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SiC_3N: A Promising Interstellar Molecule with Stable Cyclic Isomers

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The potential energy surface of SiC_3N is investigated at various levels. A total of 33 isomers are located connected by 44 interconversion transition states. At the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d) level, the lowest lying isomer is linear SiCCCN with a $^2\Pi$ electronic state whose structure mainly resonates between $^{\bullet}|\mathrm{Si{-}C{\equiv}C{-}C{\equiv}N}|$ and $|\mathrm{Si{=}C{=}C^{\bullet}{-}C{\equiv}N}|$. The chainlike low-energy structures SiCCNC (25.0 kcal/mol), SiNCCC (33.9 kcal/mol), CCSiCN (42.9 kcal/mol), and CCSiNC (45.7 kcal/mol) possess large kinetic stability also. Another two kinetically very stable three-membered-ring structures with $^2A'$ electronic states are located, i.e., CN-cCCSi (33.2 kcal/mol) and CN-cSiCC (40.7 kcal/mol), with a kinetic stability of 40.3 and 128.4 kcal/mol, respectively. Except for CN-cSiCC, other isomers mentioned above contain conjugative or hyperconjugative multiple bonding. Among the SiC_nN series, SiC_3N may be the first radical with stable cyclic isomers that can be detected in interstellar space. For the relevant structures, the higher level CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) and CASPT2(13,13)/6-311G(2df)// CASSCF(13,13)/6-311G(2df) calculations are performed to obtain more reliable structures, relative energies, vibrational spectra, dipole moments, and rotational constants. The similarities and discrepancies of SiC_3N, analogous C_4N and SiC_nN series, i.e., SiCN and SiC_2N, are compared and analyzed.

1. Introduction

Silicon and nitrogen chemistry have received considerable attention from various aspects. One area of interest is their potential importance in interstellar space. Up to now, several Si- or N-containing molecules such as C_nN ($n = 1, 3, 5$), SiC_n ($n = 1-4$), SiN, SiO, SiS, and PN have been detected in interstellar medium.[1]

Recently, the Si-, C-, and N-containing species have received experimental and theoretical attention. Particularly, two new silicon-bearing isomers, i.e., the closed-shell asymmetric tops cyanosilylene (HSiCN) and its isomer HSiNC, have been detected in a laboratory discharge by molecular beam Fourier transform microwave spectroscopy.[2] Both isomers are good candidates for astronomical detection, closely related in structure and composition to known astronomical molecules. The detection of the SiCN radical in an astronomical source has been reported and the microwave spectrum of it was recently reported in the laboratory also.[3−5] The geometrical parameters showed that only two chainlike structures, i.e., SiCN and SiNC, have kinetic stability connected by two transition states.[6] At the same time, the analogues SiC_2N have recently received theoretical consideration.[7] Although several cyclic forms have been identified as energy minima on the PES of SiC_2N, they are kinetically unstable toward isomerization. Generally, SiC_3N is a member of the SiC_nN series to be detected soon. HC_4N isomers have been detected in the laboratory.[8] The C_4N species has already been experimentally generated via mass spectrometry methods[9] and detected in a supersonic molecular beam by Fourier transform microwave spectroscopy.[10] The study of C_4N structure, energy, and kinetic stability showed that both chainlike and cyclic structures can be located as kinetically stable isomers on its PES.[11] SiC_3N, which is analogous to SiCN, SiC_2N, and isovalent C_4N, is expected to exist in interstellar space.

On the other hand, Si- or N-containing species have been believed to play important roles in materials chemistry. Binary silicon carbides are commonly used in microelectronic and photoelectronic applications.[12] Nitrogen is usually used as a minute dopant. During the N-doped SiC vaporization process, the smaller pentaatomic species SiC_3N may be generated. The knowledge about the structures, energies, and bonding nature of various SiC_3N isomers may be helpful in understanding the initial step of the growing mechanism during the N-doped SiC vaporization process.

In this paper, we choose to study the pentaatomic molecule SiC_3N, and mainly want to resolve the following questions: (1) Does it have stable cyclic forms such as C_4N, or only chainlike structures such as SiCN and SiC_2N? (2) What is the bonding nature of the most important isomers? (3) What are the similarities and discrepancies among SiCN, SiC_2N, SiC_3N, and C_4N?

2. Computational Methods

All calculations are carried out with the GAUSSIAN 98[13] and MOLCAS 5.2[14] (for CASSCF and CASPT2) program packages. The optimized geometries and harmonic vibrational frequencies of the local minima and transition states are obtained at the B3LYP/6-311G(d)[15] theory level. To get reliable energies, the CCSD(T)/6-311G(2d)[16] single-point energy calculations are further performed based on the B3LYP/6-311G(d) geometries. To confirm whether the obtained transition states connect the right isomers, the intrinsic reaction coordinate (IRC) calculations are performed at the B3LYP/6-311G(d) level. Furthermore, for the relevant species, the calculations on the structures, frequen-

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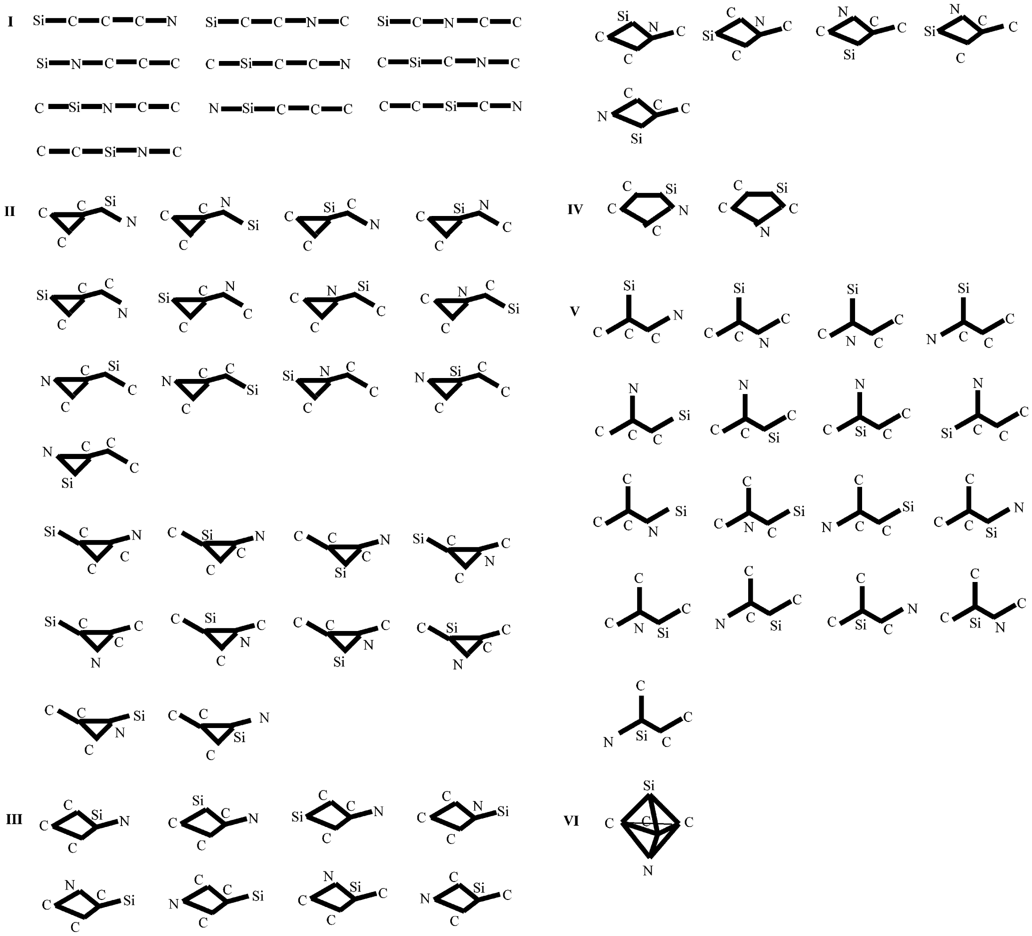


