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Theoretical Study on Potential Energy Surface of the Interstellar Molecule SiC_2N

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The potential energy surface of the interstellar molecule SiC_2N is explored at the B3LYP/6-311G(d), QCISD/6-311G(d), and CCSD(T)/6-311G(2d) (single-point) levels. Eleven species including the chainlike, three-membered ring and four-membered ring structures are located as energy minima connected by twenty interconversion transition states. At the CCSD(T)/6-311G(2d) level, the lowest-lying isomer is linear SiCCN **1** with $^2\Pi$ state followed by linear SiCNC **2** with $^2\Pi$ state at 23.2 kcal/mol and two close-energy isomers, i.e., cyclic SiCCN with SiC cross-bonding **9** with $^2A''$ state at 28.0 kcal/mol and bent SiNCC **5** with $^2A'$ state at 29.5 kcal/mol. The potential energy surface of SiC_2N indicates that only the three chainlike isomers **1**, **2**, and **5** are kinetically stable, whereas the low-lying cyclic isomer **9** and other isomers are kinetically unstable toward conversion to more stable isomers. The results are compared with those of the well-known analogous interstellar C_3N radical. The calculated bond lengths, harmonic vibrational frequencies, dipole moments, rotational constants, and the first excitation energies may assist future laboratory and interstellar identification of the three SiC_2N isomers **1**, **2**, and **5**.

1. Introduction

Recently, silicon-containing species have received considerable attention in a variety of fields. One area of interest is their potential importance in interstellar space. Heretofore, many Si-containing molecules such as SiC, SiN, SiO, SiS, SiC_2, SiC_3, and SiC_4 have been detected within the interstellar medium.[1] Generally, the properties of silicon are similar to those of carbon in some ways because of their chemical similarity, yet they are very different in many other ways. The prominent point may be that carbon favors multiple bonding, whereas silicon does not.

Ab initio calculations have now been a very powerful tool in interpreting and predicting the properties of chemical systems. In this paper we choose to study the tetra-atomic SiC_2N radical, the Si-analogue of the well-known C_3N radical that has been detected in space for several decades.[3a] A large number of theoretical and experimental studies have dealt with the structures, spectroscopies, and heat of formation of two linear isomers CCCN and CCNC of the C_3N radical.[3b,c] No cyclic isomers could be located on the potential energy surface. On the other hand, many Si, C containing molecules have been found to have low-lying cyclic isomers such as SiC_2,[4] SiC_3,[5] Si_2C_2,[6] etc., among which cyclic SiC_2 and SiC_3 are two known interstellar molecules. Then, some differences between the analogous SiC_2N and C_3N radicals are expected to exist. Also, the SiC_2N radical may have isomers with either SiC or SiN multiple bonding and may thus be a good target for exploring the stability of SiC or SiN multiple bonding. Indeed, the chemistry of SiC and SiN multiple bonding has been attracting growing interest in comparison to the corresponding CC and CN multiple bonding, recently.[2] Because SiC, CN, C_2, and SiN have all been discovered in interstellar space, their direct addition may possibly lead to the formation of several SiC_2N isomers, presumably as SiCCN, SiCNC, and SiNCC. It should be noted that the smaller SiCN radical, which is isovalent to C_2N, has been discussed as a possible origin of some unidentified spectral bands.[7] Despite the potential importance, however, to our best knowledge, we are not aware of any literature reports on the SiC_2N radical, both experimental and theoretical.

In view of the possible existence of the SiC_2N radical in interstellar space, we decided to carry out a detailed theoretical study on its potential energy surface. As many structural forms and interconversion transition states as possible are considered. We wanted to mainly resolve the following questions: (1) Are there any cyclic forms of SiC_2N, such as SiC_3 and SiC_2? (2) What is the bonding nature of the most important isomers? (3) If there are cyclic forms as energy minima, can they be kinetically stable enough to allow for future laboratory or interstellar observation? (4) What are the similarities and discrepancies between SiC_2N and the well-known C_3N radical?

