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Theoretical Study on Structures and Stability of NC_3S Isomers

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A rather exhaustive theoretical study is performed on the doublet potential energy surface (PES) of the NC_3S system at the B3LYP/6-311G(d), QCISD/6-311G(d), and single-point CCSD(T)/6-311G(2df) levels. A total of 40 minimum isomers are located including chainlike, cyclic, cagelike, and weakly bound species, which are connected by 81 interconversion transition states. At the CCSD(T)/6-311G(2df)//QCISD/6-311G(d)+ZPVE level, the lowest-lying isomer is a linear structure NCCCS **1** (0.0 kcal/mol). Its calculated vibrational frequencies and rotational constant are in good agreement with recent experimental values. Additionally, eight new isomers with high kinetic stability are predicted to be possible candidates for future experimental and astrophysical detection. They include five chainlike species, i.e., linear CNCCS **2** (26.9), bent CCNCS **3** (56.9), bent CCSCN **4** (62.7), bent CCSNC **5** (85.4), linear CCCNS **6** (67.0), and three three-membered ring species NC-cCCS **9** (34.2), **9′** (40.9), and CN-cCCS **10** (57.1). Structural analysis show that these isomers can be considered as adducts formed by various S atom attacks (terminal atomic-addition, side C≡C addition and internal single-bond insertion) to the C_3N radical (CCCN or CCNC). The present NC_3S potential energy surface represents the first detailed study on the isomerization and dissociation mechanism of the NC_nS series, and it is expected be useful and informative for further investigation of even larger NC_nS species for which complete isomeric survey is very expensive.

1. Introduction

Nitrogen and sulfur chemistry have received considerable attention from various aspects. One particular interest is their possible role in astrophysical chemistry. Larger C_nN[1] and C_nS[2] species have been extensively studied both theoretically and experimentally and have been expected to be carriers of some interstellar bands. The mixed NC_nS species may present a bridge between the C_nN and C_nS clusters. Understanding the structural, bonding, and stability properties of NC_nS clusters may be helpful for future identification of new N-, C-, and S-containing species either in the laboratory or in space. On the other hand, NC_nS can formally be considered as N-doped C_nS clusters or S-doped C_nN clusters. Knowledge of the structures and stability of NC_nS can help gain insight into the doping effect of C_nN and C_nS materials. However despite the potential importance, the ternary series NC_nS ($n > 1$) have received very little attention.[3−5] Pedersen et al.[3] found NCCCS and NCCCCS to possess high stability in gas phase by using neutralization-reionization experiments. McCarthy et al.[4] observed the detailed spectroscopic constants of NC_nS ($n = 1-7$) in a supersonic jet by Fourier transform microwave spectroscopy. Nakajima et al.[5] obtained the pure rotational spectrum of the NCCS radical by Fourier transform microwave spectroscopy. The structures and spectroscopies of the chainlike NC_nS ($n = 1-7$) forms were also calculated by the latter two groups.[4,5]

However, the isomeric mechanisms of NC_nS ($n > 1$) are completely unknown. For such polyatomic radicals, various isomeric forms are expected to exist as energy minima and some may possess considerable kinetic stability for detection. As a typical example, the well-known C_2N_2 molecule has four kinetically stable isomers NCCN, CNCN, CNNC, and CCNN, among which the former three have been experimentally characterized.[6] Since the temperature in the dense interstellar clouds is very low, some high-energy yet kinetically stable species could exist. For a recently studied penta-atomic system C_4N that contains all the first-row elements, the cyclic forms NC-cC_3 and CN-cC_3 as well as the linear forms CCCCN, CCCNC, and CCNCC were theoretically found to be kinetically stable.[1r] It is highly possible that there will be various kinetically stable NC_3S species of experimental and astrophysical interest when one C atom is replaced by one second-row S atom. In light of the rather limited knowledge of NC_nS radicals, we initiated systematic theoretical studies on the potential energy surfaces of NC_nS. In this paper, we report our work on the pentaatomic NC_3S radical. We want to resolve the following problems: (1) Is linear or chainlike NCCCS the ground-state structure of the NC_3S radical? (2) Are there any other isomers that possess considerable kinetic stability to allow experimental and astrophysical detection? (3) Are there any cyclic or cagelike species that are kinetically stable? As expected, besides the experimentally known linear NCCCS isomer, we indeed find that eight new NC_3S isomers have high kinetic stability and could be promising candidates for future identification. Their possible formation strategies in the laboratory and space are discussed.

2. Computational Methods

All computations are carried out using the GAUSSIAN 98[7] program package. The optimized geometries and harmonic

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vibrational frequencies of the local minima and transition states are initially obtained at the B3LYP/6-311G(d) level followed by CCSD(T)/6-311G(2d) single-point calculations using the B3LYP/6-311G(d) optimized geometries. To confirm whether the obtained transition states connect the right isomers or fragments, the intrinsic reaction coordinate (IRC) calculations are performed at the B3LYP/6-311G(d) level. Further, for the relevant species, the structures and frequencies are refined at the QCISD/6-311G(d) level and the energetics at the CCSD(T)/6-311G(2df) level with inclusion of QCISD/6-311G(d) zero-point vibrational energies (ZPVE). For conciseness, the levels CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE and CCSD(T)/6-311G(2df) //QCISD/6-311G(d)+ZPVE are simplified as CCSD(T)//B3LYP and CCSD(T)//QCISD.

3. Results and Discussions

After numerous searches, 40 doublet NC$_3$S minimum isomers (**m**) and 81 doublet interconversion transition states (**TSm/n**) are obtained at the B3LYP/6-311G(d) level. The optimized geometries of the NC$_3$S isomers, transition states, and fragments are shown in Figures 1−3, respectively. The most feasible pathways of the kinetically stable and unstable NC$_3$S species are presented in Figures 4 and 5, respectively. The harmonic vibrational frequencies as well as the infrared intensities, dipole moments, and rotational constants of the relevant doublet NC$_3$S species are listed in Table 1, while the total and relative energies of all species are collected in Table 2. The relative energies of various dissociation fragments of NC$_3$S are listed in Table 3.

3.1. Doublet NC$_3$S isomers. The 40 doublet minimum isomers can be sorted into five categories, i.e., 11 chainlike species **1**−**8′** (linear or bent), 20 cyclic species **9**−**21** (three-, four-, and five-membered ring), three branched-chain species **22**−**24**, three cagelike species **25**−**27** and three weakly bound species **28**−**30**. By comparison of the geometrical parameters of the isomers (in Figure 1) with fragments (in Figure 3), all the isomers except the cagelike species **25**−**27** can generally be conceived as adducts between the fragments C$_3$N + S, C$_2$S + CN, and C$_2$N + CS via terminal- and side-attack or atomic insertion processes. We take the S atom attacks on the linear CCCN as an example. Attack at the C-terminal and N-terminal sides can lead to the isomers NCCCS **1** and CCCNS **6**, respectively. Alternatively, the insertion of an S atom into the internal C−C single bond of CCCN leads to isomer CCSCN **4**. On the other hand, the side-attack of S atom at the terminal $C\equiv C$ triple bonding of CCCN leads to the three-membered ring NC-cCSC **9**, **9′**, and **9″**.

Of the 11 linear or chainlike isomers NCCCS **1** (0.0), CNCCS **2** (26.3, *26.9*), CCNCS **3** (56.7, *56.9*), **3′** (57.0), CCSCN **4** (60.5, *62.7*), **4′** (68.3), CCSNC **5** (82.9, 85.4), CCCNS **6** (66.3, *67.0*), NCCSC **7** (109.5), and NSCCC **8** (134.6), **8′** (133.7), we find that the species with $-S=C$ (**7**) and $-S=N$ (**8, 8′**) have higher energies than other chainlike forms. Optimization of the other structures CSCNC and CSCCN that contain $-S=C$ bonding even leads to the fragments CNC + CS and CCN + CS, respectively. The isomers NCCCS **1** and CNCCS **2** are lower in energy than all the other chainlike species because they contain better atomic arrangements like −CN (−NC) plus −CCS, −CCN (−CNC) plus −CS, or −CCCN (−CCNC) plus S combinations. **1** and **2** are also the former two low-lying forms of all the NC$_3$S isomers. The first and second (italic) values in parentheses are relative energies with reference to isomer **1** (0.0, *0.0*) at the CCSD(T)//B3LYP and CCSD(T)//QCISD levels. Note that the isomers **3′** and **4′** each have one imaginary frequency (118*i* and 332*i* cm^{-1}, respectively) at the QCISD level and relaxation of symmetry leads to **3** and **4**. Thus, both are artifacts of B3LYP.

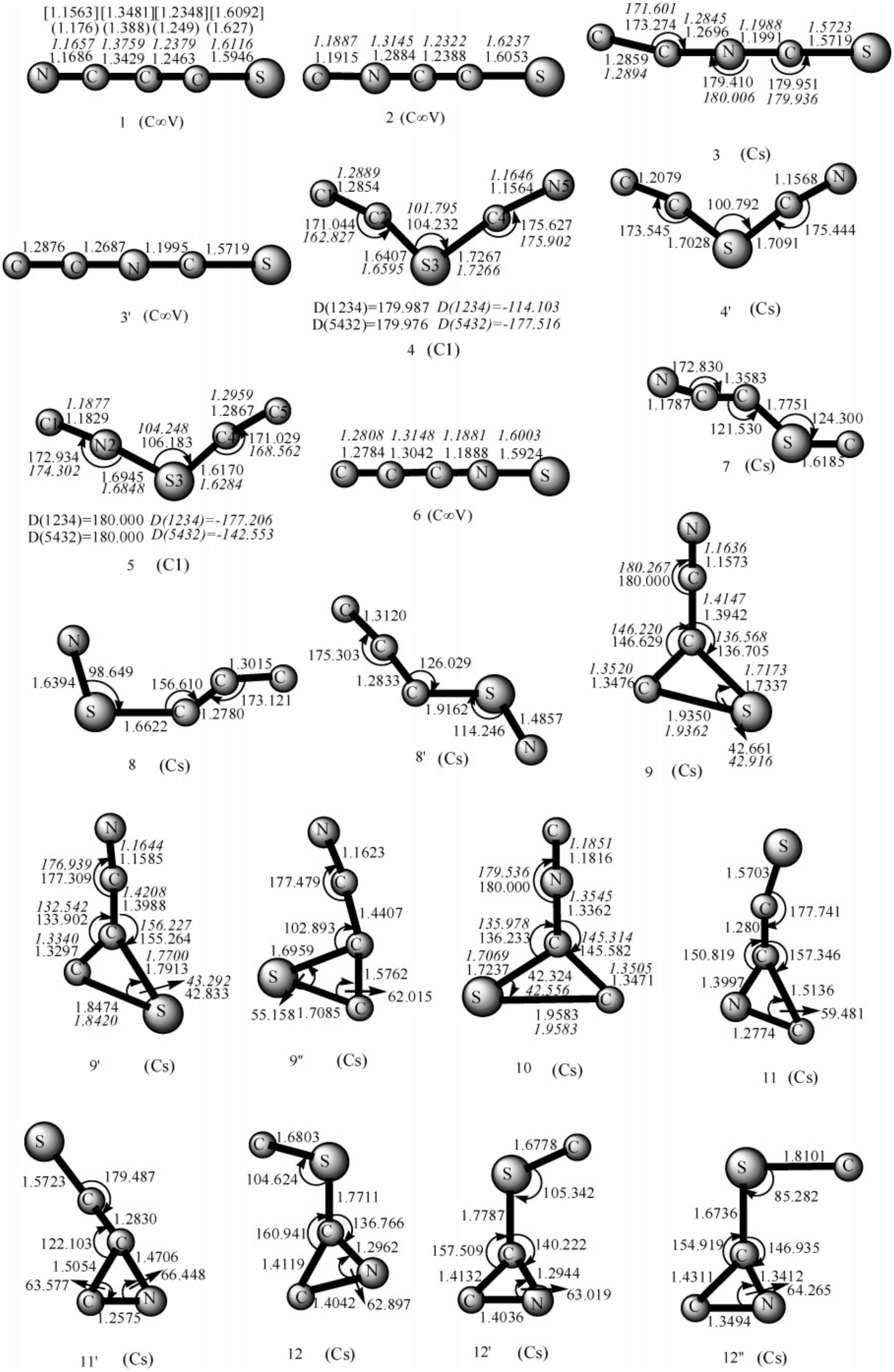
There are in total 12 three-membered ring species **9**−**15**. The species NC-cCCS **9** (32.5, *34.2*), **9′** (39.3, *40.9*), and **9″** (75.7) all contain CCS three-membered ring with exocyclic $-C\equiv N$ bonding and all have the $^2A''$ electronic state. **9′** has very similar structural parameters to **9**. Isomer **9″**is nearly twice higher in energy than **9** and **9′** because the C−C bonding within the ring of **9″** is single-bonded, whereas that is double-bonded in **9** and **9′**, as shown in Figure 1. However, **9″** is not a minimum isomer at the QCISD level. Isomer CN-cCCS **10** (55.4, *57.1*) has a CCS three-membered ring with exocylic $-N\equiv C$ bonding. It is energetically less stable than **9** and **9′**, as is consistent with the relative stability between $-C\equiv N$ and $-N\equiv C$ groups. The species SC-cCNC **11** (49.0), **11′** (57.8), CS-cCNC **12** (120.8), **12′** (120.9), and **12″**(142.1) all have a CNC three-membered ring with $-N=C-$ double bonding in the ring (the bond distances in **12″** are more averaged). **12** and **12′** are cis−trans forms with almost the same energies. The species SC-cNCC **13** (96.9) and NS-cCCC **14** (135.0) contain the CCN and CCC-ring, respectively. Isomer S-cNCC−C **15** (136.0) is a branched NCC ring with two exocylic bonds (N−S and C−C). Because in C$_4$N, the CCC ring isomer is energetically low-lying and kinetically stable,[1r] we intend to locate the CCC three-membered ring with exocyclic $-N=S$ bond. Yet it is intrinsically unstable with an imaginary frequency 50i cm^{-1} which indicates a ring-opening to the more stable linear CCCNS **6**.