Figure 1. Scheme for isomeric species.

cies, and energies are carried out at the QCISD/6-311G(d)[17] and CCSD(T)/6-311+G(2df) (energy only) levels, including the zero-point vibrational energies (ZPVE) at the 6-311G(d) B3LYP and QCISD levels for energy correction. The CASPT2(13,13)/6-311G(2df)//CASSCF(13,13)/6-311G(2df) method is used to test the relevant species' multiconfigurational effects.

3. Results and Discussion

To include as many isomeric forms as possible, we initially considered six types of isomers, i.e., chainlike species (**I**), three-membered ring species (**II**), four-membered ring species (**III**), five-membered ring species (**IV**), cage-like species (**V**), and branched-chain species (**VI**), as depicted in Figure 1. Among those possible structures, 33 isomers are located connected by 44 interconversion transition states at the B3LYP/6-311G(d) level.

The letter **m** is used to denote various SiC_3N isomers, and **TSm/n** denotes the transition states connecting the species **m** and **n**. The optimized geometrical parameters of the SiC_3N isomers and transition states are shown in Figures 2 and 3, respectively. The harmonic vibrational frequencies as well as the infrared intensities, dipole moments, and rotational constants of the relevant SiC_3N species are listed in Table 1, while the relative energies of all the structures are collected in Table 2. The possible dissociation products' energies are shown in Table 3 and their structures are shown in Figure 4. A schematic potential energy surface (PES) of SiC_3N is presented in Figure 5a, and in addition Figure 5b shows all the most relevant isomers together with the transition states governing their kinetic stability. Unless otherwise specified, the relative energies are at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE level (simplified as CCSD(T)//B3LYP).

3.1. SiC_3N PES. Among the 33 isomers, 11 have chainlike structures, i.e., SiCCCN **1** (0.0), SiCCNC **2** (25.0), SiNCCC **3** (33.9), CCSiCN **4** (42.9), CCSiNC **5** (45.7), SiNCCC **6** (49.6), SiCNCC **7** (66.3), NCCSiC **8** (101.5), NCCSiC **8′** (101.2), CSiCNC **9** (130.9), and CSiCNC **9′** (123.9). Among these, **1**, **2**, **3**, and **7** are all linear forms with $^2\Pi$ electronic states, and **4**, **5**, **6**, **8**, and **9** with Si located inside are bent forms with $^2A'$ electronic states. Two structures, i.e., **8′** and **9′**, are found for the isomers **8** and **9**, respectively, with different electronic states ($^2A''$). Neither CSiNCC nor NSiCCC can be located as a minimum.

Nine isomers on the PES include three-membered rings. NC-cCCSi **10** (9.6) and CN-cCCSi **11** (33.2) are CCSi three-membered ring structures with an exocyclic NCC bond and an exocyclic CNC bond, respectively. CN-cSiCC **12** (40.7) is a SiCC three-membered-ring structure with an exocyclic CNSi bond. SiC-cCNC **14** (50.8), CSi-cCNC **17** (148.1), and CSi-cNCC **18** (175.1) have NCC three-membered-ring structures. SiN-cCCC **13** (47.8) and NSi-cCCC **16** (121.6) including a CCC three-membered ring are of C_{2v} symmetry with $^2B_2$ electronic states. Only CC-cNSiC **15** (94.2) has an NSiC three-membered-ring structure. Note that only **10**, **11**, and **12** are energetically low lying.

Except for C-cCCSiN **23** (108.0), the other four-membered-ring species all have CC or CSi cross-bonding. N-cCCCSi **19** (50.9) and N-cCCCSi **20** (54.3) both include a CCCSi four-membered ring as well as an exocyclic NC bond, while N-cSiCCC **24** (120.4) includes a CCCSi four-membered ring

