. Yet, the remaining isomers **7**, **8**, **9**, **10**, **11**, **12**, and **13** reside in much shallower wells with the barriers 5.7 (**7** → **2**), 13.5 (**8** → **3**), 8.6 (**9** → **1**), 15.3 (**10** → **5**), 4.8 (**11** → **5**), 0.4

**TABLE 1: Harmonic Vibration Frequencies (cm$^{-1}$) and Infrared Intensities in Parentheses (km/mol) of $HC_2N_2^+$ Isomers at the B3LYP/6-311G(d,p) Level**

| species | harmonic vibration frequencies (infrared intensities) |
|---|---|
| $HNCCN^+$ **1** | 229 (0) 559 (0) 603 (151) 899 (16) 2279 (26) 2458 (245) 3607 (1017) |
| $HNCNC^+$ **2** | 169 (2) 502 (144) 540 (22) 1013 (3) 2041 (567) 2474 (523) 3645 (1027) |
| $HCNCN^+$ **3** | 230 (2) 508 (11) 755 (26) 948 (9) 2249 (107) 2393 (23) 3323 (369) |
| $HCNNC^+$ **4** | 164 (8) 428 (1) 711 (30) 1014 (2) 2054 (637) 2381 (58) 3346 (397) |
| $HCCNN^+$ **5** | 221 (4) 534 (5) 793 (23) 978 (4) 2203 (227) 2375 (243) 3381 (127) |
| $HNNCC^+$ **6** | 138 (2) 156 (0) 535 (37) 572 (3) 794 (524) 991 (36) 1854 (173) 2308 (1183) 3358 (681) |
| $NC(H)NC^+$ **7** | 154 (4) 236 (17) 305 (15) 871 (17) 913 (10) 1091 (5) 1730 (46) 1940 (535) 3174 (145) |
| $CN(H)CN^+$ **8** | 154 (8) 352 (9) 386 (9) 680 (94) 952 (1) 1199 (11) 1641 (185) 2363 (29) 3207 (376) |
| $CN(H)NC^+$ **9** | 104 (4) 184 (24) 271 (25) 687 (80) 944 (4) 1240 (5) 1624 (211) 2083 (180) 3241 (328) |
| $CC(H)NN^+$ **10** | 226 (11) 424 (5) 472 (8) 650 (38) 942 (1) 1092 (3) 1603 (268) 2382 (63) 3064 (168) |
| $HC{-}cCN_2^+$ **11** | 242 (11) 343 (4) 536 (1) 658 (51) 764 (24) 894 (7) 1757 (222) 2112 (107) 3357 (149) |
| $C{-}cC(H)N_2^+$ **12** | 143 (3) 247 (20) 446 (0) 627 (26) 802 (53) 1078 (5) 1499 (258) 1984 (17) 3138 (119) |
| $C{-}cCN_2(H)^+$ **13** | 164 (1) 276 (10) 308 (23) 670 (85) 841 (18) 1150 (62) 1600 (84) 1849 (63) 3278 (501) |
| $CNHCN^+$ **14** | 103 (1) 139 (31) 143 (30) 190 (31) 377 (0) 381 (0) 1534 (482) 1534 (482) 2195 (4) 2307 (190) |
| $HN{-}cNC_2^+$ **15** | 721i (107) 567i (185) 216i (186) 496 (12) 508 (2) 818 (67) 1592 (12) 2097 (212) 3517 (1440) |
| $NC(H)CN^+$ **16** | 1064i (875) 218 (27) 246 (54) 457 (2) 506 (0) 870 (3) 1853 (198) 2114 (116) 2288 (6) |
| $NCHCN^+$ **17** | 618i (17) 161 (16) 270 (0) 397 (0) 1638 (1020) 2250 (0) 2329 (109) |
| $CNHNC^+$ **18** | 713i (442) 133 (13) 244 (0) 468 (0) 858 (10) 2186 (0) 2221 (37) |