2. Computational Methods

All calculations are carried out using the Gaussian 98 program package.[8] The geometries of the SiC_2N structures and interconversion transition states are fully optimized at the B3LYP/6-311G(d) level. Harmonic vibrational frequencies are calculated at the same level to check whether the obtained structure is an energy minimum (frequencies are all real) or a first-order saddle point (only one imaginary frequency). To get reliable energies, the CCSD(T)/6-311G(2d) calculations are performed at the B3LYP/6-311G(d) geometries. Intrinsic reaction coordinate (IRC) calculations are also carried out to test whether the transition state connects the right minima at the B3LYP/6-311G(d) level. Furthermore, QCISD/6-311G(d) calculations are performed on the structures and spectroscopies of some relevant SiC_2N species so as to aid in their future laboratory or interstellar detection.

3. Results and Discussions

Thirteen SiC_2N structural forms are optimized and twenty interconversion transition states are obtained at the B3LYP/6-

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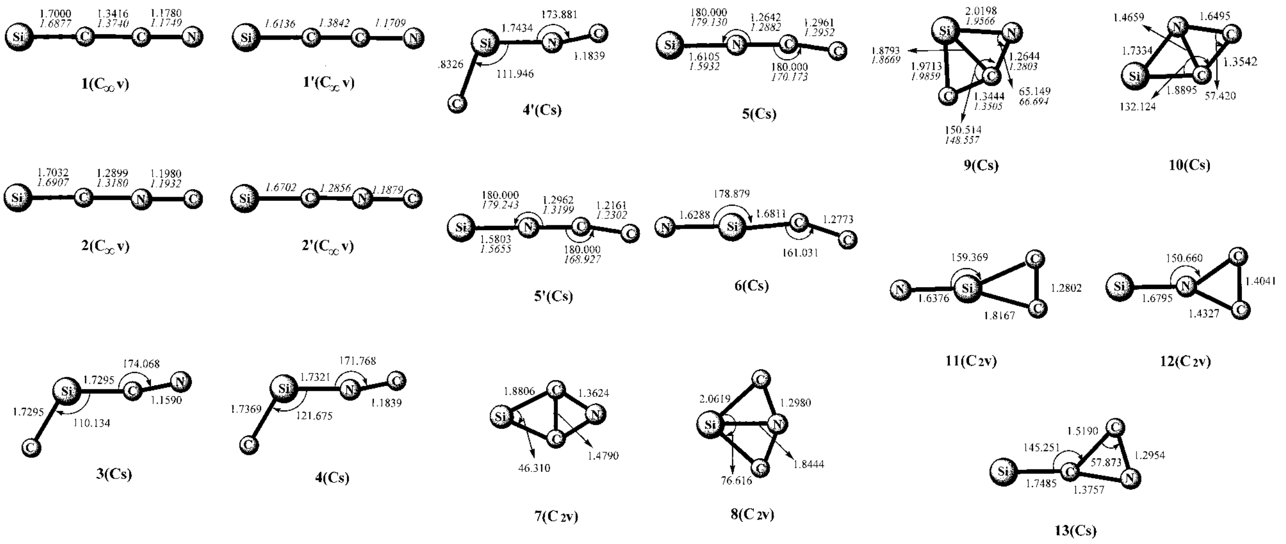

Figure 1. Optimized SiC_2N structures at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees. The values calculated at the QCISD/6-311G(d) level for some structures are also given in italics.

TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in parentheses), Dipole Moment (Debye), and Rotational Constant (GHz) of SiC_2N Structures at the B3LYP/6-311G(d) Level

species	frequencies (infrared intensity)	dipole moment	rotational constant
SiCCN **1**	152 (1) 168 (1) 489 (10) 559 (25) 626 (26) 1453 (34) 2060 (3)	3.7296	2.644203
SiCNC **2**	163 (1) 183 (0) 396 (3) 460 (11) 638 (21) 1475 (14) 1981 (116)	2.7730	2.827604
CSiCN **3**	97 (14) 286 (0) 288 (13) 585 (41) 912 (5) 2259 (13)	2.6590	29.35289, 3.85920, 3.41077
CSiNC **4**	120 (12) 198 (1) 222 (12) 641 (75) 913 (21) 2096 (352)	1.7990	41.44480, 3.92781, 3.58779
CSiNC**4′**	156 (10) 217 (332) 379 (1086) 647 (310) 784 (176)	1.4979	28.54978, 4.12498, 3.60423
SiNCC **5**	133 (12) 188 (0) 302 (51) 469 (12) 712 (7) 1360 (47) 1961 (145)	5.5862	2.965953
SiNCC **5′**	197 (12) 197 (12) 669 (12) 670 (12) 738 (11) 1480 (13) 2180 (16)	2.1684	3.046125
NSiCC **6**	54 (9) 276 (50) 201 (36) 711 (3) 1089 (20) 1913 (349)	1.4406	728.13336, 3.22449, 3.21027
cSiCNC**7**	329 (18) 375 (1) 631 (28) 720 (25) 934 (36) 1446 (37)	1.9364	38.50501, 5.86845, 5.09234
cSiCNC**8**	393i (8) 425 (22) 465 (13) 759 (74) 1125 (0) 1189 (149)	*a*	*a*
cSiCCN**9**	158 (12) 383 (47) 534 (34) 848 (48) 1171 (2) 1507 (23)	2.5935	12.74415, 10.85913, 5.86318
cSiCCN**10**	155 (17) 251 (0) 453 (3) 712 (3) 904 (70) 1502 (48)	3.8621	36.60972
N-cSiCC **11**	196 (55) 204 (42) 410 (24) 693 (42) 1117 (43) 1733 (13)	0.5043	51.39209, 4.95057, 4.51559
Si-cNCC **12**	100i (4) 316 (0) 625 (10) 662 (2) 726 (3) 1394 (1)	*a*	*a*
Si-cCCN **13**	155 (0) 311 (1) 578 (3) 758 (67) 1014 (4) 1623 (20)	2.7540	46.21422, 4.04979, 3.72349

[a] The species **8** and **12** are not energy minima at the B3LYP level, so their dipole moments and rotational constants are not presented.

311G(d) level. The letter **m** is used to denote various SiC_2N structures, and **TSm/n** denotes the transition states connecting the species **m** and **n**. The optimized geometrical parameters of the SiC_2N structures and transition states are shown in Figure 1 and Figure 2, respectively. The harmonic vibrational frequencies as well as the infrared intensities, dipole moments and rotational constants of the SiC_2N species are listed in Table 1, while the frequencies and intensities of all transition states are given Table 2. The total and relative energies of all energy minima and transition states are collected in Table 3. For the species **1**, **1′**, **2**, **2′**, **5**, **5′**, and **9**, the QCISD/6-311G(d) calculations are performed to obtain more reliable frequencies, dipole moments, and rotational constants, as listed in Table 4. Finally, a schematic potential energy surface (PES) of SiC_2N showing the isomerization process is given in Figure 3.

3.1. SiC_2N Species. Our considered thirteen SiC_2N species can be classified into three groups, i.e., chainlike, four-membered ring, and three-membered ring forms. The discussion will follow the three groups.

The species SiCCN **1**, SiCNC **2**, CSiCN **3**, CSiNC **4**, SiNCC **5**, and NSiCC **6** have chainlike structures. At the B3LYP level, the species **1**, **2,** and **5** with Si located outside are all linear with $^2\Pi$ electronic state, whereas **3**, **4**, and **6** with Si located inside are bent with $^2A'$ state. Frequency calculations show that the six structures are local minima with all real frequencies. In addition, for the species **4** and **5**, two respective structures with different electronic states are found, which are denoted as **4′** with $^2A''$ state and **5′** with $^2\Sigma$ state. Yet, optimization of the SiCCN and SiCNC structures with $^2\Sigma$ state often leads to the lower-lying $^2\Pi$ state structures at the B3LYP/6-311G(d) level. On the other hand, at the QCISD/6-311G(d) level, the $^2\Sigma$ state structures SiCCN **1′** and SiCNC **2′** can be truly obtained. Noticeably at the QCISD/6-311G(d) level, both $^2\Sigma$ and $^2\Pi$ state structures of SiNCC have one imaginary frequency (297*i* and 206*i* cm^{-1}, respectively) and relaxation of $C_{\infty v}$ symmetry leads to bent forms with the $^2A'$ state, which are also denoted as **5** and **5′**, respectively. Yet, the corresponding bending energies are just 0.2 and 0.1 kcal/mol.