The four-membered ring species **16** (97.8) with the $^2A''$ state and **17** (102.7) with the $^2A'$ state possess the CCCN ring with exocyclic CS bonding and CCCS ring with exocyclic CN bonding, respectively. Note that $^2A'$ and $^2A''$ represent the doublet state of A′ and A″ symmetries, respectively, which belong to the "C_s" point group. Isomer **16** has a very long crossed N−C single bond (1.6126 Å), whereas **17** has a very short crossed C−C bond (1.3840 Å). Isomer **16** can be viewed as a 2 + 2 cycloadduct between the C$_2$ and NCS radicals. The isomers **18** (113.8) and **19** (148.9) both have the CCNS ring with exocyclic $C=C$ bonding. Isomer **19** has a crossed C−N bond, whereas **18** does not.

In the five-membered ring species cSCCNC **20** (93.0), **20′** (106.5), and **20″** (122.3), each have a planar SCCNC ring with the N and S atoms separated by one or two C atoms. In another five-membered ring form **21** (93.1), the N and S atoms are neighbors to each other. All the four five-membered ring species have no crossed bonding character and could be viewed as adducts of S atom bridging to the terminus of CCNC or CCCN.

The isomers **22** (63.3), **23** (186.2), and **24** (193.2) belong to the branched description. Isomer **22** has a main part CCCN (low-lying) while **23** and **24** have a main part CSCN and CSNC (high-lying), respectively. As a result, **23** and **24** are energetically much less stable than **22**.

The isomers **25** (132.9), **26** (150.0), and **27** (154.7) may be seen as interesting cagelike species. The species **25** and **27** have the $^2A'$ and $^2A''$ states, respectively. Isomers **25** and **27** are both made by single bonds as shown in Figure 1. Isomer **26** has one $C=C$ (1.3736 Å) double bond, and one of its CN bonds is as short as 1.3377 Å, containing somewhat $C=N$ double bonding character. Similar to the case of the C$_4$N radical,[1r] the three NC$_3$S cagelike species are relatively very high-lying (and also kinetically unstable as will be discussed in the next section). It is understandable that for such a small molecule, the "cage" is rather strained with the composed bonding angle being very acute, and no or few multiple bonds are formed.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(1.176) (1.388) (1.249) (1.627)
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1.1686 1.3429 1.2463 1.5946
N C C C S
1 (C∞V)
1.1887 1.3145 1.2322 1.6237
1.1915 1.2884 1.2388 1.6053
C N C C S
2 (C∞V)
171.601
173.274
1.2845
1.2696
1.1988
1.1991
1.5723
1.5719
1.2859
1.2894
179.410
180.006
179.951
179.936
C C N C S
3 (Cs)
1.2876 1.2687 1.1995 1.5719
C C N C S
3' (C∞V)
1.2889
1.2854
1.1646
1.1564
C1 C2 S3 C4 N5
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104.232
171.044
162.827
175.627
175.902
1.6407
1.6595
1.7267
1.7266
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D(5432)=179.976 D(5432)=-177.516
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1.1568
100.792
173.545
175.444
1.7028
1.7091
C C S C N
4' (Cs)
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1.1829
1.2959
1.2867
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106.183
171.029
168.562
172.934
174.302
1.6945
1.6848
1.6170
1.6284
C1 N2 S3 C4 C5
D(1234)=180.000 D(1234)=-177.206
D(5432)=180.000 D(5432)=-142.553
5 (C1)
1.2808 1.3148 1.1881 1.6003
1.2784 1.3042 1.1888 1.5924
C C C N S
6 (C∞V)
172.830
1.3583
1.1787
1.7751
124.300
121.530
1.6185
N C C S C
7 (Cs)
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1.1573
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180.000
1.4147
1.3942
146.220
146.629
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136.705
1.3520
1.3476
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1.7337
1.9350
1.9362
42.661
42.916
N C C C S
9 (Cs)
98.649
1.6394
156.610
1.3015
173.121
1.2780
1.6622
N S C C C
8 (Cs)
1.3120
175.303
126.029
1.2833
1.9162
114.246
1.4857
C C C S N
8' (Cs)
1.1644
1.1585
176.939
177.309
1.4208
1.3988
132.542
133.902
156.227
155.264
1.3340
1.3297
1.7700
1.7913
43.292
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1.8474
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N C C C S
9' (Cs)
1.1623
177.479
1.4407
102.893
1.6959
1.5762
62.015
55.158
1.7085
N C C S C
9" (Cs)
1.1851
1.1816
179.536
180.000
1.3545
1.3362
135.978
136.233
145.314
145.582
1.7069
1.7237
42.324
42.556
1.3505
1.3471
1.9583
1.9583
C N C S C
10 (Cs)
1.5703
177.741
1.280
150.819
157.346
1.3997
1.5136
59.481
1.2774
S C C N C
11 (Cs)
1.5723
179.487
1.2830
122.103
1.4706
1.5054
66.448
63.577
1.2575
S C C C N
11' (Cs)
1.6803
104.624
1.7711
160.941
136.766
1.2962
1.4119
1.4042
62.897
C S C N C
12 (Cs)
1.6778
105.342
1.7787
157.509
140.222
1.4132
1.2944
63.019
1.4036
S C C C N
12' (Cs)
1.8101
85.282
1.6736
154.919
146.935
1.4311
1.3412
64.265
1.3494
S C C C N
12" (Cs)

Figure 1.

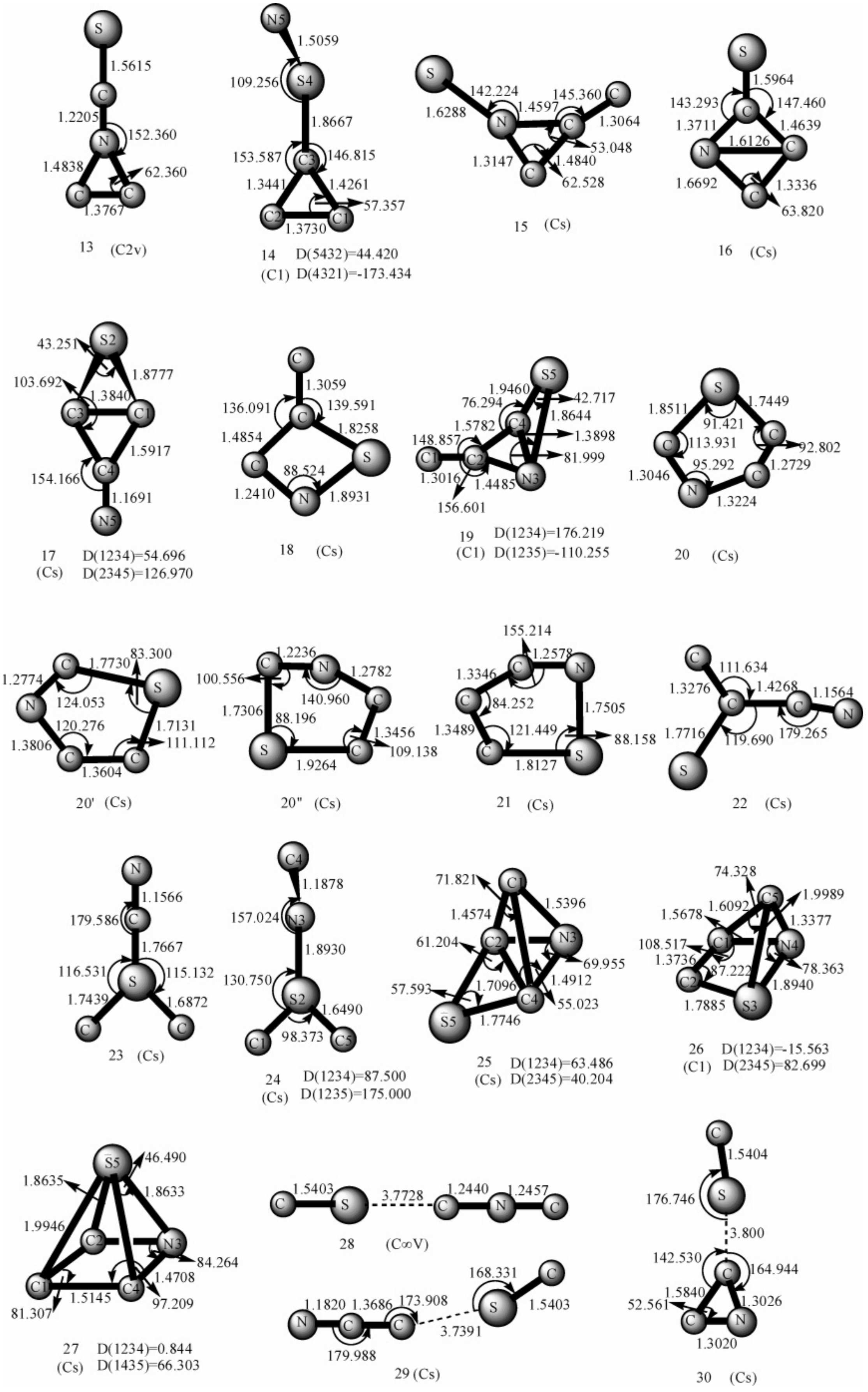


Figure 1. (continued).