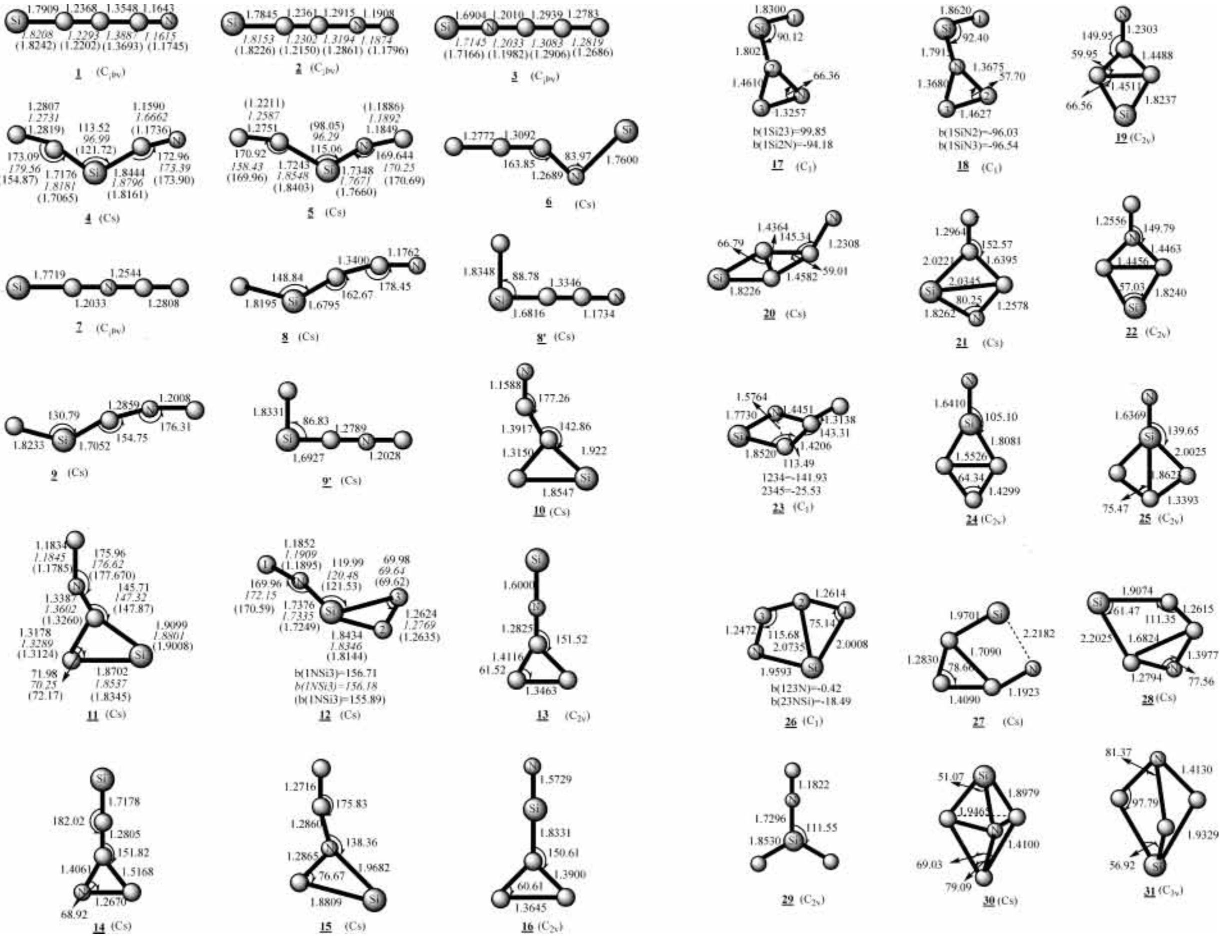


Figure 2. Optimized geometries of SiC$_3$N isomers at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees. The values obtained at the QCISD/6-311G(d) level and with the CASSCF(13,13)/6-311g(2df) method for some relevant isomers are also given in italics and in parenthese, respectively.

and an exocyclic SiN bond. **19**, **20**, and **24** all have CC cross-bonding. N-cSiCCC **25** (134.2), which has a CCCSi four-membered ring just like **24**, however, has SiC cross-bonding while **24** does not. C-cCCNSi **21** (55.8), C-cNCSiC **22** (104.6), and C-cCCSiN **23** (108.0) are all CCNSi four-membered-ring forms with exocyclic CC, CN, and CC bonds, respectively. Among the 7 four-membered-ring isomers, **19**, **22**, **24**, and **25** are of C_{2v} symmetry with $^2B_2$ electronic states, while **20** and **21** are of C_s symmetry with $^2A''$ and $^2A'$ electronic states, respectively.

Total three five-membered-ring isomers cSiNCCC **26** (53.3), cSiCCCN **27** (56.6), and cSiCCNC **28** (77.0) are all searched as minima. Both **27** and **28** are C_s symmetrized with $^2A''$ electronic states. CSi, CC, and CC cross-bonding are found in **26**, **27**, and **28**, respectively.

Finally, isomer **29** (173.3) is a C_{2v}-symmetried branched-chain structure with a $^2A_2$ state. Both isomers **30** (105.5) and **31** (131.0) may be viewed as cage-like species of respective C_s and C_{3v} symmetry, $^2A'$ and $^2A_1$ electronic states. All three possess very high relative energies, so they may be of minute importance.

It is worthy of note that we performed additional calculations to test the doublet instability of the seven C_{2v} systems **13**, **16**, **19**, **22**, **24**, **25**, and **29**. The results show that all of them are stable. In case they could have lower energy C_s or even C_1 structures, we adjusted the seven isomers to C_s and C_1 symmetry. Fortunately, all final optimizations are converged to the more symmetrized C_{2v} structures.

To discuss the kinetic stability, we need to consider as many various isomerization and dissociation pathways as possible. Since the relative energies of the dissociation products are rather high (more than 89 kcal/mol at the CCSD(T)//B3LYP level) as shown in Table 3, we do not attempt to search any dissociation transition states. So the isomerization barriers govern the kinetic stability of SiC$_3$N isomers. From the isomerization process of the SiC$_3$N isomers depicted in Figure 5a, we can see that most of the high-energy isomers can convert to the low-energy isomers. Then, the kinetic stability order of all the SiC$_3$N isomers can be obtained as **12** (128.4, **12**→**17**) > **11** (40.3, **11**→**14**) > **2** (25.9, **2**→**14**) > **15** (25.2, **15**→**6**) > **7** (24.7, **7**→**2**) > **17** (21.0, **17**→**12**) > **4** (20.4, **4**→**5**) > **1** (16.9, **1**→**10**) > **3** (15.°7, **3**→**6**) = **5** (15.7, **5**→**21**) > **25** (11.7, **25**→**1**) > **24** (9.0, **24**→**16**) > **18** (8.2, **18**→**17**) > **10** (7.3, **10**→**1**) > **16** (5.5, **16**→**11**) > **9′** (5.0, **9′**→**11**) > **23** (3.8, **23**→**28**) > **19** (3.7, **19**→**10**) = **13** (3.7, **13**→**3**) > **26** (2.2, **26**→**1**) > **28** (1.0, **28**→**2**) > **21** (0.8, **21**→**26**) > **14** (0.1, **14**→**2**) > **6** (0.0, **6**→**3**) > **22** (−0.2, **22**→**11**) > **27** (−0.6, **27**→**1**). The values in parentheses are in kcal/mol. Yet, no transition states connecting isomers **8** (101.2), **8′** (101.5), **9** (123.9), **20** (54.3), **29** (173.3), **30** (105.5), and **31** (131.0) can be located. These isomers are expected to be of little importance in the investigation of SiC$_3$N isomerizations due to their high-lying energies.

From the order of kinetic stability, we can see that the cyclic isomer **12** has the highest kinetic stability (128.4, *137.3*), the italic values in parentheses are for CCSD(T)/6-311G+(2df)//QCISD/6-311G(d)+ZPVE single-point calculations. **1**, **2**, **3**, **4**, **5**, **7**, **11**, **15**, and **17** all have considerable kinetic stability (more than 15 kcal/mol). But the isomers **7** (66.3), **15** (94.2), and **17** (148.1) possess high energies (more than 65 kcal/mol). So **1** (0.0), **2** (25.0), **3** (33.9), **4** (42.9), **5** (45.7), **11** (33.2), and **12**