The species **7**, **8**, **9**, and **10** can be described as four-membered ring structures. The species **7** and **8** contain a cyclic SiCCN skeleton with CC and SiN cross bonding, respectively, as indicated by the transannular bond lengths (in Figure 1). The species **7** is an energy minimum with all real frequencies, whereas **8** possesses one imaginary frequency 393*i* cm^{-1} indicating a ring-open process. The species **9** and **10** with $^2A''$ state are interesting cyclic SiCCN structures with SiC and CN cross bonding, respectively. Both are predicted to be local

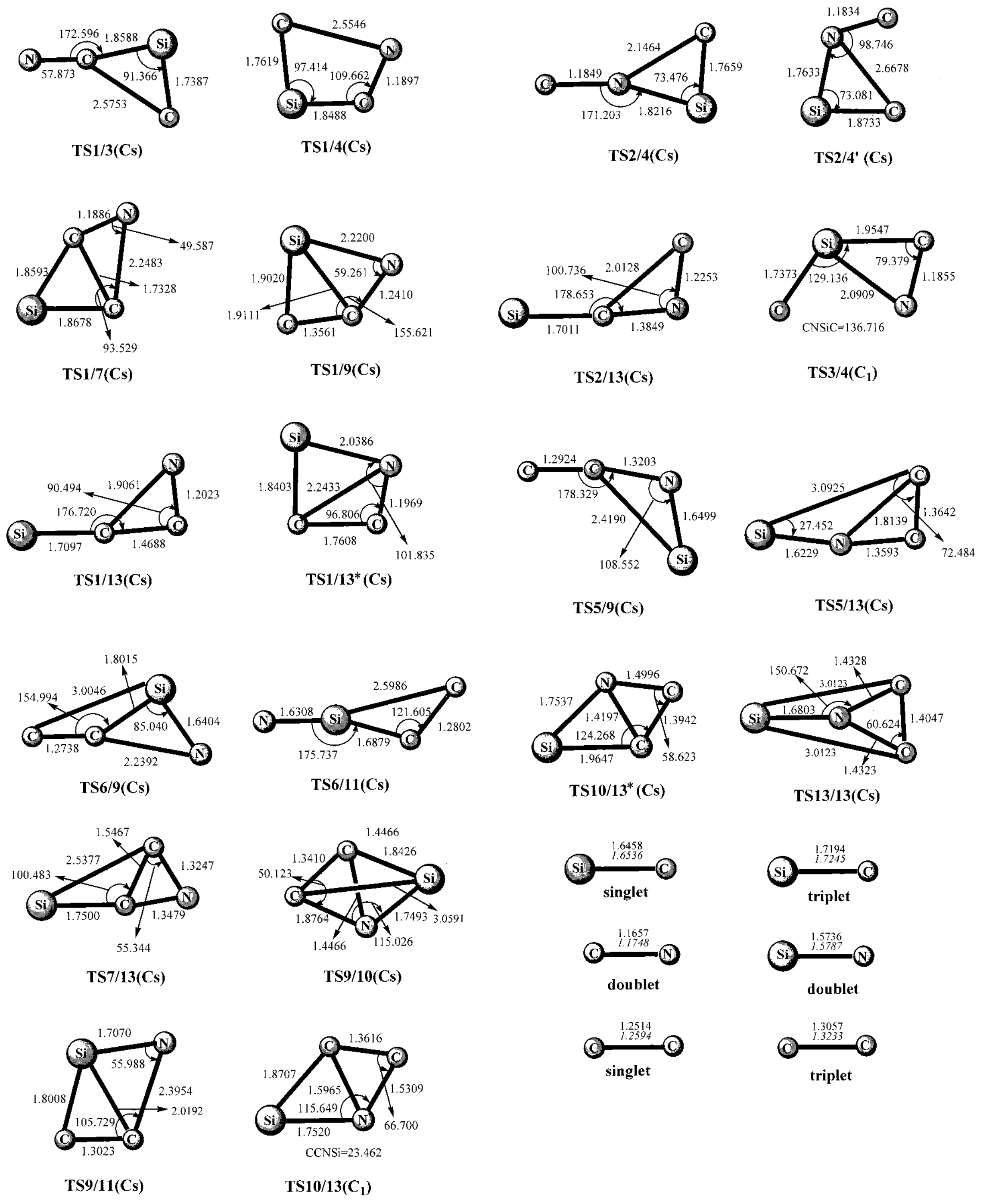

Figure 2. Optimized geometries of interconversion transition states between SiC_2N isomers and of the dissociation products. Bond lengths are in angstroms and angles in degrees.

minima on the potential energy surface. The energy minimum nature of **9** is also confirmed by QCISD/6-311G(d) calculations.

The species **11**, **12**, and **13** are CCSi, CCN, and NCC three-membered ring forms, respectively. Species **11** and **12** have C_{2v} symmetry with exocyclic SiN and NSi bonding, respectively, while **13** is of C_s symmetry with exocyclic CSi bonding. The two species **11** and **13** have all real frequencies and are thus local minima, whereas **12** has one imaginary frequency 100*i* cm^{-1} indicative of a ring-open process.