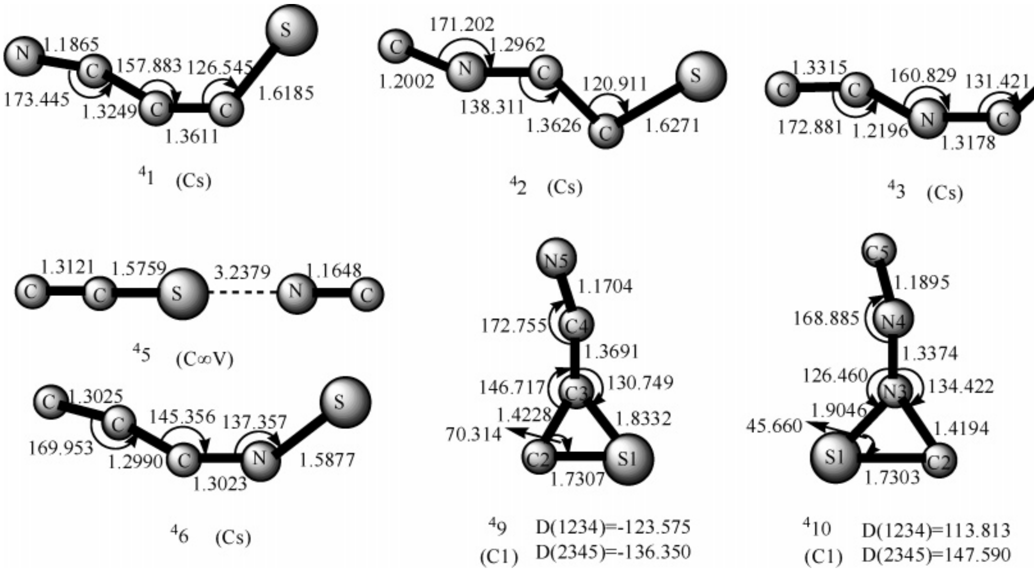


Figure 1. Optimized geometries of doublet NC_3S isomers and quartet species corresponding to the most stable doublet isomers at the B3LYP/6-311G(d) level. The values in italics are at the QCISD/6-311G(d) level. For isomer **1**, the values in parentheses and those in square brackets are at the QCISD/cc-pVDZ and MRSDCI/cc-pVTZ levels, respectively. Bond lengths are in angstroms and angles in degrees.

Finally, the species CS···CNC **28** (97.8), CS···CCN **29** (99.6) and CS···cCNC **30** (111.8) are of the weakly bound complexes between the C_2N radical and the CS molecule. As shown in Table 3, they are unstable with respect to the direct dissociation to the corresponding fragmented radicals and molecules.

3.2. Doublet NC_3S Isomerization and Dissociation Stability. For the isomerization and dissociation processes of various doublet NC_3S isomers, a total of 81 transition states are located at the B3LYP/6-311G(d) level. For simplicity, their structural details (in Figure 2) are not discussed here. The lowest isomerization or dissociation barrier governs the kinetic stability of an isomer. An isomer with such a higher barrier is expected to have a relatively higher kinetic stability. Nine doublet NC_3S isomers NCCCS **1**, CNCCS **2**, CCNCS **3**, CCSCN **4**, CCSNC **5**, CCCNS **6**, NC-cCCS **9**, **9′**, and CN-cCCS **10** are of interest with considerable kinetic stability. They have the kinetic stability of around or more than 20 kcal/mol as 54.8 (*58.7*) (**1** → **9**), 26.2 (*27.4*) (**2** → **11**), 47.1 (*48.5*) (**3** → **18**), 34.5 (*33.5*) (**4** → **9**), 19.6 (*20.2*) (**5** → **4**), 33.9 (*34.5*) (**6** → **21**), 22.3 (*24.5*) (**9** → **1**), and 20.8 (*21.2*) (**10** → **2**) kcal/mol, respectively, as can be deduced from Figure 4. Despite a lot of attempts, the transition state **TS9/9′** and other transition states associated with **9′** are not able to be located. Yet we feel it is safe to consider it as having similar kinetic stability to **9**. The italic values in parentheses are for CCSD(T)//QCISD single-point calculations.

However, the other doublet isomers have much lower kinetic stability, as shown in Figure 5. At the CCSD(T)//B3LYP level, the least isomerization barriers are −5.3 (**7** → **29**), 0.5 (**8** → **6**), 3.5 (**11** → **2**), 7.1 (**12** → **30**), 6.2 (**12′** → **30**), 1.2 (**12″** → **10**), 1.1 (**13** → **3′**), 0.9 (**14** → **C_3+NS**), 0.5 (**15** → **6**), −0.6 (**16** → **11**), 1.6 (**17** → **9**), −0.4 (**18** → **22**), 5.9 (**19** → **15**), 3.9 (**20** → **2**), 2.1 (**20′** → **3**), 0.6 (**20″** → **3**), 7.0 (**21** → **1**), 3.8 (**22** → **1**), 12.1 (**23** → **9**), 11.1 (**24** → **23**), 6.1 (**25** → **1**), 0.7 (**26** → **11**), 2.1 (**27** → **9**), 1.0 (**28** → **CS + CNC**), 1.5 (**29** → **CS + CCN**), 0.8 (**30** → **CS + cCNC**) kcal/mol, respectively. Coupled with their high energy, they may be of little interest as observable species either in the laboratory or in space. The negative values for **7** and **16**, resulting from the CCSD(T) single-point calculations using the B3LYP optimized geometries, just indicate that the two isomers may have zero or very small conversion barriers. Surely, it is probable that at higher optimization levels, the B3LYP-minima **7**, **12″**, **15**, **16**, **18**, **20″**, and **26** with minute barriers may disappear on exact potential-energy surface (PES). Yet, this will not affect the main features of the NC_3S PES.

3.3. Properties of Stable NC_3S Isomers and Their Experimental and Astrophysical Implications. We now analyze the structural and bonding properties of the kinetically stable isomers in more detail. At the B3LYP/6-311G(d) level, the spin density distribution of NCCCS **1** is 0.256, −0.127, 0.471, −0.169, and 0.569e for N, C, C, C, and S, respectively. Isomer **1** can be viewed as resonating between three forms: (1) $|N{\equiv}C{-}C{\equiv}C{-}\overline{\underline{S}}\bullet$, (2) $|N{\equiv}C{-}C\bullet{=}C{=}\overline{\underline{S}}$ and (3) $|N\bullet{=}C{=}C{=}C{=}\overline{\underline{S}}$, with form 1 having the most weight, form 2 less weight, and form 3 the least. The symbols "•" and "|" denote the single electron and lone-pair electrons, respectively. The second low-lying isomer CNCCS **2** also has the $^2\Pi$ electronic state. Similar to isomer **1**, based on the bond lengths (in Figure 1) and the spin density distribution (0.153, −0.041, 0.401, −0.119, and 0.607e for C, N, C, C, and S, respectively), isomer **2** has resonance structures of (1) $|C{\equiv}N{-}C{\equiv}C{-}\overline{\underline{S}}\bullet$, (2) $|C{\equiv}N{-}C\bullet{=}C{=}\overline{\underline{S}}$, and (3) $|C\bullet{=}N{=}C{=}C{=}\overline{\underline{S}}$, with form 1 having the most weight, form 2 less weight, and form 3 the least. As a result, structurally the two low-lying forms **1** and **2** can be considered as the combination between the doublet C_3N radical (CCCN and CCNC form) and triplet S atom or between doublet CN radical and triplet CCS radical. Another possibility is the combination between the doublet C_2N radical (CCN and CNC) and singlet CS molecule.

The slightly bent isomer CCNCS **3** has the spin density distribution 0.392, 0.310, 0.068, −0.035, and 0.265e for C, C, N, C, and S, respectively. Its possible resonance structures are (1) $\bullet C{\equiv}N{-}\overline{N}{=}C{=}\overline{\underline{S}}$, (2) $|C{=}C\bullet{-}\overline{N}{=}C{=}\overline{\underline{S}}$, and (3) $|C{=}C{=}\overline{N}{-}C{\equiv}S\bullet$. The weight of three forms decreases slightly from form 1 to form 3. It could be thought of the direct quasi-linear addition of the C_2 radical to the NCS radical at N-site or the addition of CCN radical (N-site) to the CS molecule.

The two bent isomers CCSCN **4** and CCSNC **5** with internal S atom have the corresponding spin density distributions as 0.410, 0.303, 0.251, −0.047, and 0.083e for C, C, S, C, N in **4** and 0.436, 0.222, 0.303, −0.023, and 0.062e for C, C, S, N, and C in **5**. They have similar types of resonance structures between forms 1, 2, 3, and 4 with (X,Y) = (C,N) for **4** and (X,Y) = (N,C) for **5**. Form 4 has the least contribution. For

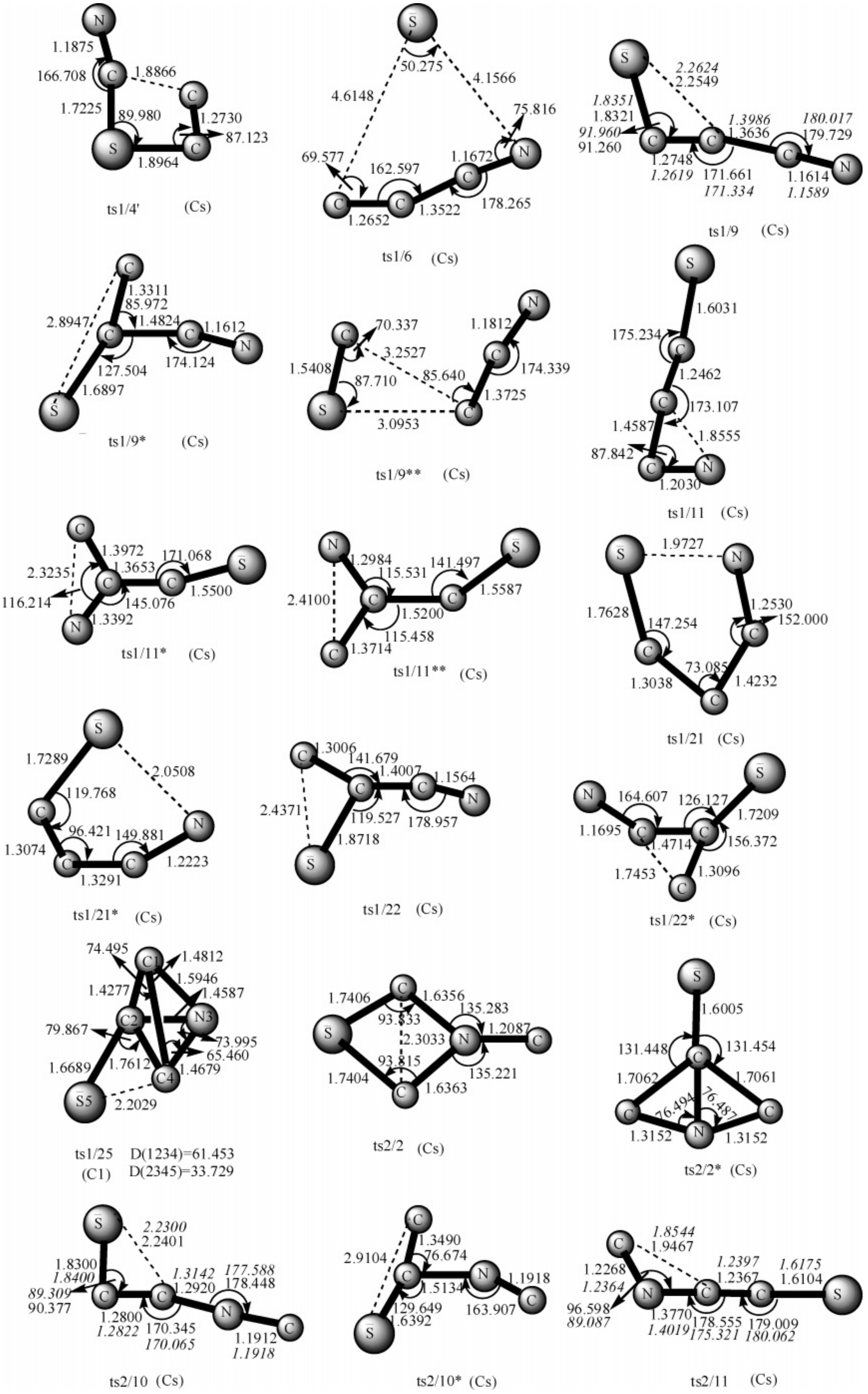
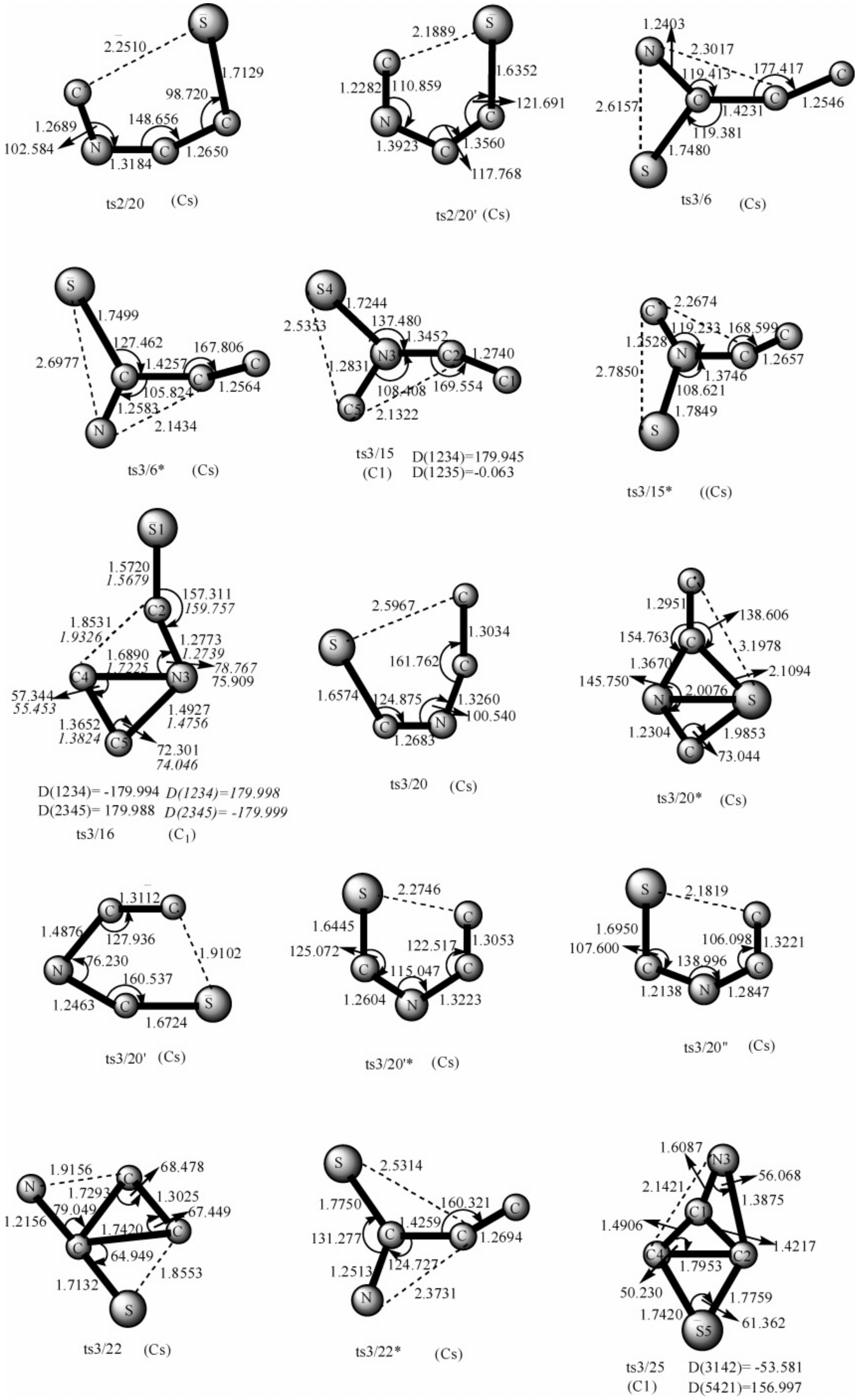