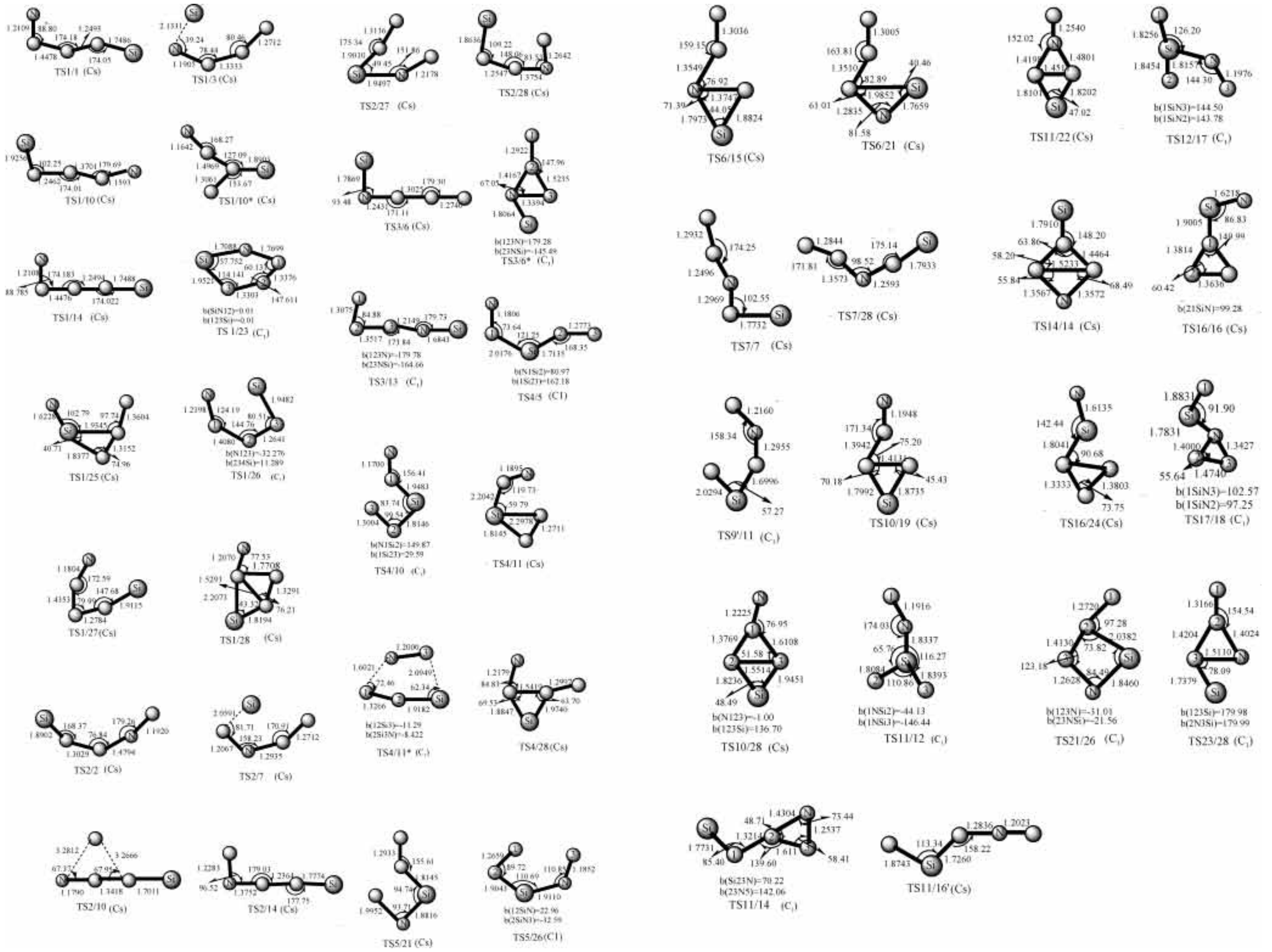


Figure 3. Optimized geometries of interconversion transition states between SiC_3N isomers at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees.

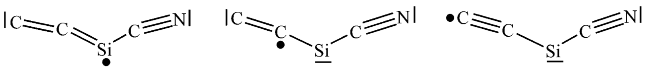
(40.7), with large thermodynamic and kinetic stabilities, may stimulate great interest in the scientific domain. Note that the values in parentheses are relative energies (in kcal/mol) with reference to isomer **1**. To get more accurate structures, energies, vibrational spectra, dipole moments, and rotational constants, CCSD(T)/6-311+G(2df)// QCISD/6-311G(d) level calculations have been performed on the seven isomers.

3.2. Properties and Implication of the Relevant Species. From above, we know that the seven isomers **1**, **2**, **3**, **4**, **5**, **11**, and **12** possessing large kinetic and thermodynamic stabilities may be observable in the laboratory and in interstellar space. So their structures and bonding natures are analyzed and discussed at the B3LYP/6-311G(d) level.

Both ground-state SiCCCN **1** and isomer SiCCNC **2** have linear structures and $^2\Pi$ electronic states. Their calculated SiC bond lengths lie between the typical SiC single bond and Si═C double bond.[18] Their CC bonds connecting to the Si atom are closer to the C≡C bond than to the C═C bond. Their CN bond lengths are a little longer than that of the C≡N triple bond. Then isomer **1** may be best described as a resonant structure between •|Si—C≡C—C≡N| and |Si═C═C•—C≡N| (where "|" denotes the lone electron pair, and "•" denotes the single electron). The spin densities (0.7514, −0.1350, 0.3100, −0.0799, and 0.1535 e for Si, C, C, C, and N, respectively) suggest the former bears somewhat more weight. For isomer **2**, the spin densities (0.7698, −0.1373, 0.2701, −0.0654, and 0.1628 *e* for Si, C, C, N, and C, respectively) suggest a resonant structure among •|Si—C≡C—N|═C|, |Si═C═C•—N|═C|, and |Si═C═C═N|—C|• with the first one having the most weight and the last one the least. The unpaired electron is mainly located at the terminal Si atom.

SiNCCC **3** has a linear structure with a $^2\Pi$ electronic state also. The terminal SiN bond is longer than the typical Si═N bond, and the NC bond is shorter than the typical NC double bond. Both of the CC bonds are a little shorter than the typical CC double bond. The spin densities (0.7583, −0.1237, 0.2148, −0.0826, and 0.2332 e for Si, N, C, C, and C respectively) suggest a resonant structure among three forms: (1) •|Si—N|═C═C═C|, (2) |Si═N|—•C═C═C|, and (3) |Si═N|—C|—C≡C•, with the former (1**)** having the most weight, (3) less, and (2) the least.

The bend structures of CCSiCN **4** and CCSiNC **5** with $^2A'$ electronic states may be attributed to their internal Si atom. For isomer **4**, the CC bond is just between C═C and C≡C bond values, the SiC bond connecting to the N atom is a little shorter than the typical SiC single bond, while the other one is very close to the typical Si═C bond. Its NC bond length is close to that of the N≡C bond. So CCSiCN **4** can be viewed as a superposition of the following structures:



(1) (2) (3)

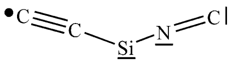
The spin densities (0.2976, 0.1462, 0.4867, 0.0475, and 0.0221 e for C, C, Si, C, and N, respectively) suggest form (1**)** having

TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in Parentheses), Dipole Moment (D), and Rotational Constants (GHz) of the Relevant SiC$_3$N Structures at the B3LYP/6-311G(d) and QCISD/6-311G(d) Level