From Table 3, we can obtain the energetic ordering of the obtained SiC_2N minimum isomers at the single-point CCSD(T)/6-311G(2d) level. Note that for the species **1**, **1′**, **2**, **2′**, **5**, **5′**, and **9**, the QCISD/6-311G(d) geometries are used. Generally, the isomer with lower total energy has higher thermodynamical stability. At the CCSD(T)/6-311G(2d) level, the thermodynamical stability order is then **1** (0.0) > **2** (23.2) > **9** (28.0) > **5** (29.5) > **1′** (35.3) > **7** (38.1) > **5′** (38.3) > **13** (43.8) > **3** (57.5) > **10** (62.2) > **4** (66.1) > **4′** (69.6) > **11** (78.9)> **2′** (88.0) > **6** (88.4). The values in parentheses are relative energies in kcal/mol with reference to **1**. It is clear that the former two low energy isomers are linear SiCCN **1** and SiCNC **2**. The energies of the chainlike isomers CSiCN **3**, CSiNC **4** (**4′**), and NSiCC **6** are very high lying. An extraordinary point is that the SiCCN four-membered ring isomer **9** with SiC cross bonding lies 28.0 kcal/mol above the linear isomer **1** and is even 1.5 kcal/mol lower than the bent isomer SiNCC **5**. Another cyclic SiCNC isomer **7** has lower energy than the chainlike isomers **3**, **4** (**4′**), **5′**, and **6**. Note that the cyclic isomers **7** and **9** both

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) (in parentheses) of Interconversion Transition States between SiC_2N Isomers at the B3LYP/6-311G(d) Level