**TABLE 2: *I* Total (a.u.) and Relative (kcal/mol) (in parentheses) of the $HC_2N_2^+$ Isomers at the B3LYP/6-311G(d,p) and Single-Point CCSD(T)/6-311G(3df,2p) Levels**

| species | B3LYP/6-311G(d,p) | CCSD(T)/6-311G(3df,2p)// B3LYP/6-311G(d,p) | ΔZPVE |
|---|---|---|---|
| $HNCCN^+$ **1** | −185.9652348 (0.0) | −185.6108742 (0.0) | 0.027397 (0.0) |
| $HNCNC^+$ **2** | −185.9428200 (14.1) | −185.5851452 (16.1) | 0.026418 (−0.6) |
| $HCNCN^+$ **3** | −185.9407532 (15.4) | −185.5869191 (15.0) | 0.027105 (−0.2) |
| $HCNNC^+$ **4** | −185.8773143 (55.2) | −185.5202746 (56.9) | 0.025973 (−0.9) |
| $HCCNN^+$ **5** | −185.9214385 (27.5) | −185.5656715 (28.4) | 0.027412 (0.0) |
| $HNNCC^+$ **6** | −185.7996090 (103.9) | −185.4367742 (109.2) | 0.024388 (−1.9) |
| $NC(H)NC^+$ **7** | −185.8059162 (100.0) | −185.4543125 (98.2) | 0.023722 (−2.3) |
| $CN(H)CN^+$ **8** | −185.8406620 (78.2) | −185.4911998 (75.1) | 0.024913 (−1.6) |
| $CN(H)NC^+$ **9** | −185.7770911 (118.1) | −185.4249954 (116.6) | 0.023643 (−2.4) |
| $CC(H)NN^+$ **10** | −185.8357065 (81.3) | −185.4849578 (79.0) | 0.024729 (−1.7) |
| $HC{-}cCN_2^+$ **11** | −185.8340832 (82.3) | −185.4822353 (80.7) | 0.024290 (−1.7) |
| $C{-}cC(H)N_2^+$ **12** | −185.7626099 (127.1) | −185.4152296 (122.8) | 0.022701 (−2.9) |
| $C{-}cCN_2(H)^+$ **13** | −185.7136235 (157.9) | −185.3662951 (153.5) | 0.023096 (−2.7) |
| $CNHCN^+$ **14** | −185.6786222 (179.9) | | |
| $HN{-}cNCC^+$ **15** | −185.7135024 (158.0) | | |
| $NC(H)CN^+$ **16** | −185.8106039 (97.0) | | |
| $NCHCN^+$ **17** | −185.6807356 (178.5) | | |
| $CNHNC^+$ **18** | −185.6904789 (172.4) | | |
| $H^+ + NCCN$ | −185.7046716 (163.5) | −185.3508602 (163.2) | 0.016533 (−6.8) |
| $H^+ + CNCN$ | −185.6666144 (187.4) | −185.3122778 (187.4) | 0.015809 (−7.3) |
| $H^+ + CNNC$ | −185.5908165 (235.0) | −185.2361027 (235.2) | 0.014726 (−8.0) |
| $H^+ + CCNN$ | −185.5768491 (243.7) | −185.2170183 (247.1) | 0.015456 (−7.5) |
| $HCN^+ + CN$ | −185.6729407 (183.4) | −185.3286806 (177.1) | 0.023004 (−2.8) |
| $HNC^+ + CN$ | −185.7208018 (153.4) | −185.3761795 (147.3) | 0.021130 (−3.9) |
| $CN^+ + HCN$ | −185.6324439 (208.8) | −185.3355294 (172.8) | 0.021206 (−3.9) |
| $CN^+ + HNC$ | −185.6088149 (223.7) | −185.3117732 (187.7) | 0.020409 (−4.4) |
| $C_2H^+ + N_2$ | −185.6514263 (196.9) | −185.3178911 (183.8) | 0.021510 (−3.7) |
| $N_2^+ + C_2H$ | −185.6052516 (225.9) | −185.2682666 (215.0) | 0.019471 (−5.0) |
| $N_2H^+ + C_2$ | −185.6531670 (195.8) | −185.3504841 (163.4) | 0.020677 (−4.2) |
| $C_2^+ + N_2H$ | −185.5100885 (285.6) | −185.0705677 (339.0) | 0.016766 (−6.7) |

(**12** → **10**), and 8.4 (**13** → $N_2H^+ + C_2$) kcal/mol, respectively. Surely, the isomers **1**, **2**, **3**, **4**, **5,** and **6** may be most possibly observable since they each have the kinetic stability of more than 30 kcal/mol. It has been shown that the kinetic stability of NCCN, CNCN, CNNC, and CCNN are 59.7, 36.1, 34.2, and 42.1 kcal/mol, respectively.[7] Then, upon protonation, the kinetic stability of structure NCCN (at terminal N) is lowered by about 8 kcal/mol, whereas that of CNCN (at terminal N) and CNNC (at terminal C) is almost unchanged. Also, protonation of CNCN at terminal C is kinetically much more favorable than that at terminal N though the thermodynamical stability of the protonated forms at both sites is almost the same. Moreover, the kinetic stability of $HCCNN^+$ **5** and $HNNCC^+$ **6**, which are the respective protonated forms of CCNN at terminal carbon and terminal nitrogen, is significantly larger than that of CCNN. Similar to the isomers $HNCNC^+$ **2** and $HCNCN^+$ **3**, the isomers $HCCNN^+$ **5** and $HNNCC^+$ **6** are separated from conversion to each other by very high barriers.