N
1.1875
166.708
C
1.8866
C
1.7225
89.980
1.2730
87.123
S
C
1.8964
ts1/4' (Cs)
S̄
50.275
4.6148
4.1566
75.816
N
1.1672
C
162.597
69.577
C
C
1.2652
1.3522
178.265
ts1/6 (Cs)
S̄
2.2624
2.2549
1.8351
1.8321
91.960
91.260
C
C
1.3986
1.3636
180.017
179.729
C
N
1.2748
1.2619
171.661
171.334
1.1614
1.1589
ts1/9 (Cs)
C
1.3311
85.972
2.8947
1.4824
1.1612
C
C
N
127.504
174.124
1.6897
S̄
ts1/9* (Cs)
C
70.337
1.1812
N
3.2527
C
1.5408
85.640
174.339
87.710
1.3725
S
C
3.0953
ts1/9** (Cs)
S
1.6031
175.234
C
1.2462
C
173.107
1.4587
1.8555
87.842
C
N
1.2030
ts1/11 (Cs)
C
1.3972
171.068
1.3653
S̄
2.3235
C
C
1.5500
116.214
145.076
N
1.3392
ts1/11* (Cs)
N
1.2984
141.497
S̄
115.531
2.4100
C
C
1.5587
1.5200
115.458
C
1.3714
ts1/11** (Cs)
S
1.9727
N
1.7628
147.254
1.2530
152.000
C
C
73.085
1.3038
1.4232
C
ts1/21 (Cs)
S̄
1.7289
2.0508
119.768
C
N
96.421
149.881
1.3074
C
C
1.2223
1.3291
ts1/21* (Cs)
C
1.3006
141.679
1.4007
1.1564
C
C
N
2.4371
119.527
178.957
1.8718
S̄
ts1/22 (Cs)
S̄
N
164.607
126.127
1.7209
1.1695
C
C
1.4714
156.372
1.7453
1.3096
C
ts1/22* (Cs)
74.495
C1
1.4812
1.5946
1.4277
1.4587
C2
N3
79.867
73.995
65.460
1.7612
1.6689
C4
1.4679
S5
2.2029
ts1/25 D(1234)=61.453
(C1) D(2345)=33.729
1.7406
C
1.6356
135.283
93.833
S̄
2.3033
N
1.2087
C
93.815
1.7404
C
1.6363
135.221
ts2/2 (Cs)
S
1.6005
131.448
C
131.454
1.7062
1.7061
C
76.494
76.487
C
1.3152
N
1.3152
ts2/2* (Cs)
S̄
2.2300
2.2401
1.8300
1.3142
177.588
1.8400
1.2920
178.448
89.309
C
C
N
90.377
1.2800
1.2822
170.345
170.065
1.1912
1.1918
C
ts2/10 (Cs)
C
1.3490
2.9104
76.674
C
N
1.1918
1.5134
129.649
1.6392
163.907
C
S̄
ts2/10* (Cs)
1.8544
1.9467
C
1.2397
1.6175
1.2268
1.2367
1.6104
1.2364
N
C
C
S
96.598
89.087
1.3770
1.4019
178.555
175.321
179.009
180.062
ts2/11 (Cs)

Figure 2.



ts2/20 (Cs)

ts2/20' (Cs)

ts3/6 (Cs)

ts3/6* (Cs)

ts3/15 (C1) D(1234)=179.945 D(1235)=-0.063

ts3/15* ((Cs)

D(1234)= -179.994 *D(1234)=179.998*
D(2345)= 179.988 *D(2345)= -179.999*
ts3/16 (C_1)

ts3/20 (Cs)

ts3/20* (Cs)

ts3/20' (Cs)

ts3/20'* (Cs)

ts3/20" (Cs)

ts3/22 (Cs)

ts3/22* (Cs)

ts3/25 (C1) D(3142)= -53.581 D(5421)=156.997

Figure 2. (continued).

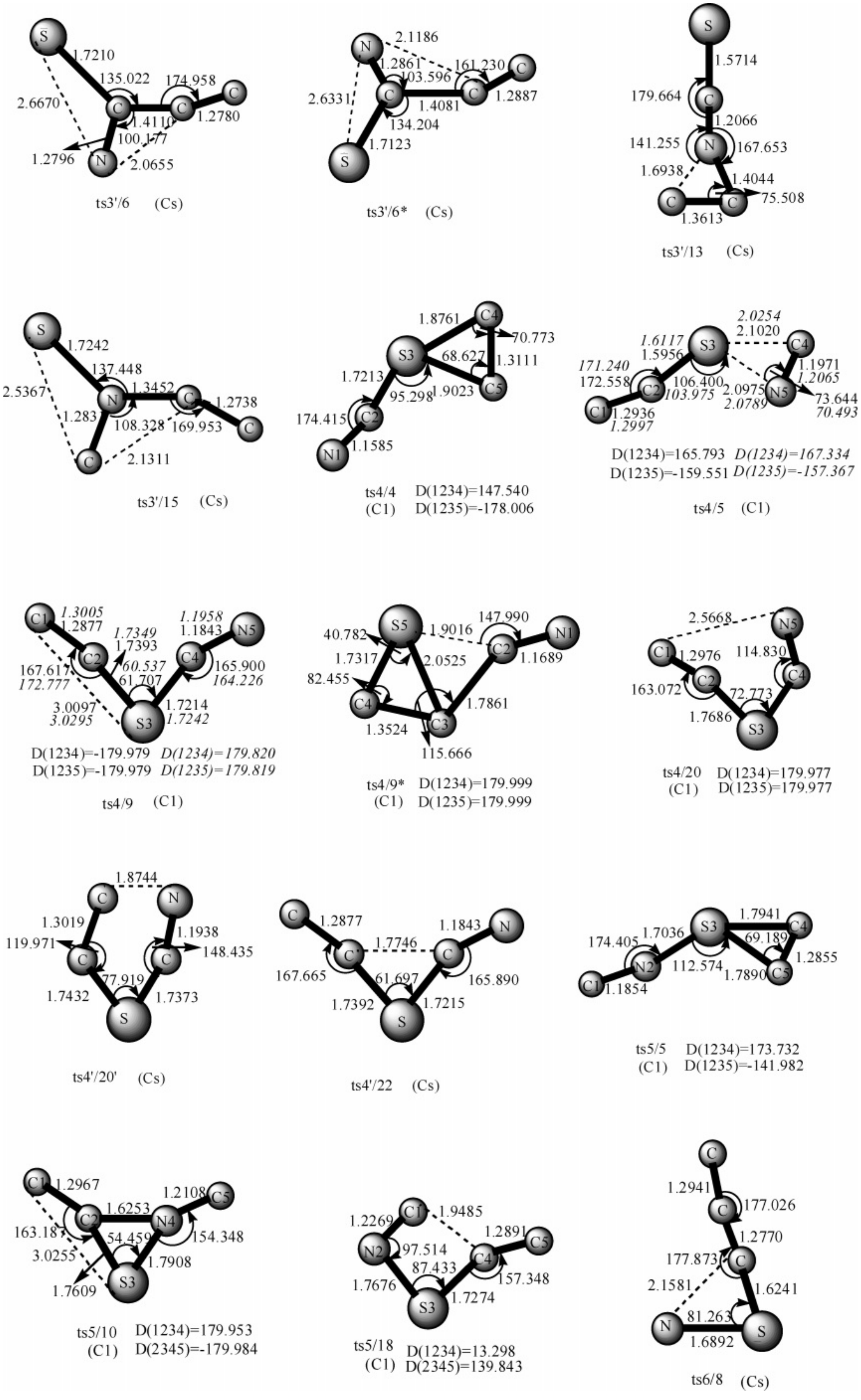


Figure 2. (continued).