species	frequencies (infrared intensity)	dipole moment	rotational constant
SiCCCN1	98 (1), 97 (0), 115 (1), 294 (8), 323 (6), 481 (21), 511 (4), 586 (0), 1032 (18), 2023 (0), 2259 (74)	3.6088	1.418980
SiCCCN1^a	97 (0), 113 (1), 244 (4), 262 (7), 465 (32), 492 (6), 560 (1), 990 (48), 2095 (0), 2376 (47)	3.6097	1.390604
SiCCNC2	99 (0), 120 (0), 254 (5), 300 (6),397 (0), 490 (20), 523 (4), 1095 (11), 2014 (16), 2080 (32)	2.2914	1.499760
SiCCNC2^a	97 (0), 118 (0), 235 (4), 267 (5), 382 (0), 475 (45), 495 (5), 1061 (25), 2070 (24)	2.2979	1.471050
SiNCCC3	96 (1), 119 (2), 206 (7), 265 (7), 493 (14), 532 (22), 594 (23), 1039 (7), 1867 (37), 2093 (585)	5.5647	1.574248
SiNCCC3^a	83 (1), 108 (1), 163 (3), 223 (3), 505 (91), 516 (23), 590 (33), 1023 (61), 1901 (0)	5.9754	1.553837
CCSiCN4	69 (11), 116 (0), 215 (8), 234 (2), 362 (20), 554 (100), 743 (22), 1807 (94), 2265 (59)	3.4468	15.85766, 2.23128, 1.95605
CCSiCN4^a	72 (9), 124 (0), 195 (23), 226 (3), 380 (2), 573 (61), 625 (54), 1690 (244), 2269 (37)	3.1164	9.33758, 2.69063, 2.08875
CCSiNC5	71 (11), 108 (0), 164 (0), 183 (5), 335 (26), 593 (117), 760 (75), 1793 (15), 2092 (558)	3.3824	18.82232, 2.33141, 2.07446
CCSiNC5^a	103 (3), 107 (0), 165 (1), 226 (0), 405 (9), 636 (206), 659 (151), 1832 (37), 2091 (492)	2.1735	11.99191, 2.65001, 2.17039
CN-cCCSi11	169 (3), 201 (3), 372 (8), 468 (0), 599 (4), 728 (46), 942 (9), 1681 (4), 2135 (226)	2.6998	20.06309, 2.63942, 2.33256
CN-cCCSi11^a	165 (3), 188 (2), 376 (10), 449 (0), 617 (2), 737 (55), 970 (16), 1672 (5), 2165 (294)	2.9421	20.22717, 2.62196, 2.32109
CN-cSiCC12	103 (1), 132 (7), 154 (2), 278 (56), 310 (13), 610 (54), 791 (210), 1823 (9), 2089 (490)	2.1430	20.43512, 2.82211, 2.73641
CN-cSiCC12^a	113 (2), 130 (7), 174 (0), 314 (15), 319 (68), 630 (69), 822 (240), 1785 (13), 2086 (511)	2.2035	18.07124, 2.78018, 2.40949

[a] At the QCISD/6-311G(d) level.

most weight, (3**)** less, and (2**)** the least. For isomer **5**, the CC and CN bond are a little longer than the CC and CN triple bond. Its respective spin densities (0.2056, 0.0789, 0.6531, 0.0128, and 0.0495 e for C, C, Si, N, and C, respectively) suggest a resonant structure between the following two forms and the latter bears more weight.



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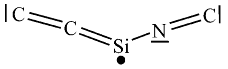
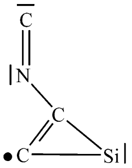


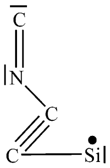
A hyperconjugative bonding is formed by the CC multiple bonding, the lone electron pair on the Si atom, and the CN multiple bonding, and this hyperconjugative bonding together with conjugative multiple bonding makes isomers **4** and **5** show higher stability although containing an internal Si atom.

Isomer **11** includes a SiCC three-membered ring. All five of the atoms are on the same plane. The CC bond value is pretty much the same as the normal C═C bond value. The CSi bond connecting to the N atom is a little longer than the typical CSi single bond, while the other one is close to it. The terminal CN bond length is longer than the normal C≡N triple bond, and the other one is between that of the CN double and single bond. Isomer **11** can be view as a superposition of the following Lewis structures:



(1)

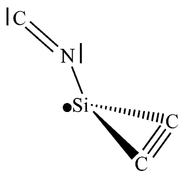
and



(2)

The conjugative multiple bonding formed by the terminal CN and the CC multiple bonding enhances the stability of cyclic isomer **11**. Considering the spin densities (0.0539, −0.0229, 0.0882, 0.6001, and 0.2795 e for C, N, C, C, and Si, respectively), form (1) should bear more weight than form (2).

Isomer **12** including a SiCC three-membered ring as well as exocyclic CNSi bond is of C_s symmetry with a $^2A'$ electronic state. The three C, N, and Si atoms form a plane and the other two C atoms lie symmetrically on the two sides of it. The CC bond value is just between that of the C═C and C≡C bonds. While the two SiC bond lengths are close to that of the SiC single bond, the CN bond value lies between that of the C≡N bond and the C═N bond. Its SiN bond length is very close to the typical SiN single bond. Considering the spin densities (0.0559, 0.0123, 0.6133, 0.0159, and 0.0159 e for C, N, Si, C, and C, respectively), isomer **12** can be viewed as the dominant structure:



The unpaired electron is mainly located at the center Si atom.

From the bonding natures discussed above, we can see that C≡C and C≡N triple bonds widely exist in the stable isomers of SiC$_3$N. No an Si≡C or Si≡N bond could be found in the above seven isomers. Except for isomer **5**, other valence structures are confirmed by the natural bond orbital (NBO) analysis.

To aid future identification of the SiC$_3$N isomers either in the laboratory or in interstellar space, the calculated vibrational frequencies, dipole moments, and rotational constants for the relevant isomers at the QCISD/6-311G(d) level are presented in Table 1. We can see that the dominant frequencies of isomers **1**, **2**, **3**, **4**, **5**, **11**, and **12** are 990, 475, 505, 1690, 2091, 2165, and 2086 cm^{-1}, respectively, with the corresponding infrared

TABLE 2: Relative Energies (kcal/mol) of the SiC_3N Structures and Transition States at the B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2d) Levels[f]