**3.3. Laboratory and Interstellar Implications.** Now we know that for the protonated system $[HC_2N_2]^+$, the six chainlike isomers $HNCCN^+$ **1**, $HNCNC^+$ **2**, $HCNCN^+$ **3**, $HCNNC^+$ **4**, $HCCNN^+$ **5,** and $HNNCC^+$ **6** may be observable either in laboratory or in interstellar space due to their considerable kinetic stability. The lowest-lying isomer **1** has been studied experimentally[11−19] and expected to have great abundance in interstellar space. However, the remaining four isomers are still unknown. Since Petrie has discussed the properties of the isomers **1**, **2**, **3,** and **4** in great detail,[22] we focus on the isomers **5** and **6**.

At the CCSD(T)/6-311G(3df,2p)//B3LYP/6-311G(d,p) +

**TABLE 3: Total (a.u.) and Relative (kcal/mol) (in parentheses) of the $HC_2N_2^+$ Interconversion Transition States at the B3LYP/6-311G(d,p) and Single-Point CCSD(T)/6-311G(3df,2p) Levels**

| species | B3LYP/6-311G(d,p) | CCSD(T)/6-311G(3df,2p)//B3LYP/6-311G(d,p) | ΔZPVE |
|---|---|---|---|
| **TS1/1** | −185.8106034 (97.0) | −185.4569131 (96.6) | 0.019483 (−5.0) |
| **TS1/2** | −185.8762026 (55.9) | −185.5256492 (53.5) | 0.023961 (−2.2) |
| **TS1/3** | −185.8330623 (89.9) | −185.4775344 (83.7) | 0.022943 (−2.8) |
| **TS1/8** | −185.8191962 (91.6) | −185.4698237 (88.5) | 0.023171 (−2.7) |
| **TS1/9** | −185.7563559 (131.1) | −185.4096649 (126.3) | 0.021769 (−3.5) |
| **TS2/3** | −185.7763959 (118.5) | −185.4284855 (114.5) | 0.019779 (−4.8) |
| **TS2/7** | −185.8028970 (101.9) | −185.4443233 (104.5) | 0.022784 (−2.9) |
| **TS2/8** | −185.8071484 (99.2) | −185.4647809 (91.7) | 0.022972 (−2.8) |
| **TS2/8*** | −185.7714972 (121.6) | −185.4155646 (122.6) | 0.018835 (−5.4) |
| **TS2/9** | −185.7529263 (133.2) | −185.4001480 (132.2) | 0.020896 (−4.1) |
| **TS3/4** | −185.8122501 (96.0) | −185.4620777 (93.4) | 0.022971 (−2.8) |
| **TS3/4*** | −185.7907035 (109.5) | −185.4441141 (104.6) | 0.022954 (−2.8) |
| **TS3/7** | −185.7849354 (113.1) | −185.4373192 (108.9) | 0.022490 (−3.1) |
| **TS3/8** | −185.8174769 (92.7) | −185.4650562 (91.5) | 0.020149 (−4.5) |
| **TS4/7** | −185.7872486 (111.7) | −185.4344072 (110.7) | 0.022053 (−3.4) |
| **TS4/9** | −185.7574151 (130.4) | −185.4025103 (130.7) | 0.019088 (−5.2) |
| **TS5/10** | −185.8091174 (98.0) | −185.4560497 (97.1) | 0.020262 (−4.5) |
| **TS5/10*** | −185.8047419 (100.7) | −185.4561834 (97.1) | 0.022893 (−2.8) |
| **TS5/11** | −185.8261690 (87.3) | −185.4737587 (86.0) | 0.023847 (−2.2) |
| **TS6/13** | −185.6739276 (182.8) | −185.3230523 (180.6) | 0.020796 (−4.1) |
| **TS7/9** | −185.7002322 (166.3) | −185.3506230 (163.3) | 0.018249 (−5.7) |
| **TS9/9** | −185.6998835 (166.5) | −185.3426384 (168.3) | 0.017378 (−6.3) |
| **TS9/13** | −185.6837908 (176.6) | −185.3418042 (168.8) | 0.023581 (−2.4) |
| **TS10/11** | −185.7838299 (113.8) | −185.4402547 (107.0) | 0.023138 (−2.7) |
| **TS10/12** | −185.7597628 (128.9) | −185.4137773 (123.7) | 0.021915 (−3.4) |
| **TS10/13** | −185.6672167 (187.0) | −185.3206695 (182.1) | 0.018633 (−5.5) |