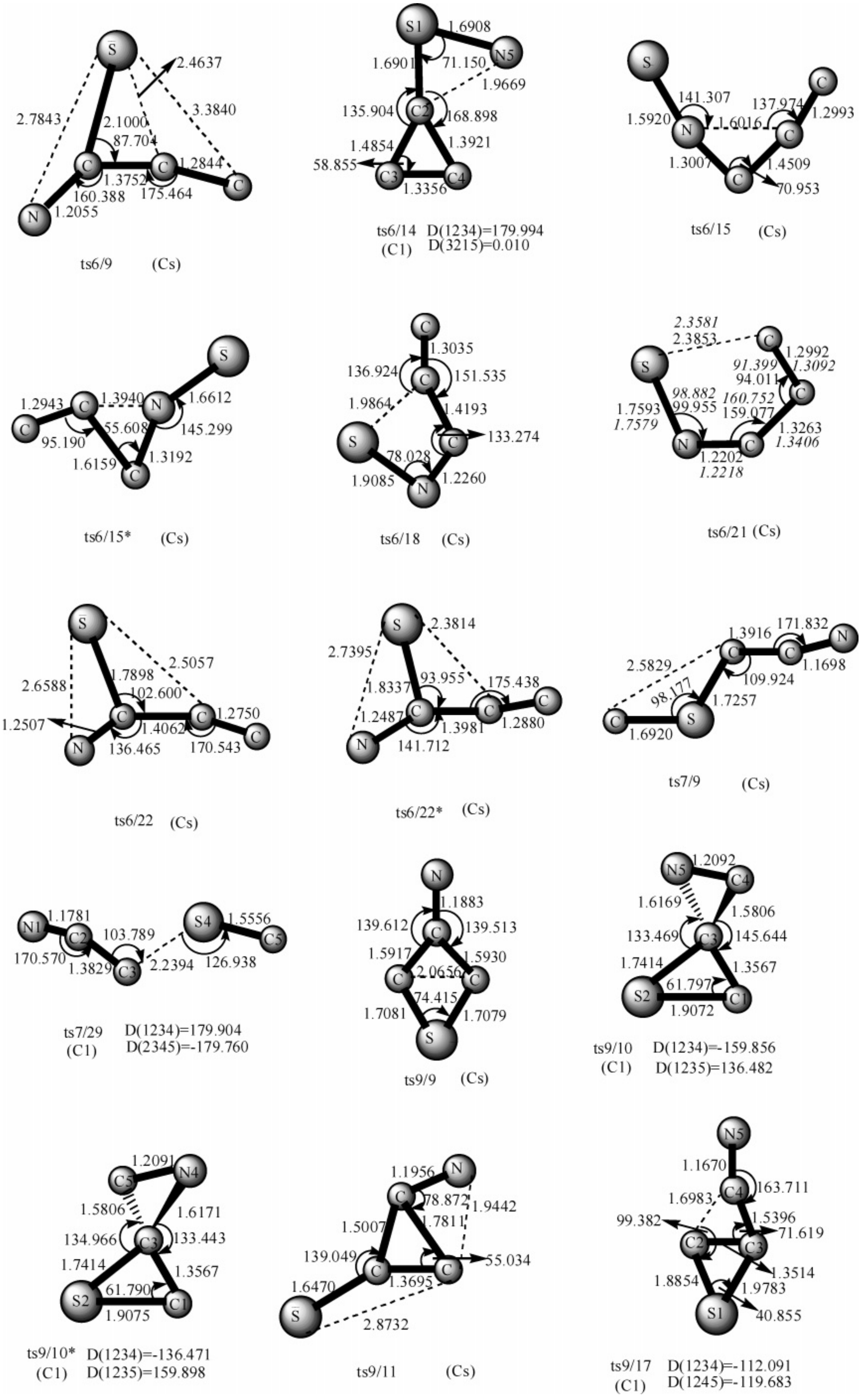


Figure 2. (continued).

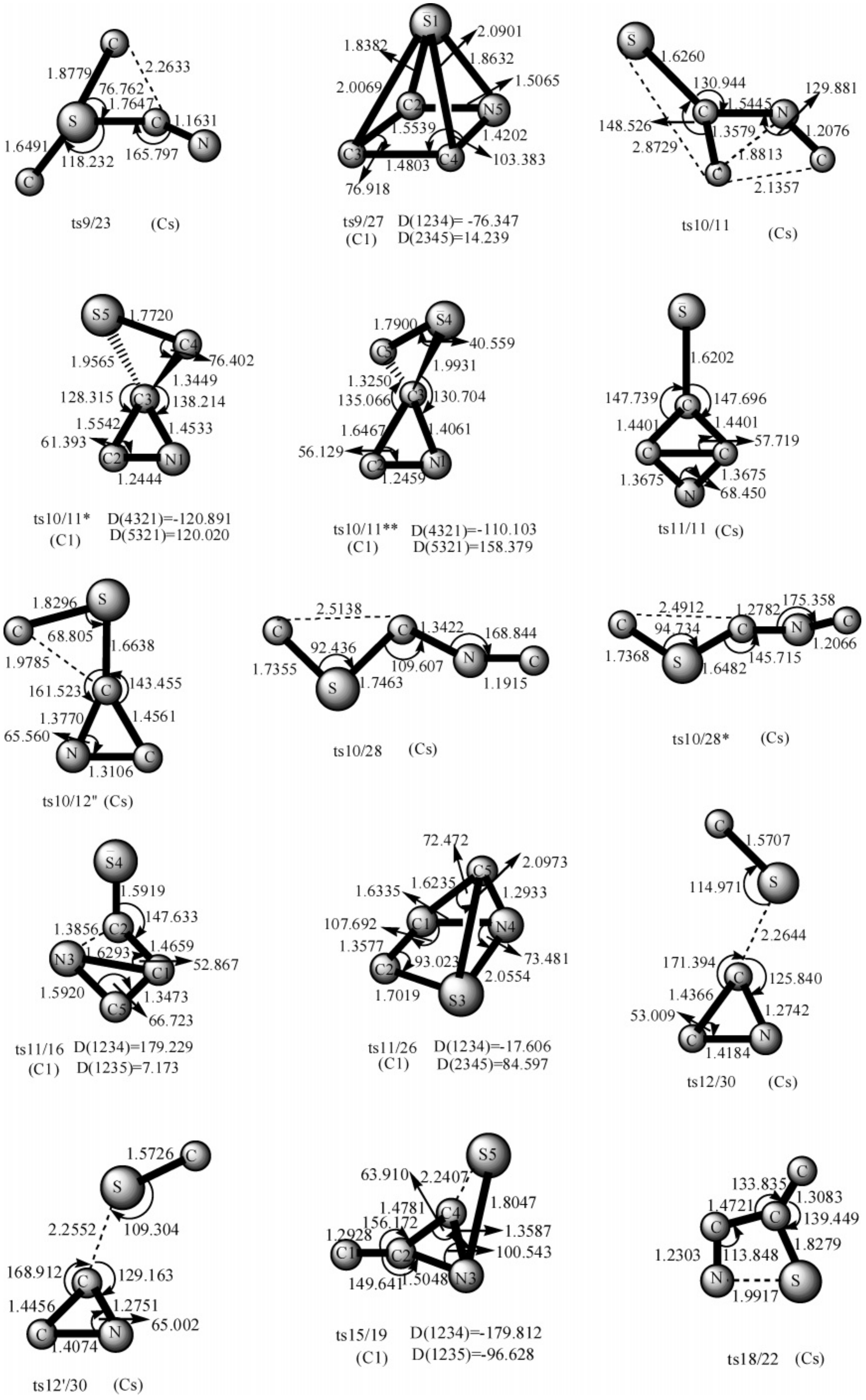


Figure 2. (continued).

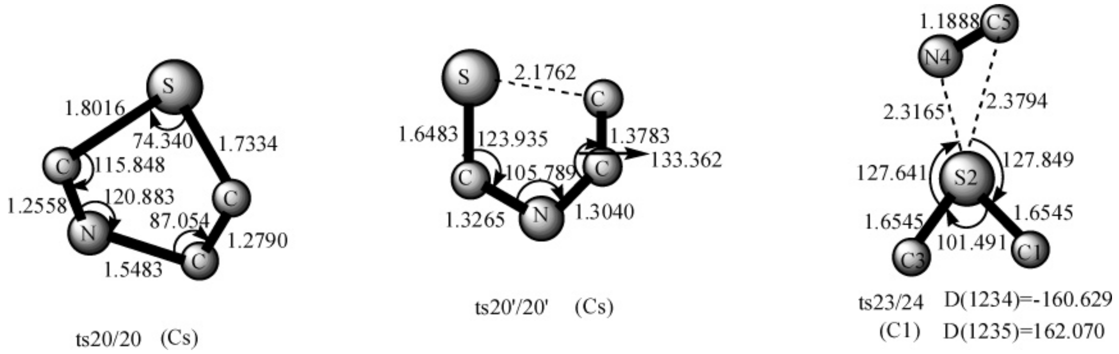


Figure 2. Optimized geometries and of doublet NC_3S transition states at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees.

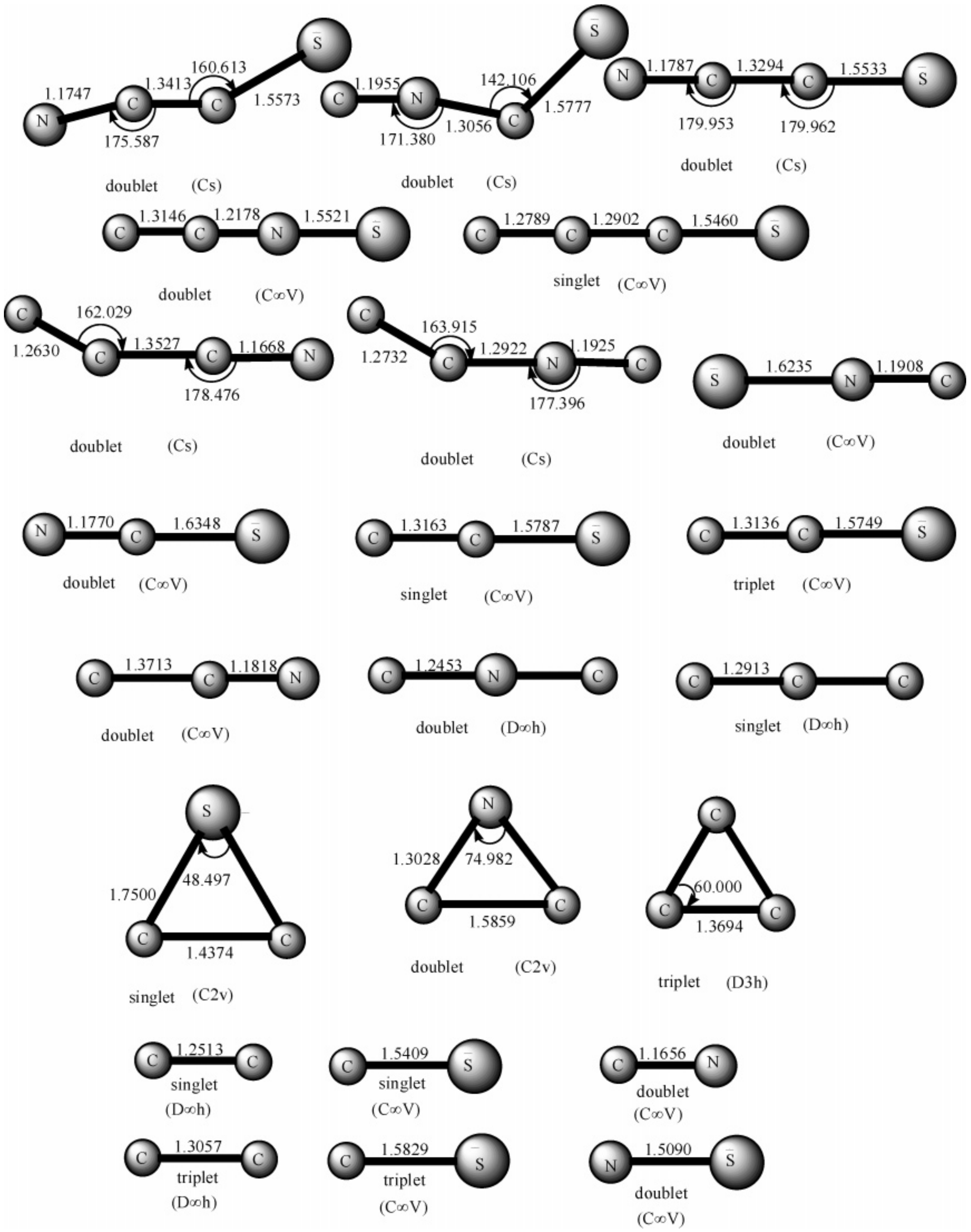


Figure 3. Optimized fragments of the dissociations of NC_3S at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees.