species	state	B3LYP[b]	ΔZPVE B3LYP[b]	CCSD(T)[c]// B3LYP[b]	total 1	QCISD[b]	CCSD(T)[d]// QCISD[b]	ΔZPVE QCISD[b]	total 2	CASPT2// CASSCF[e](13,13)
SiCCCN1[a]	$^2\Pi$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SiCCNC2	$^2\Pi$	25.4	−0.5	25.5	25.0	25.4	25.5	−0.3	25.2	32.0
SiNCCC3	$^2\Pi$	28.9	−0.6	34.5	33.9	36.9	32.7	−0.7	32.0	51.1
CCSiCN4	$^2A'$	49.4	−1.9	44.9	42.9	42.6	47.5	−2.2	45.3	41.8
CCSiNC5	$^2A'$	52.5	−2.3	48.0	45.7	45.8	49.7	−2.1	47.6	49.8
SiNCCC6	$^2A'$	48.7	−1.3	51.0	49.6					
SiCNCC7	2Π	61.7	−0.7	67.0	66.3					
NCCSiC8	$^2A'$	110.1	−1.7	103.2	101.5					
NCCSiC8′	$^2A''$	107.9	−2.0	103.1	101.2					
CSiCNC9	$^2A'$	133.2	−2.6	133.5	130.9					
CSiCNC9′	$^2A''$	129.4	−2.0	126.0	123.9					
NC-cCCSi10	$^2A'$	13.7	−0.2	9.8	9.6					
CN-cCCSi11	$^2A'$	37.3	−0.6	33.8	33.2	33.0	33.1	−0.5	32.6	55.4
CN-cSiCC12	$^2A'$	52.5	−2.0	42.7	40.7	44.1	41.7	−1.9	39.8	67.6
SiN-cCCC13	$^2B_2$	46.6	−1.5	49.2	47.8					
SiC-cCNC14	$^2A'$	50.0	−1.5	52.3	50.8					
CC-cNSiC15	$^2A'$	93.3	−1.4	95.6	94.2					
NSi-cCCC16	$^2B_2$	131.9	−3.2	124.8	121.6					
CSi-cCNC17		142.4	−3.0	151.1	148.1					
CSi-cNCC18		178.0	−3.9	178.5	175.1					
N-cCCCSi19	$^2B_2$	54.0	−1.1	52.0	50.9					
N-cCCCSi20	$^2A''$	57.8	−1.2	55.5	54.3					
C-cCCNSi21	$^2A'$	61.7	−2.1	57.9	55.8					
C-cNCSiC22	$^2B_2$	110.1	−2.7	107.3	104.6					
C-cCCSiN23		114.1	−2.8	110.8	108.0					
N-cSiCCC24	$^2B_2$	130.0	−2.4	122.8	120.4					
N-cSiCCC25	$^2B_2$	142.7	−3.0	137.1	134.2					
cSiNCCC26		61.3	−1.4	54.8	53.3					
cSiCCCN27	$^2A''$	63.5	−1.4	58.0	56.6					
cSiCCNC28	$^2A''$	82.9	−1.9	78.9	77.0					
CNSiCC29	2A2	188.0	−4.0	177.3	173.3					
pSiNCCC30	$^2A'$	114.1	−2.2	107.7	105.5					
pSiCCCN31	2A1	144.5	−2.9	133.9	131.0					
TS1/1	$^2A'$	59.3	−2.1	59.0	56.8					
TS1/3	$^2A''$	61.4	−1.3	56.7	55.4					
TS1/10	$^2A'$	28.3	−0.5	17.4	16.9	26.2	25.2	−0.2	25.0	
TS1/10*	$^2A'$	63.8	−2.1	57.7	55.6					
TS1/14	$^2A'$	59.3	−2.1	67.1	65.0					
TS1/23		127.7	−3.5	122.1	118.7					
TS1/25	$^2A''$	159.1	−3.1	149.0	145.9					
TS1/26		62.5	−2.1	57.6	55.5					
TS1/27	$^2A''$	63.7	−1.7	57.8	56.0					
TS1/28	$^2A''$	89.6	−2.6	82.9	80.3					
TS2/2	$^2A''$	108.5	−2.8	95.7	92.9					
TS2/7	$^2A''$	96.8	−1.7	92.7	91.0					
TS2/10	$^2A'$	155.2	−3.2	156.5	153.3					
TS2/14	$^2A'$	55.3	−1.9	52.8	50.9	53.5	48.8	−1.5	47.3	
TS2/27	$^2A''$	109.9	−3.5	102.7	99.2					
TS2/28	$^2A''$	83.4	−2.1	80.1	78.0					
TS3/6	$^2A'$	48.9	−1.4	51.1	49.6	55.0	53.8	−2.1	51.7	
TS3/6*		127.5	−3.3	119.3	116.0					
TS3/13		52.3	−1.7	53.2	51.5					
TS4/5		72.5	−3.0	66.3	63.3	69.5	66.3	−2.9	63.4	
TS4/10		77.4	−2.7	71.2	68.5					
TS4/11	$^2A'$	89.7	−3.1	80.7	77.6					
TS4/11*		111.5	−3.4	104.3	100.9					
TS4/28	$^2A''$	99.3	−3.1	108.1	105.1					
TS5/21	$^2A'$	70.5	−2.9	64.3	61.4	67.0	64.7	−2.8	61.9	
TS5/26		81.6	−3.2	71.0	67.8					
TS6/15	$^2A'$	122.9	−3.1	122.5	119.4					
TS6/21	$^2A'$	63.5	−2.1	62.0	59.9					
TS7/7		102.4	−2.0	94.5	92.5					
TS7/28	$^2A''$	82.9	−1.9	105.0	103.1					
TS9′/11	$^2A''$	137.9	−2.8	131.7	128.9					
TS10/19	$^2A'$	58.6	−1.9	56.5	54.6					
TS10/28		98.4	−2.3	93.6	91.3					
TS11/12		186.2	−4.2	180.3	176.1					
TS11/14		78.1	−2.7	76.3	73.5	76.9	74.2	−2.6	71.6	
TS11/16	$^2A'$	134.9	−3.2	130.3	127.1					
TS11/22	$^2A'$	110.1	−2.9	107.3	104.4					
TS12/17		181.0	−4.3	173.4	169.1	181.6	181.2	−4.1	177.1	

TABLE 2 (Continued)

species	state	B3LYP[b]	ΔZPVE B3LYP[b]	CCSD(T)[c]// B3LYP[b]	total 1	QCISD[b]	CCSD(T)[d]// QCISD[b]	ΔZPVE QCISD[b]	total 2	CASPT2// CASSCF[e](13,13)
TS14/14	$^2A'$	83.7	−2.7	81.5	78.8					
TS16/16	$^2A''$	140.1	−0.7	134.1	133.4					
TS16/24	$^2A''$	138.7	−3.2	132.6	129.4					
TS17/18		180.5	−3.9	187.2	183.3					
TS21/26		63.1	−1.7	58.4	56.6					
TS23/28	$^2A''$	117.3	−2.9	114.7	111.8					

[a] The total energy of reference isomer **1** at the B3LYP/6-311G(d) level is −458.4800977 au, at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d) level it is −457.5933461 au, at the QCISD/6-311G(d) level it is −457.5186127 au, at the CCSD(T)6-311+G(2df)//QCISD/6-311G(d) level it is −457.6632811 au, and at the CASPT2//CASSCF(13,13) level it is −456.8243249599 au. The ZPVE at the B3LYP and QCISD levels is 0.017594 and 0.017529 au, respectively. [b] The basis set is 6-311G(d) for B3LYP and QCISD. [c] The basis set is 6-311G(2d) for CCSD(T). [d] The basis set is 6-311+G(2df) for CCSD(T). [e] The 6-311G(2df) basis set and 13*13 electrons and active orbitals are used for the the CASSCF and CASPT2 methods. [f] For the relevant isomers, the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) and CASPT2(13,13)/6-311G(2df)//CASSCF(13,13)/6-311G(2df) values are included also.

TABLE 3: Relative Energies (kcal/mol) of Possible Dissociation Products of SiC_3N Isomers at the B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2d) Levels