ΔZPVE level, the calculated proton affinities (PA) for the isomers NCCN at terminal N, CNCN at terminal C, CNCN at terminal N, and CNNC at terminal C are 156.4 (*156.3*, *156.5*, *156.6*, *156.6*), 165.3 (*165.0*, *165.8*, *164.5*, *166.3*), 164.6 (*165.7*, *165.6*, *164.7*, *165.2*), and 171.2 (*172.0*, *171.7*, *172.1*, *172.9*) kcal/mol, respectively. Surely, our values are very comparable to Petrie's corresponding ones (in italics) at the G2 (the first italic), G2(QCI) (the second italic), CBS-Q (the third italic), and CBS-APNQ (the fourth italic) levels.[22] It is now clear that all theoretical PAs of NCCN are in excellent agreement with the experimentally determined value 155.6 kcal/mol by Milligan et al.[18] For the isomer CCNN, protonation at terminal C and N gives the respective proton affinities 211.2 and 132.3 kcal/mol. Interestingly, the PA value of CCNN at terminal C is the largest of all $C_2N_2$ isomers. This phenomenon is well characteristic of carbene protonation such as c-$C_3H_2$ (227.3) and CCCO (210.4), etc. The values in parentheses are PAs in kcal/mol taken from ref 24.

Due to the rather large PA value, it is very natural that one effective pathway to form the isomer HCCNN$^+$ is via proton transfer to the neutral CCNN. In the ion−molecule reactions involving NCCN, Amano and Scappini found a very poor yield of HNCCN$^+$.[16] They thought that two possible reasons might be ascribed to this, i.e., (1) many CN containing species such as HCN (170.4), HNC (184.6), and $HC_3N$ (179.5) produced from secondary reactions have larger PA values (from ref 24) than NCCN, and proton transfer to these species may be more competitive than to NCCN; (2) once HNCCN$^+$ is formed, fast dissociation recombination of HNCCN$^+$ with electrons and proton transfer reactions may occur to give NCCN again. Accordingly, they proposed a mechanism of HNCCN$^+$ for its formation and depletion via the reactions (I) and (II), respectively:

$$\mathrm{HX^+ + NCCN \rightarrow HNCCN^+ + X\ [X = H_2\ (100.9),\ N_2\ (118.0),\ CO\ (142.0),\ OCS\ (150.2),\ C_2H_2\ (153.3),\ OH\ (141.8),\ etc.,\ with\ smaller\ PAs\ than\ NCCN]} \quad \text{(I)}$$

$$\mathrm{HNCCN^+ + Y \rightarrow NCCN + HY^+\ [Y{=}C_2H_4\ (162.6),\ H_2O\ (165.0),\ H_2S\ (168.0),\ CH_3OH\ (180.3),\ NH_2\ (184.8),\ NH_3\ (204.0),\ etc.,\ with\ larger\ PAs\ than\ NCCN]} \quad \text{(II)}$$

However, the situation might be somewhat different for CCNN. The very large PA value (211.2 kcal/mol) at the C-site of CCNN, which is larger than many gas-phase neutral species, enables us to predict that CCNN can very efficiently abstract proton from the other neutral species to form HCCNN$^+$, but it can very difficultly lose a proton to form CCNN. Then, the species HCCNN$^+$ **5** may be very stable against proton-loss process once it is formed. The observation of the high-lying isomer HNNCC$^+$ may also be possible in the laboratory due to its very high kinetic stability. However, proton transfer from HNNCC$^+$ to other neutral species with larger PAs may also easily take place to recycle CCNN, and then CCNN further abstracts a proton to form HCCNN$^+$. This may be indicative of the much less abundance of HNNCC$^+$ than HCCNN$^+$.