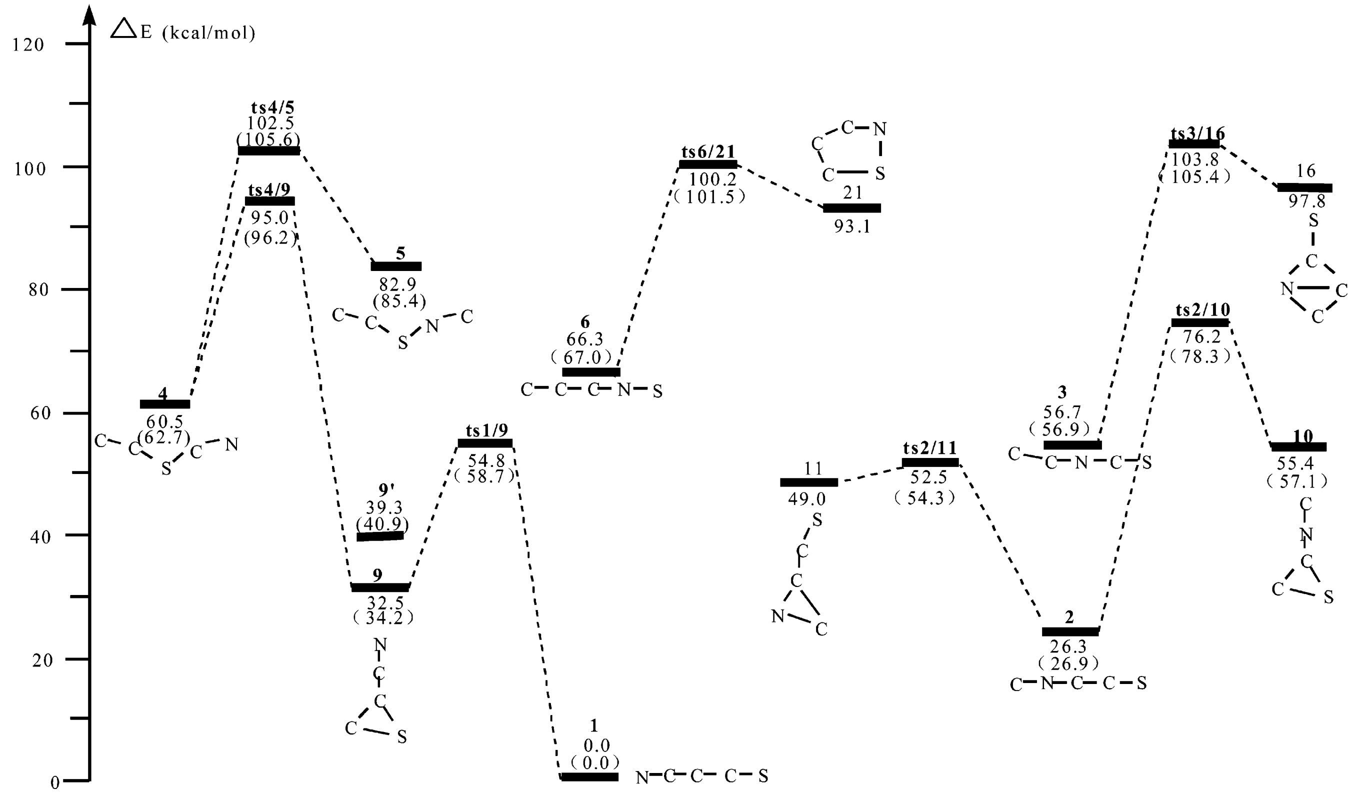


Figure 4. Schematic potential-energy surface of NC$_3$S including the most feasible pathways of the kinetically stable at the CCSD(T)/6-311G-(2d)//B3LYP/6-311G(d)+ZPVE level. The relative values in parentheses are at the CCSD(T)/6-311G(2df)//QCISD/6-311G(d)+ZPVE level.

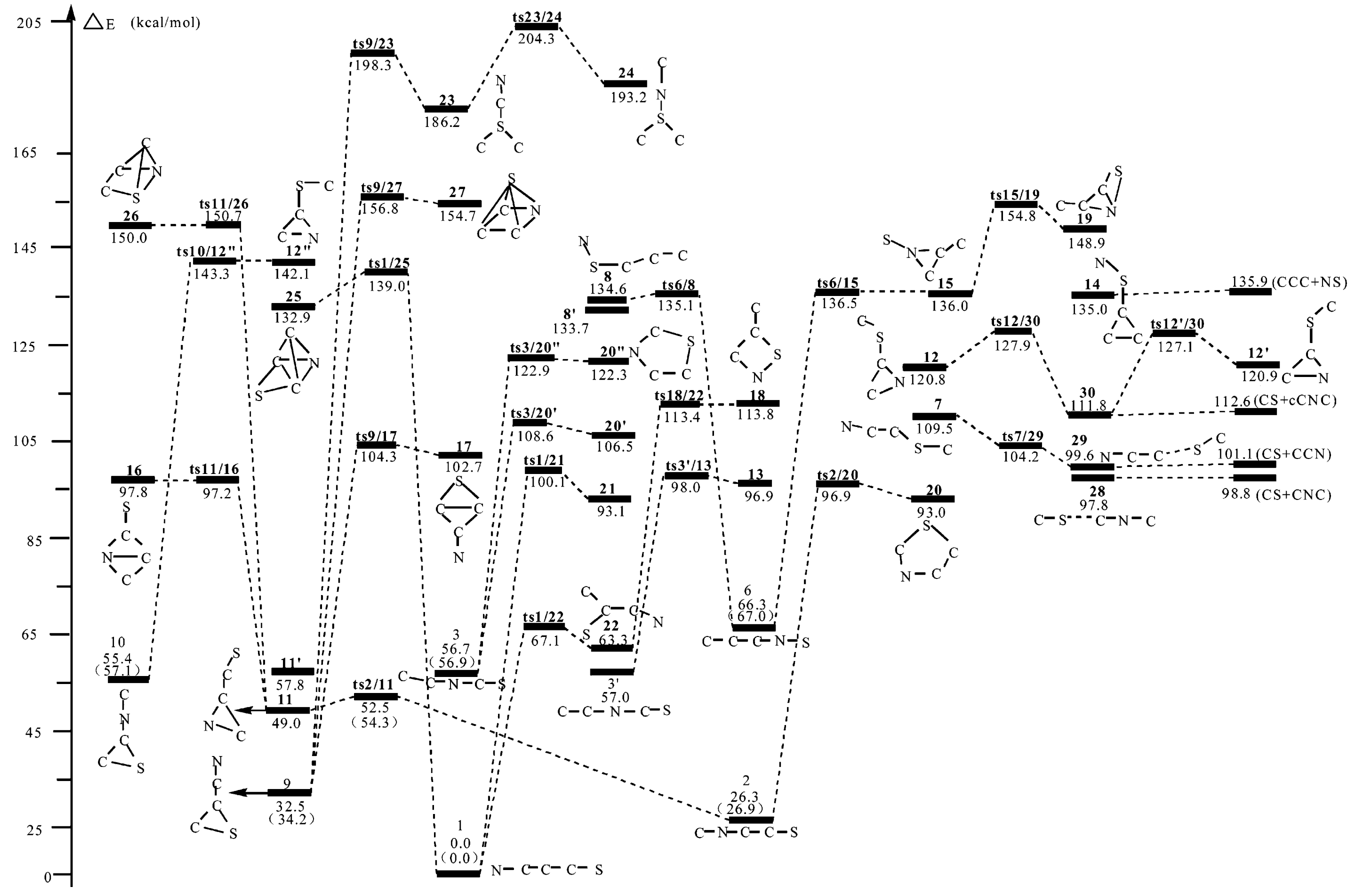


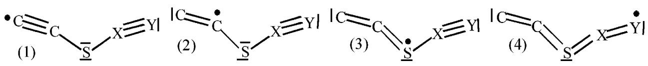
Figure 5. Schematic doublet potential-energy surface of NC$_3$S including all unstable species at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE level. The relative values in parentheses are at the CCSD(T)/6-311G(2df)//QCISD/6-311G(d)+ZPVE level.

TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in Parentheses), Dipole Moment (D), and Rotational Constants (GHz) of the Relevant Doublet NC_3S Structures at the B3LYP/6-311G(d) Level[b]

species	frequencies (infrared intensity)	dipole moment	rotational constant	$\langle S^2 \rangle$ value
NCCCS **1**	113 (1), 132 (3), 369 (6), 380, (0), 512 (10), 533 (1), 575 (1), 1170 (22), 1978 (53), 2183 (2)	2.8529	1.442315	0.7720
NCCCS **1**[a]	10 (0), 130 (2), 257 (0), 302 (3), 489 (2), 490 (10), 554 (0), 1116 (2), 2017 (38), 2306 (15)	3.1557	1.420481	
NCCCS **1**[c,d]	∼550,[c] 939,[c] 2139[c]	2.97[d]	1.43918582(8)[d]	
CNCCS **2**	122 (1), 138 (3), 319 (2), 352 (1), 382 (1), 466 (2), 585 (2), 1195 (20), 2008 (143), 2119 (42)	1.6411	1.517481	0.7638
CNCCS **2**[a]	121 (1), 133 (2), 295 (2), 312 (1), 353 (1), 430 (3), 566 (1), 1149 (4), 2046 (76), 2254 (315)	1.8893	1.495929	
CCNCS **3**	99 (25), 231 (50), 266 (0), 381 (0), 459 (4), 629 (16), 1182 (12), 1908 (244), 2181 (378)	3.8046	5028.52287, 1.57840, 1.57791	0.7619
CCNCS **3**[a]	91 (20), 149 (13), 244 (107), 375 (1), 438 (3), 634 (13), 1186 (18), 1950 (20), 2263 (2746)	3.8357	2615.03848, 1.56970, 1.56876	
CCSCN **4**	40 (17), 107 (6), 253 (4), 333 (2), 471 (6), 644 (26), 739 (5), 1873 (163), 2274 (4)	3.1696	12.31998, 2.68061, 2.20159	0.7534
CCSCN **4**[a]	109 (4), 255 (23), 269 (20), 327 (3), 476 (6), 673 (18), 744 (16), 1703 (248), 2219 (12)	2.9877	11.25091, 2.77997, 2.23602	
CCSNC **5**	94 (4), 145 (11), 182 (0), 194 (1), 420 (20), 607 (87), 772 (2), 1855 (300), 2088 (346)	3.0271	13.88028, 2.73822, 2.28704	0.7539
CCSNC **5**[a]	90 (7), 115 (16), 190 (1), 208 (0), 439 (18), 658 (86), 760 (1), 1842 (121), 2100 (346)	3.1174	13.00031, 2.80673, 2.30983	
CCCNS **6**	110 (7), 122 (3), 230 (6), 249 (4), 476 (14), 519 (12), 586 (0), 1116 (4), 1945 (373), 2246 (367)	4.0897	1.554165	0.7648
CCCNS **6**[a]	101 (4), 113 (2), 193 (3), 216 (1), 486 (26), 520 (22), 581 (13), 1104 (85), 1979 (242), 2357 (2073)	4.7901	1.542362	
NC-cCCS **9**	184 (8), 227 (10), 416 (2), 529 (2), 536 (3), 670 (6), 962 (13), 1596 (31), 2314 (3)	2.3652	15.77299, 2.66112, 2.27696	0.7540
NC-cCCS **9**[a]	185 (9), 225 (8), 419 (2), 523 (3), 528 (2), 686 (3), 996 (8), 1614 (39), 2342 (5)	2.5951	15.66741, 2.64671, 2.26421	
NC-cCCS **9′**	183 (8), 198 (8), 412 (0), 498 (4), 578 (3), 614 (19), 985 (20), 1615 (26), 2285 (2)	3.0935	22.10107, 2.37345, 2.14328	0.7568
NC-cCCS **9′**[a]	183 (8), 183 (5), 429 (1), 472 (5), 577 (3), 618 (12), 1018 (9), 1630 (36), 2303 (5)	3.4307	22.29711, 2.35857, 2.13295	
CN-cCCS **10**	171 (4), 207 (6), 387 (3), 462 (2), 479 (1), 702 (11), 993 (33), 1614 (33), 2148 (294)	1.8908	15.50660, 2.89356, 2.43852	0.7531
CN-cCCS **10**[a]	163 (4), 195 (5), 395 (5), 444 (2), 479 (2), 715 (5), 1029 (29), 1633 (41), 2173 (344)	2.2011	15.41290, 2.88641, 2.43113	

[a] At the QCISD/6-311G(d) level. [b] For the relevant isomers, the QCISD/6-311G(d) values are included also. [c] Reference 8. [d] Reference 4.