species	B3LYP[b]	ΔZPVE B3LYP[b]	CCSD(T)[c]// B3LYP[b]	total
$C(^1\Sigma)+SiCCN(^2\Pi)$[a]	197.8	−3.2	223.5	220.3
$C(^1\Sigma)+SiCNC(^2\Pi)$	221.6	−3.5	207.2	203.7
$C(^1\Sigma)+SiNCC(^2\Pi)$	226.8	−3.7	193.0	189.3
$C(^3\Pi)+SiCCN(^2\Pi)$	155.8	−3.2	187.3	184.1
$C(^3\Pi)+SiCNC(^2\Pi)$	179.6	−3.5	170.9	167.4
$C(^3\Pi)+SiNCC(^2\Pi)$	184.8	−3.7	156.8	153.1
$N(^2\Pi)+SiCCC(^1\Sigma)$	244.6	−3.9	229.6	225.7
$N(^2\Pi)+SiCCC(^3\Pi)$	229.6	−3.9	221.6	217.7
$N(^2\Pi)+CSiCC(^1\Sigma)$	332.2	−5.6	290.9	285.3
$N(^2\Pi)+CSiCC(^3\Pi)$	332.4	−4.8	342.7	337.9
$N(^2\Pi)+SiCCCa(^1A1)$	237.6	−4.2	209.6	205.4
$N(^2\Pi)+SiCCCa(^3B1)$	255.5	−4.6	232.0	227.4
$N(^2\Pi)+SiCCCb(^1A1)$	242.5	−4.4	237.9	233.5
$N(^2\Pi)+SiCCCb(^3B1)$	249.2	−4.4	232.1	227.7
$SiC(^1\Sigma)+NCC(^2\Pi)$	209.6	−4.1	191.1	187.0
$SiC(^1\Sigma)+CNC(^2\Pi)$	207.6	−5.2	433.6	428.4
$SiC(^3\Pi)+NCC(^2\Pi)$	182.9	−4.3	235.9	231.6
$SiC(^3\Pi)+CNC(^2\Pi)$	180.9	−4.7	478.4	473.7
$NSi(^2\Sigma)+CCC(^1\Sigma g)$	156.7	−4.2	166.3	162.1
$NSi(^2\Sigma)+CCC(^3\Pi u)$	206.9	−5.8	221.3	215.5
$CC(^1\Sigma g)+SiCN(^2\Pi)$	173.7	−3.8	136.6	132.8
$CC(^1\Sigma g)+SiNC(^2\Pi)$	175.1	−4.0	138.8	134.8
$CC(^3\Pi u)+SiCN(^2\Pi)$	151.1	−4.5	170.6	166.1
$CC(^3\Pi u)+SiNC(^2\Pi)$	152.5	−4.3	172.8	168.5
$NC(^2\Sigma)+SiCC(^1\Sigma)$	110.9	−3.9	99.9	96.0
$NC(^2\Sigma)+SiCC(^3\Pi)$	156.9	−3.8	145.3	141.5
$Si(^1\Sigma)+NCCC(^2\Pi)$	148.2	2.4	111.3	113.7
$Si(^3\Pi)+NCCC(^2\Pi)$	122.2	2.4	87.2	89.6
$Si(^1\Sigma)+CNCC(^2A')$	170.7	−2.8	128.5	125.7
$Si(^3\Pi)+CNCC(^2A')$	144.7	−2.9	104.5	101.6

[a] 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 *a* of Table 2. The symbols in parentheses in column one denote the electronic states. [b] The basis set is 6-311G(d) for B3LYP. [c] The basis set is 6-311G(2d) for CCSD(T).

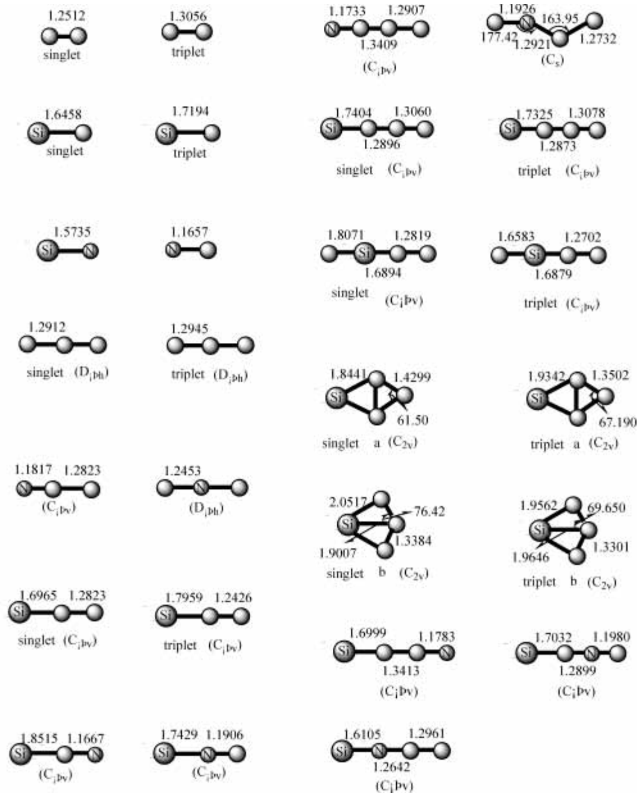


Figure 4. Optimized geometries of possible dissociation products of SiC_3N isomers at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees.

intensities 48, 45, 91, 244, 492, 294, and 511 km/mol. All seven isomers have very large dipole moments (3.6097, 2.2979, 5.9754, 3.1164, 2.1735, 2.9421, and 2.2035 D, respectively), making them very promising for microwave detection. The calculated CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) energies of **1, 2**, **3**, **4**, **5**, **11**, and **12** may also be helpful for their experimental characterization.

Furthermore, CASPT2//CASSCF calculations are performed to check the multiconfigurational properties of the above seven isomers, considering 13 frontier orbitals as active space and allowing 13 electrons to be excited within them, denoted as (13,13). The optimized geometrical structures at the CASSCF-(13,13) level of **1**, **2**, **3**, **4**, **5**, **11**, and **12** are given in Figure 2. The relative energies at the CASPT2//CASSCF(13,13)/6-311G-(2df) level for them are collected in Table 2. We can see that the geometrical structures and relative energies at the CASPT2//CASSCF level are in good agreement with the B3LYP- and QCISD/6-311G(d)-based calculated results. The leading electronic configurations occupied by **1**, **2**, **3**, **4**, **5**, **11**, and **12** (82.80%, 83.43%, 81.95%, 81.61%, 80.30%, 84.94% and 82.47%, respectively) are the same as those that spanned the Slater Determinant of B3LYP, indicating that the SiC_3N system has negligible multiconfigurational effect, and the CCSD(T)//B3LYP method is adequate for calculation of the structures, vibrational spectra, and energies.

3.3. Comparison to SiCN, SiC_2N, and C_4N. Generally, isovalent or same series' molecules are expected to possess similar chemical properties. SiCN, SiC_2N, and SiC_3N all belong to the SiC_nN series, and SiC_3N also can be viewed as one C-atom of C_4N replaced by the second-row Si atom. So SiCN, SiC_2N, C_4N, and SiC_3N may have much similarity on the PES.