It is interesting to compare the interconversion between the two terminus-protonated isomers of both CNCN and CCNN. Surely, the conversion between HNCNC$^+$ **2** and HCNCN$^+$ **3** and that between HCCNN$^+$ **5** and HNNCC$^+$ **6** is kinetically prohibited via intramolecular processes as shown in Figure 3. Yet, such conversion might be realized via intermolecular processes following the so-called "forth-and-back proton transfer",[25] "proton shuttling",[26] or "proton transport catalysis"[27] mechanism as:

$$\mathrm{ABH^+ + Y \rightarrow [AB...HY]^+ \rightarrow [BA...HY]^+ \rightarrow [BAH...Y]^+ \rightarrow BAH^+ + Y} \quad \text{(III)}$$

Since HNCNC$^+$ **2** and HCNCN$^+$ **3** are virtually identical in energy, the conversion between them seems unlikely to take place. Then, it may represent "a significant experimental challenge to distinguish between the two CNCN protonated isomers, or to characterize the true preferred site of protonation" as stated by Petrie.[22] However, reaction III is very viable from HNNCC$^+$ **6** to HCCNN$^+$ **5** due to the overall large exothermicity 78.9 kcal/mol, and the C-protonation is surely the most feasible.

In addition to the protonation of CCNN, the species HCCNN$^+$ **5** and HNNCC$^+$ **6** may be formed alternatively via the dissociative electron impact of relevant larger neutral compounds possessing the HCCNN connectivity as a structural component. In fact, many cations (recent examples are $C_5H_2^+$,[28] SiNCO$^+$,[29] $C_3N_2^+$,[30] etc.) have been proven to be efficiently generated via such methods. In view of the fact that formation of the neutral CCNN is thermodynamically much less favorable than other dicyanogen isomers, such methods may offer the most probable route to the experimental generation of HCCNN$^+$ **5** and HNNCC$^+$ **6**.

To aid their future characterization either in laboratory or in interstellar space, the knowledge about the structural and spectroscopic features HCCNN$^+$ **5** and HNNCC$^+$ **6** is useful. As shown in Figure 1, the CC and NN bonds of linear HCCNN$^+$ **5** are very short as 1.2058 and 1.1114 Å, respectively, very close to the corresponding triple bonds in acetylene HC≡CH (1.203 Å)[31] and nitrogen N≡N (1.095 Å).[32] The B3LYP/6-311G(d,p) Mulliken charges are 0.2347, 0.3440, 0.2220, −0.0078, and 0.2070 *e* for H, C, C, N, and N, respectively, placing most of the positive charge on $C_2H$ part. Then, isomer **5** can be viewed as consisting of HCC$^+$ and $N_2$ components. The calculated dipole moment of HCCNN$^+$ **5** is considerable as 2.4538 D, pointing to the terminal H-end away from the N-end. For the bent isomer $HNNCC^+$ **6** with $C_s$ symmetry, the CC (1.1634 Å) and NN (1.3198 Å) bond lengths are longer than those in isomer **5**. The B3LYP/6-311G(d,p) Mulliken charge distribution for H, N, N, C, and C is 0.3675, 0.3828, −0.0062, 0.3279, and 0.2955 *e*, respectively, with comparable positive charge placed on $N_2H$ and $C_2$ parts. The electronic dipole moment of $HNNCC^+$ **6** is large as 3.5255 D with its direction pointing from the terminal C-atom to the terminal H-atom. As listed in Table 1, the dominant vibration frequencies for $HCCNN^+$ **5** are at 2203 and 2375 $cm^{-1}$ with the corresponding infrared intensities 227 and 243 km/mol. One sideband is at 3381 $cm^{-1}$ with the intensity 127 km/mol. For $HNNCC^+$ **6**, the strongest vibration is at 2308 $cm^{-1}$ with the intensity 1183 km/mol. Yet, the 794, 1854, and 3358 $cm^{-1}$ bands are also very strong with the intensities 524, 173, and 681 km/mol, respectively. In a word, we expect that while the high-lying yet kinetically very stable neutral species CCNN is still experimentally and astrophysically unknown, its low-lying protonated form $HCCNN^+$ **5** may be a very promising target for future laboratory and astrophysical detection.