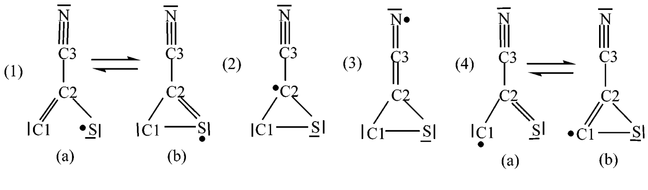
isomer **4**, form 2 is preferred over form 3, whereas for isomer **5**, the order is reversed.



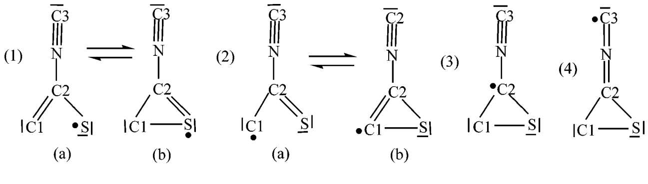
Thus, we suggest that the isomers **4** and **5** can be obtained via the direct addition between CCS and CN radicals or between C_2 and NCS/CNS radicals. Formation via the insertion of the S atom into the internal C−C/C−N single bond of CCCN/CCNC is also probable.

The linear isomer CCCNS **6** with the $^2\Pi$ electronic state has the spin density distribution 0.202, 0.141, −0.014, 0.043, and 0.629e for C, C, C, N, and S, respectively. Thus, isomer **6** can be viewed as a resonance structure between three forms: (1) |C═C═C═N═$\overline{\text{S}}$•, (2) •C≡C−C≡N−$\overline{\text{S}}$|, and (3) |C═C•−C≡N−$\overline{\text{S}}$| with form 1 having the predominant weight.

The three-membered ring NC-cCCS **9** and **9′** energetically follows the linear **1** and **2**. We take **9** as an example. Its spin density distribution is 0.664, 0.093, 0.198, −0.058, and 0.104e for S, C1, C2, C3, and N, respectively. Isomer **9** can be seen as having four resonance structures:



Because isomer **10** has the spin density distribution 0.632, 0.163, 0.162, −0.029, and 0.072e for S, C1, C2, N, and C3, respectively, it could also be taken to resonate between four forms:



Notice that the resonance structures 1 and 4 for isomer **9** and 1 and 2 for isomer **10** each have two substructures a and b with substructure a bearing more weight. We can find that formally, the three-membered ring isomers **9**, **9′**, and **10** can be considered as the products when the S atom attacks the terminal C≡C bond of chainlike CCCN or CCNC. This is consistent with the structural comparison between the isomers and fragments. Surely, an alternative formation procedure is the direct addition of −CN or −NC group to the cyclic C_2S molecule at one C atom. Interestingly, the structural features of the C_2S ring of **9**, **9′**, and **10** are quite different from those of the naked cyclic C_2S molecule (see Figure 3). In **9**, **9′**, and **10**, the C−C bond is very short (around 1.34 Å) with strong π-bonding character. One of the two C−S bonds is longer than normal C−S single bond, yet the other C−S lies between the C═S double and C−S single bonds. However in the cyclic C_2S molecule, the C−S and C−S bonds have averaged values 1.750 and 1.437 Å, all with considerable double bonding character. The difference could be ascribed to that when the highly electron-withdrawing group −CN/−NC is bonded to one C atom of C_2S, the π-electron densities are highly localized within the C−C and C−S bonds closer to the −CN or −NC group.

Only the lowest-energy doublet isomer NCCCS **1** has been characterized by experiments[3,4,8] and theoretically studied.[4,8] As shown in Table 1, the three experimentally[8] determined vibrational modes at 550, 939, and 2139 cm^{-1}, are in agreement with our QCISD/6−311(d) values 554, 1116, and 2017 cm^{-1}, respectively. Also, the experimental[4] rotational constant 1.4391858 GHz is consistent with our calculated value 1.420481 GHz. Also, the agreement between our calculated results and the available theoretical reference data is generally good. Our QCISD/6-311G(d) bond distances (in Figure 1) for $NC_1C_2C_3S$ **1** are $r(N-C_1) = 1.1657$, $r(C_1-C_2) = 1.3759$, $r(C_2-C_3) = 1.2379$, and $r(C_3-S) = 1.6116$ Å. The referenced QCISD/cc-pVDZ values[4] are 1.176, 1.388, 1.249, and 1.627 Å, and the referenced MRSDCI/cc-pVTZ values[8] are 1.1563, 1.3481, 1.2348, and 1.6092 Å. Our calculated dipole moment 3.1557 D at the QCISD/6-311G(d) level is well comparable to the referenced QCISD/cc-pVDZ value of 2.97 D.[4] We are aware that in one experiment,[3] isomer **1** was produced from the parent molecules that contain the NCCCS atomic arrangement, while in the others[8] it was generated from the mixture of CH_3CN with CS_2. It is reasonable for us to speculate that under certain laboratory conditions, the other eight kinetically stabilized doublet isomers **2**, **3**, **4**, **5**, **6**, **9**, **9′**, and **10** could be generated. The isomerism is particularly important in interstellar space

TABLE 2: Total (au) and Relative (kcal/mol) Energies of the NC_3S Structures and Transition States at the B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2d) Levels[a]

species	B3LYP^c	ΔZPVE B3LYP^c	CCSD(T)^d//B3LYP^c	total 1	QCISD^c	ΔZPVE QCISD^c	CCSD(T)^e//QCISD^c	total 2
NCCCS **1**^{b} ($^2\Pi$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNCCS **2** ($^2\Pi$)	27.6	−0.4	26.7	26.3	27.6	0.0	26.9	26.9
CCNCS **3** ($^2A'$)	55.3	−0.9	57.6	56.7	60.7	−0.5	57.4	56.9
CCNCS **3′** ($^2\Pi$)	55.3	−0.6	57.6	57.0				
CCSCN **4**	73.2	−1.7	62.2	60.5	62.8	−1.3	64.0	62.7
CCSCN **4′** ($^2A'$)	85.2	−0.7	69.0	68.3				
CCSNC **5**	95.5	−2.3	85.2	82.9	87.9	−1.8	87.2	85.4
CCCNS **6** ($^2\Pi$)	64.4	−0.5	66.8	66.3	72.4	0.0	67.0	67.0
NCCSC **7** ($^2A''$)	118.5	−3.1	112.6	109.5				
NSCCC **8** ($^2A''$)	139.6	−2.9	137.5	134.6				
NSCCC **8′** ($^2A'$)	146.2	−2.3	136.0	133.7				
NC-cCCS **9** ($^2A''$)	43.0	−0.7	33.2	32.5	34.4	−0.2	34.4	34.2
NC-cCCS **9′** ($^2A''$)	49.5	−0.8	40.1	39.3	41.7	−0.4	41.3	40.9
NC-cCCS **9″** ($^2A''$)	88.0	−2.1	77.8	75.7				
CN-cCCS **10** ($^2A''$)	65.7	−1.1	56.5	55.4	58.6	−0.6	57.7	57.1
SC-cCNC **11** ($^2A''$)	51.0	−1.3	50.3	49.0				
SC-cCNC **11′** ($^2A''$)	61.1	−1.5	59.3	57.8				
CS-cCCN **12** ($^2A'$)	134.8	−2.5	123.3	120.8				
CS-cCCN **12′** ($^2A'$)	135.1	−2.6	123.5	120.9				
CS− cCCN **12″** ($^2A''$)	154.6	−2.8	144.9	142.1				
SC-cNCC **13** ($^2B_1$)	100.4	−2.1	99.0	96.9				
NS-cCCC **14**	148.9	−3.2	138.2	135.0				
S-cNCC−C **15** ($^2A''$)	138.4	−2.4	138.4	136.0				
S-cCNCC **16** ($^2A''$)	108.1	−2.5	100.3	97.8				
N-cCCSC **17** ($^2A'$)	114.0	−1.2	103.9	102.7				
C-cCCNS **18** ($^2A'$)	125.9	−2.0	115.8	113.8				
C-cCNSC **19**	161.0	−3.1	152.0	148.9				
cSCCNC **20** ($^2A'$)	102.0	−0.8	93.8	93.0				
cSCCNC **20′** ($^2A'$)	115.7	−1.2	107.7	106.5				
cSCCNC **20″** ($^2A'$)	133.0	−0.7	123.0	122.3				
cSCCCN **21** ($^2A'$)	102.3	−0.7	93.8	93.1				
CC(S)CN **22** ($^2A'$)	77.1	−1.1	64.4	63.3				
CS(C)CN **23** ($^2A''$)	206.1	−4.2	190.4	186.2				
CS(C)NC **24** ($^2A''$)	217.2	−4.9	198.1	193.2				
cageCCSCN **25** ($^2A'$)	146.7	−1.5	134.4	132.9				
cageCCCSN **26**	167.0	−2.7	152.7	150.0				
cageSCCCN **27** ($^2A''$)	172.1	−2.3	157.0	154.7				
CS···CNC **28** ($^2\Pi$)	116.8	−4.4	102.2	97.8				
CS···CCN **29** ($^2A'$)	118.8	−3.9	103.5	99.6				
CS···cCNC **30** ($^2A'$)	132.1	−4.7	116.5	111.8				
TS1/4′ ($^2A'$)	127.6	0.9	115.5	116.4				
TS1/6 ($^2A''$)	121.9	−2.9	113.3	110.4				
TS1/9 ($^2A''$)	62.1	−1.3	56.1	54.8	61.5	−0.9	59.6	58.7
TS1/9*($^2A''$)	69.9	−2.0	60.7	58.7				
TS1/9** ($^2A''$)	118.6	−3.8	103.1	99.3				
TS1/11 ($^2A''$)	65.1	−1.9	61.1	59.2				
TS1/11* ($^2A''$)	124.5	−3.0	122.9	119.9				
TS1/11** ($^2A''$)	136.9	−3.8	130.7	126.9				
TS1/21 ($^2A'$)	110.5	−2.0	102.1	100.1				
TS1/21* ($^2A'$)	112.9	−1.5	104.2	102.7				
TS1/22 ($^2A'$)	80.1	−1.4	68.5	67.1				
TS1/22* ($^2A'$)	79.6	−1.8	69.6	67.8				
TS1/25	152.3	−2.5	141.5	139.0				
TS2/2 ($^2A''$)	159.4	−4.2	148.0	143.8				
TS2/2* ($^2A''$)	154.3	−3.2	147.2	144.0				
TS2/10 ($^2A''$)	83.3	−1.8	78.0	76.2	81.0	−1.1	79.4	78.3
TS2/10* ($^2A''$)	97.3	−2.9	89.5	86.6				
TS2/11 ($^2A''$)	58.3	−1.8	54.3	52.5	55.3	−1.6	55.9	54.3
TS2/20 ($^2A'$)	104.9	−1.5	98.4	96.9				
TS2/20′ ($^2A'$)	121.9	−2.1	112.4	110.3				
TS3/6 ($^2A'$)	135.5	−2.6	120.1	117.5				
TS3/6* ($^2A'$)	126.8	−2.9	120.9	118.0				
TS3/15	155.8	−2.7	152.1	149.4				
TS3/15* ($^2A'$)	164.5	−3.1	160.0	156.9				
TS3/16	112.7	−2.7	106.5	103.8	110.1	−2.3	107.7	105.4
TS3/20 ($^2A'$)	128.8	−1.8	123.6	121.8				
TS3/20* ($^2A'$)	159.5	−3.2	150.3	147.1				
TS3/20′ ($^2A'$)	120.6	−2.0	110.6	108.6				
TS3/20′* ($^2A'$)	130.6	−2.0	126.5	124.5				
TS3/20″ ($^2A'$)	133.8	−1.4	124.3	122.9				
TS3/22 ($^2A'$)	125.8	−2.6	115.1	112.5				
TS3/22* ($^2A'$)	127.0	−2.6	120.6	118.0				
TS3/25	163.4	−3.3	152.6	149.3				