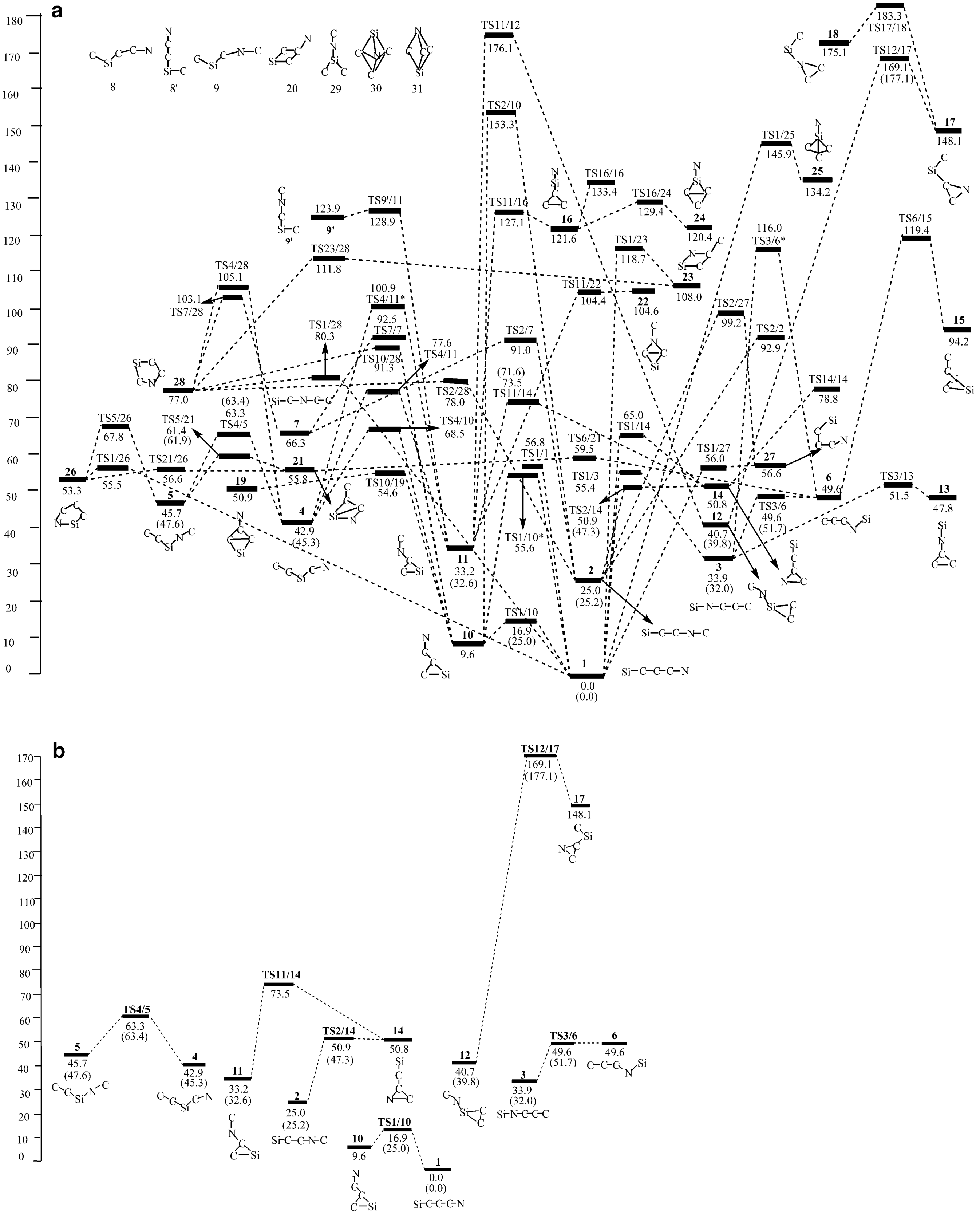


Figure 5. (a) Schematic potential energy surface of SiC_3N at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE level. The values in parentheses for the relevant species **1**, **2**, **3**, **4**, **5**, **11**, and **12** are obtained at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level. (b) The lowest ismoerization channels for the relative isomers. The values in parentheses for the relevant species **1**, **2**, **3**, **4**, **5**, **11**, and **12** are obtained at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level.

The structures and stability of SiCN, SiC_2N, and C_4N molecules have been extensively studied.[10,13] Chainlike structures can be located as stable isomers on the PES of the SiCN, SiC_2N, C_4N, and SiC_3N molecules. The linear SiCCCN **1,** SiCCNC **2**, and SiNCCC **3** of SiC_3N can be found similar to their analogous structures in SiCN, SiC_2N, and C_4N isomers.

All of the isomers contain conjugative multiple bonding. The bent forms CCSiCN **4** and CCSiNC **5** can exist as kinetically and thermodynamically stable structures mainly because of their hyperconjugative multiple bonding. Both C_4N and SiC_3N molecules have three-membered-ring isomers with large kinetic stability, yet no ring forms can be located as kinetically stable isomers on the SiCN and SiC_2N PES. The kinetic barriers of CN-cCCSi **11** and CN-cSiCC **12** (40.3 and 128.4 kcal/mol, respectively) are much higher than those of CN−CCC and NC−CCC (23.7 and 23.2 kcal/mol, respectively). This may attribute to the decrease of the three-membered-ring's tension when one C atom of the CCC ring is replaced by the second-row element Si.

For SiCN, SiC_2N, C_4N, and SiC_3N respective lowest lying isomers, SiCN, SiCCN, CCCCN, and SiCCCN are all linear structures with a $^2\Pi$ electronic state. The dominant structure of SiCN is $^{\bullet}$|Si−C≡N|, and that of SiCCN can be described as |Si=C$^{\bullet}$−C≡N|, while CCCCN can be viewed as a resonant structure between |C=C=C$^{\bullet}$−C≡N| and $^{\bullet}$|C−C≡C−C≡N|. The counterpart of SiC_3N, SiCCCN **1**, can be viewed as a resonant structure between $^{\bullet}$|Si−C≡C−C≡N| and |Si=C=C$^{\bullet}$−C≡N|. Since the second-row element Si atom is shown to have much less tendency to form π-bonding than the first-row C-atom, the cumulene structure |C=C=C$^{\bullet}$−C≡N| is the main structure of the two resonant structures in CCCCN while the conjugative triple bonding structure $^{\bullet}$|Si−C≡C−C≡N| is the main structure of the two resonant structures in SiCCCN.

4. Conclusions

The structures, energies, vibrational spectra, dipole moments, rotational constants, and isomerization of SiC_3N isomeric species are explored at various levels. Among the 33 minimum isomers, seven isomers may be kinetically stable toward isomerization and dissociation. The lowest lying linear isomer SiCCCN **1** with a $^2\Pi$ electronic state can be described as resonant forms between $^{\bullet}$|Si−C≡C−C≡N| and |Si=C=C$^{\bullet}$−C≡N|, and the former bears somewhat more weight. Five chainlike forms, i.e., SiCCCN **1**, SiCCNC **2**, SiNCCC **3**, CCSiCN **4**, and CCSiCN **5,** possess considerable kinetic stability toward either isomerization or dissociation. In contrast to the SiCN and SiC_2N molecules which have no kinetically stable cyclic structures, SiC_3N has two kinetically very stable cyclic forms, i.e., CN-cCCSi **11** and CN-cSiCC **12**. SiC_3N is a promising interstellar molecule with two stable cyclic isomers of the SiC_nN series. The bonding property suggests that the conjugative bonding and hyperconjugative multiple bonding are the main structures of the seven stable isomers.

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Supporting Information Available: Table 4 showing the harmonic vibrational frequencies and corresponding infrared intensities of the unstable SiC_3N isomers at the B3LYP/6-311G-(d) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) For parallel comparison, the bond distances Si−C (1.8850 Å), Si=C (1.7070 Å), Si≡C (1.6118 Å), C−C (1.5304 Å), C=C (1.3269 Å), C≡C (1.1983 Å), C−N (1.4661 Å), C=N (1.2656 Å), C≡N (1.1487 Å), Si−N (1.7291 Å), Si−N (1.5702 Å), and Si≡N (1.5641 Å) are calculated at the B3LYP/6-311G(d,p) (p for H-atom) calculations (with frequency confirmation as stationary points) for the model systems SiH_3CH_3, SiH_2CH_2, SiHCH, CH_3CH_3, CH_2CH_2, CHCH, CH_3NH_2, CH_2NH, CHN, SiH_3NH_2, SiH_2N, and SiHN, respectively.