## 4. Conclusions

By building up a schematic potential energy surface of $[HC_2N_2]^+$ at the CCSD(T)/6-311G(3df,2p)//B3LYP/6-311G(d,p) level with ZPVE correction, we mainly investigate the structures, spectroscopics, and stability of the CCNN protonated forms and compare with other isomers. We find that although CCNN is energetically very high-lying (82.7 kcal/mol above NCCN), its C-end protonated isomer $HCCNN^+$ lies only 28.4 kcal/mol above the lowest-lying $HNCCN^+$ and even 27.6 kcal/mol below $HCNNC^+$. Moreover, the kinetic stability of $HCCNN^+$ is 55.4 kcal/mol, much larger than that of CCNN (42.1 kcal/mol). Then, protonation at the terminal carbon can greatly stabilize CCNN both thermodynamically and kinetically. The proton affinity of CCNN at the C-end is very large as 211.2 kcal/mol. The terminal N-protonated isomer $HNNCC^+$ is very high-lying (107.3 kcal/mol above $HNCCN^+$), yet it also possesses very high kinetic stability, 51.9 kcal/mol. Both the isomers $HCCNN^+$ and $HNNCC^+$ may represent promising targets for future laboratory and interstellar identification to provide the existing evidence of CCNN, the last kinetically stable isomer of the $C_2N_2$ family.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (No. 29892168, 20073014), Doctor Foundation of Educational Ministry, Foundation for University Key Teacher by the Ministry of Education and Key Term of Science and Technology by the Ministry of Education of China. The authors are very thankful to the reviewers for their helpful comments.

## References and Notes

(1) Gray-Lussac, L. J. *Ann. Chim.* (Paris) **1815**, *95*, 175.

(2) van der Does, T.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 936.

(3) Stroh, F.; Winnewisser, B. P.; Winnewisser, M.; Reisenauer, H. P.; Maier, G.; Goede, S. J.; Bickelhaupt, F. *Chem. Phys. Lett.* **1989**, *160*, 105.

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

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

(6) Bickelhaupt, F. M.; Bickelhaupt, F. *Chem. Eur. J.* **1999**, *5*, 162.

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

(8) Scheller, M. K.; Cederbaum, L. S.; Tarantelli, F. *J. Am. Chem. Soc.* **1990**, *112*, 9484.

(9) Maier, G.; Reisenauer, H. P.; Eckwert, J.; Sierakowski, C.; Stumpf, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1218.

(10) Winnewisser, G. *J. Mol. Struct.* **1997**, 408/409.

(11) Inoué, M.; Cotton, M. *Adv. Mass Spectrom.* **1966**, *3*, 339.

(12) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1984**, *57*, 211.

(13) Deakyne, C. A.; Meot-Ner (Mautner), M.; Buckley, T. J.; Metz, R. *J. Chem. Phys.* **1986**, *86*, 2334.

(14) Petrie, S.; Freeman, C. G.; McEwan, M. J.; Meot-Ner (Mautner), M. *Int. J. Mass Spectrom. Ion Processes* **1989**, *90*, 241.

(15) Warner, H. E.; Amano, T. *J. Mol. Spectrosc.* **1991**, *145*, 66.

(16) Amano, T.; Scappini, F. *J. Chem. Phys.* **1991**, *95*, 2280.

(17) Cazzoli, G.; Degli Esposti, C.; Scappini, F. *J. Chem. Phys.* **1992**, *97*, 6187.

(18) Milligan, D. B.; Fairley, D. A.; Meot-Ner (Mautner), M.; McEwan, M. *Int. J. Mass Spectrom.* **1998**, *179*/*180*, 285.

(19) Gottlieb, C. A.; Apponi, A. J.; McCarthy, M. C.; Thaddeus, P. *J. Chem. Phys.* **2000**, *113*, 1910.

(20) Botschwina, P.; Sebald, P. *Chem. Phys.* **1990**, *141*, 311.

(21) Haese, N. N.; Woods, R. C. *J. Chem. Phys.* **1980**, *73*, 4521.

(22) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 7835.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(25) Petrie, S.; Freeman, C. G.; Meot-Ner, M.; McEwan, M.; Ferguso, E. E. *J. Am. Chem. Soc.* **1990**, *112*, 7121.

(26) Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95.

(27) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 7573.

(28) Blanksby, S.; Dua, S.; Bowie, J. H.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1998**, *102*, 9949.

(29) Srinivas, R.; Vivekananda, S.; Schröder, D.; Schwarz, H. *Chem. Phys. Lett.* **2000**, *316*, 243.

(30) Blanksby, S.; Dua, S.; Bowie, J. H.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **2000**, *104*, 11248.

(31) Strey, G.; Mills, I. M. *J. Mol. Spectrosc.* **1976**, *59*, 103.

(32) Krummacher, S.; Schmidt, V.; Wuilleumier, F. *J. Phys. B* **1980**, *13*, 3993.