TABLE 2: Continued

species	B3LYP[c]	ΔZPVE B3LYP[c]	CCSD(T)[d]//B3LYP[c]	total 1	QCISD[c]	ΔZPVE QCISD[c]	CCSD(T)[e]//QCISD[c]	total 2
TS3′/6 (^{2}A″)	123.9	−2.9	119.5	116.6				
TS3′/6* (^{2}A″)	124.4	−3.0	120.8	117.8				
TS3′/13 (^{2}A″)	101.4	−2.3	100.3	98.0				
TS3′/15 (^{2}A″)	155.8	−2.7	152.1	149.4				
TS4/4	108.8	−2.7	95.5	92.8				
TS4/5	115.1	−3.1	105.6	102.5	110.7	−2.8	108.4	105.6
TS4/9	106.6	−2.6	97.6	95.0	99.3	−2.3	98.5	96.2
TS4/9*	117.2	−2.6	102.8	100.2				
TS4/20	132.2	−2.6	121.6	119.0				
TS4′/20′ (^{2}A′)	125.8	−2.5	112.8	110.3				
TS4′/22 (^{2}A′)	106.6	−2.6	97.6	95.0				
TS5/5	128.4	−3.2	115.4	112.2				
TS5/10	152.8	−3.1	143.7	140.6				
TS5/18	137.5	−2.9	126.5	123.6				
TS6/8 (^{2}A″)	141.8	−3.1	138.2	135.1				
TS6/9 (^{2}A″)	130.1	−2.9	127.7	124.8				
TS6/14	161.7	−3.7	153.4	149.7				
TS6/15 (^{2}A″)	139.0	−2.8	139.3	136.5				
TS6/15* (^{2}A″)	144.1	−2.5	139.5	137.0				
TS6/18 (^{2}A′)	130.7	−2.7	122.4	119.7				
TS6/21 (^{2}A′)	109.6	−1.2	101.4	100.2	110.0	−0.5	102.0	101.5
TS6/22 (^{2}A′)	127.2	−2.4	124.5	122.1				
TS6/22* (^{2}A″)	127.8	−2.7	125.8	123.1				
TS7/9 (^{2}A″)	129.5	−1.6	118.6	117.0				
TS7/29	120.2	−3.6	107.8	104.2				
TS9/9 (^{2}A″)	124.0	−3.5	111.4	107.9				
TS9/10	102.6	−2.9	92.8	89.9				
TS9/10*	102.6	−2.9	92.8	89.9				
TS9/11 (^{2}A″)	81.7	−2.1	73.3	71.2				
TS9/17	115.2	−2.4	106.7	104.3				
TS9/23 (^{2}A″)	218.5	−4.7	203.0	198.3				
TS9/27	176.3	−3.3	160.1	156.8				
TS10/11 (^{2}A″)	98.6	−2.8	89.3	86.5				
TS10/11*	107.3	−3.2	101.3	98.1				
TS10/11**	107.6	−3.1	101.5	98.4				
TS10/12″ (^{2}A″)	155.8	−3.3	146.6	143.3				
TS10/28 (^{2}A″)	150.6	−3.4	140.0	136.6				
TS10/28* (^{2}A″)	150.7	−3.1	145.0	141.9				
TS11/11 (^{2}A″)	81.1	−2.5	76.5	74.0				
TS11/16	108.2	−2.7	99.9	97.2				
TS11/26	167.7	−3.3	154.0	150.7				
TS12/30 (^{2}A′)	142.9	−3.9	131.8	127.9				
TS12′/30 (^{2}A′)	142.4	−3.9	131.0	127.1				
TS15/19	165.8	−3.6	158.4	154.8				
TS18/22 (^{2}A′)	126.0	−2.4	115.8	113.4				
TS20/20 (^{2}A′)	136.1	−2.7	125.8	123.1				
TS20′/20′ (^{2}A″)	137.2	−1.9	132.1	130.2				
TS23/24	224.5	−5.1	209.4	204.3				
NCCCS ^{4}**1** (^{4}A″)	57.6	−1.4	57.5	56.1				
CNCCS ^{4}**2** (^{4}A″)	82.4	−1.6	80.7	79.1				
CCNCS ^{4}**3** (^{4}A″)	103.1	−1.8	105.6	103.8				
CCSNC ^{4}**5** ($^4\Sigma$)	131.1	−3.5	119.4	115.9				
CCCNS ^{4}**6** (^{4}A″)	112.8	−1.7	115.5	113.8				
NC-cCCS ^{4}**9**	102.6	−1.3	96.8	95.5				
CN-cCCS ^{4}**10**	124.3	−1.8	117.5	115.7				

[a] For the relevant species, the values at the CCSD(T)/6-311G(2df)//QCISD/6-311G(d) are listed also. The symbols in parentheses of the column denote the point group symmetry. Only the electronic states of the species that are not of C_1 symmetry are given. [b] The total energies of reference isomer **1** at the B3LYP/6-311G(d) level are −567.2205525 au, at CCSD(T)/6-311G(2d)//B3LYP/6-311G(d) level is −566.2851185 au, at the QCISD/6-311G(d) level is −566.2033965 au, and at the CCSD(T)/6-311G(2df)//QCISD/6-311G(d) level is −566.3720291 au. The ZPVE at B3LYP and QCISD level are 0.018099 and 0.017476 au, respectively. [c] The basis set is 6-311G(d) for B3LYP and QCISD. [d] The basis set is 6-311G(2d) for CCSD(T). [e] The basis set is 6-311G(2df) for CCSD(T).

where the temperature is very low so that the species with high kinetic stability can have long lifetime once formed. In fact, various isomeric species with higher energy yet considerable kinetic stability are already known in space, e.g., HNC, HCCNC, and HNCCC (high-energy isomers of HCN and HCCCN, respectively), etc. Therefore, existence of our predicted kinetically stabilized isomers is promising. The QCISD/6-311G(d) harmonic vibrational frequencies, dipole moments, and rotational constants collected in Table 1 can be helpful for future experimental and interstellar characterization of the eight newly predicted doublet isomers **2**, **3**, **4**, **5**, **6**, **9**, **9′**, and **10**.

It is worth mentioning that for the nine isomers **1**, **2**, **3**, **4**, **5**, **6**, **9**, **9′**, and **10** as well as the seven transition states **TS1/9**, **TS2/10**, **TS2/11**, **TS3/16**, **TS4/5**, **TS4/9**, and **TS6/21** that govern their kinetic stability, the geometrical parameters and spectroscopic properties at the B3LYP/6-311G(d) level are generally in good agreement with those at the QCISD/6-311G(d) level (in Figure 1, and Table 1). As a result, the respective relative

TABLE 3: Relative (kcal/mol) Energies of Dissociation Fragments of the NC_3S Structures at the B3LYP/6-311G(d) and Single-Point CCSD(T)/6−311 g(2d) Levels[a]

species	B3LYP[b]	ΔZPVE B3LYP[b]	CCSD(T)[c]//B3LYP[b]	total
$CCNS(^2\Pi) + C(^3P)$	222.2	−4.0	212.8	208.8
$NCCS(^2A') + C(^3P)$	157.0	−3.4	145.8	142.4
$NCCS(^2A'') + C(^3P)$	157.0	−3.8	144.9	141.1
$CNCS(^2A') + C(^3P)$	176.4	−4.1	166.0	161.9
$CCCS(^1\Sigma) + N(^2D)$	202.7	−3.2	186.0	182.8
$CCCS(^1\Sigma) + N(^4S)$	137.7	−3.2	120.0	116.8
$CCCN(^2A') + S(^3P)$	122.1	−3.0	114.1	111.1
$CCNC(^2A') + S(^3P)$	146.1	−3.2	137.3	134.1
$CNS(^2\Pi) + CC(^1\Sigma_g^+)$	208.9	−4.0	169.2	165.2
$NCS(^2\Pi) + CC(^1\Sigma_g^+)$	178.9	−3.6	140.6	137.0
$CNS(^2\Pi) + CC(^3\Pi_u^-)$	186.3	−4.2	171.5	167.3
$NCS(^2\Pi) + CC(^3\Pi_u^-)$	156.3	−3.9	142.9	139.0
$CCS(^1\Sigma) + CN(^2\Sigma)$	152.6	−3.8	135.6	131.8
$cCCS(^1A_1) + CN(^2\Sigma)$	165.7	−4.5	145.5	141.0
$CCS(^3\Sigma) + CN(^2\Sigma)$	132.4	−3.8	121.3	117.5
$CCN(^2\Pi) + CS(^1\Sigma)$	119.5	−4.1	105.2	101.1
$CNC(^2\Pi) + CS(^1\Sigma)$	117.5	−4.6	103.4	98.8
$cCCN(^2A_1) + CS(^1\Sigma)$	132.7	−5.0	117.6	112.6
$CCC(^1\Sigma_g) + NS(^2\Pi)$	155.7	−4.5	140.4	135.9
$cCCC(^3A_1') + NS(^2\Pi)$	174.7	−4.0	162.8	158.8

[a] The symbols in parentheses of the column denote the point group symmetry. [b] The total energies of reference isomer **1** at the B3LYP and single point CCSD(T) levels as well as the ZPVE at the B3LYP level are listed in footnote b of Table 2. The basis set is 6-311G(d) for B3LYP. [c] The basis set is 6-311G(2d) for CCSD(T).

energies at the CCSD(T)//B3LYP level are very close to those at the CCSD(T)//QCISD levels (in Table 2). On the other hand, we consider the spin polarization of the wave functions here, which is important in assessment of the reliability of the spectroscopic parameters and relative energies. It is known that the DFT- and QCI (or CC)-based wave functions are subject to little spin contaminations. In fact, as shown in Table 1, the $\langle S^2 \rangle$ values (criteria for the spin contamination) for the nine species are very close to the value 0.75 for a pure doublet state.

Finally, it is useful to discuss the possibility of applying the present calculated results to larger NC_nS molecules. Generally, for all the 9 doublet NC_3S species, the resonance structure that contains the S-radical center plays an important part. So, all the 9 kinetically stable NC_3S isomers can be viewed as the combination of C_3N and S atom at various attack sites. It's better to consider NC_3S as S-doped C_3N molecules rather than the N-doped C_3S molecules. Similarly, we expect that the isomers (S-addition at terminal atoms of C_nN, S-insertion to the C−C single bonding of C_nN), and S-addition to the terminal CC π-bonding of C_nN conceived from the combination between C_nN and S atom can be kinetically stable for larger NC_nS molecules for which detailed potential energy surveys are even more cost expensive.

3.4. Wave Function Stability and Quartet NC_3S Species. It is desirable to perform an analysis of the wave function stabilities for the doublet NC_3S species. Using the "stable = opt" option, the B3LYP-wave functions of the relevant NC_3S isomers **1**, **2**, **3**, **4**, **5**, **6**, **9**, and **10** are tested and are all found to have no internal doublet instability. In fact, the quartet isomers **^{4}1**, **^{4}2**, **^{4}3**, **^{4}5**, **^{4}6**, **^{4}9,** and **^{4}10** are all energetically much high-lying than the corresponding doublet species with large double-quartet energy gaps 30−60 kcal/mol, as shown in Table 2. The quartet state species may be related to some reactions such as $N(^4S) + CCCS(^1\Sigma)$ and $S(^3P) + CCCN(^2A')$. Since we are mainly concerned with the stability of various NC3S isomers, a detailed potential energy surface survey on the higher-energy quartet state species is not decided to perform in the present article. Note that the Arabic number **4** in the top left corner means the quartet state.

4. Conclusions

A very complex potential-energy surface of NC_3S is theoretically established, involving 40 minimum isomers and 81 interconversion transition states. In addition to the experimentally known isomer NCCCS **1** (0.0), eight new isomers CNCCS **2** (26.9), CCNCS **3** (56.9), CCSCN **4** (62.7), CCSNC **5** (85.4), CCCNS **6** (67.0), NC-cCCS **9** (34.2), **9′** (40.9), and CN-cCCS **10** (57.1) are predicted to possess very high kinetic stability of around or more than 20 kcal/mol. They could be produced under certain laboratory and interstellar conditions. All the nine NC_3S isomers can mainly be considered as the different combined forms between the C_3N radical and S atom. The theoretical results in this paper are expected to be useful for understanding the isomerism of larger NC_nS radicals as well as the formation process of S-doped C_nN materials. The present study also represents the first detailed investigation on the isomerization and dissociation of NC_nS series.

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Supporting Information Available: Table 4 showing the harmonic vibrational frequencies and corresponding infrared intensities of the unstable NC_3S isomers at the B3LYP/6-311G-(d) level and Figure 6 showing all possible isomerizaiton and dissociation pathways of various NC_3S isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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