species	frequencies (infrared intensity)
TS1/3	125*i* (9) 267 (7) 295 (1) 571 (33) 898 (1) 2249 (12)
TS1/4	247*i* (4) 143 (9) 144 (5) 608 (90) 853 (0) 2004 (39)
TS1/7	279*i* (6) 275 (0) 462 (10) 526 (13) 750 (13) 1939 (10)
TS1/9	125*i* (18) 383 (47) 622 (33) 804 (36) 1135 (2) 1575 (20)
TS1/13	604*i* (118) 203 (5) 232 (0) 655 (86) 1287 (10) 1854 (57)
TS1/13*	508*i* (25) 235 (13) 418 (24) 503 (5833) 766 (10) 1829 (128)
TS2/4	192*i* (0) 177 (1) 231 (0) 546 (52) 868 (6) 2062 (297)
TS2/4′	74*i* (21) 181 (1) 227 (9) 621 (80) 698 (7) 2087 (269)
TS2/13	456*i* (55) 223 (10) 262 (1) 670 (90) 1382 (72) 1749 (37)
TS3/4	313*i* (151) 21 (1) 126 (17) 507 (80) 881 (6) 1963 (310)
TS5/9	408*i* (17) 190 (28) 324 (0) 872 (13) 1084 (59) 1861 (30)
TS5/13	320*i* (41) 229 (10) 262 (0) 764 (52) 1252 (14) 1407 (25)
TS6/9	224*i* (47) 189 (12) 202 (0) 645 (2) 1004 (4) 1671 (180)
TS6/11	86*i* (3) 169 (48) 199 (31) 817 (10) 1120 (12) 1827 (183)
TS7/13	176*i* (1) 332 (0) 677 (52) 687 (36) 1124 (52) 1568 (31)
TS9/10	162*i* (11) 253 (0) 529 (4) 702 (31) 944 (51) 1534 (79)
TS9/11	329*i* (9) 226 (17) 432 (14) 720 (18) 822 (1) 1585 (9)
TS10/13	312*i* (6) 358 (14) 416 (7) 711 (67) 851 (27) 1453 (102)
TS10/13*	265*i* (197) 310 (1) 362 (50) 630 (46) 920 (34) 1400 (12)
TS13/13	99*i* (4) 316 (0) 624 (10) 663 (2) 725 (4) 1392 (1)

TABLE 3: Total (a.u.) and Relative (kcal/mol) (in parentheses) of the SiC_2N Structures and Transition States at the B3LYP/6-311G(d) and Single-Point CCSD(T)/ 6-311G(2d) Levels

species	B3LYP/6-311G(d)	CCSD(T)/6-311G(2d)[a]
SiCCN **1** ($^2\Pi$)	−420.3759033 (0.0)	−419.5828689 (0.0)
SiCCN **1′** ($^2\Sigma$)	*b*	−419.5266398 (35.3)
SiCNC **2** ($^2\Pi$)	−420.3379587 (23.8)	−419.5459582 (23.2)
SiCNC **2′** ($^2\Sigma$)	*b*	−419.4425831 (88.0)
CSiCN **3** ($^2A'$)	−420.2627599 (71.0)	−419.4911947 (57.5)
CSiNC **4** ($^2A'$)	−420.2517812 (77.9)	−419.4774633 (66.1)
CSiNC**4′** ($^2A''$)	−420.2476784 (80.5)	−419.4718865 (69.6)
SiNCC **5** ($^2A'$)	*c*	−419.5357797 (29.5)
SiNCC **5′** ($^2A'$)	*c*	−419.5218023 (38.3)
NSiCC **6** ($^2A'$)	−420.2278098 (92.9)	−419.4419709 (88.4)
cSiCNC **7** ($^2B_1$)	−420.3079202 (42.7)	−419.5221239 (38.1)
cSiCNC **8** ($^2A_1$)	−420.2676408 (67.9)	*d*
cSiCCN **9** ($^2A''$)	−420.3221949 (33.7)	−419.5381899 (28.0)
cSiCCN **10** ($^2A''$)	−420.2679522 (67.7)	−419.4837676 (62.2)
N-cSiCC **11** ($^2B_1$)	−420.2378568 (86.6)	−419.4571880 (78.9)
Si-cNCC **12** ($^2B_1$)	−420.2563659 (75.0)	*d*
Si-cCCN **13** ($^2A''$)	−420.3029471 (45.8)	−419.5129986 (43.8)
SiC($^1\Sigma$)+CN($^2\Sigma$)	−420.0989754 (173.8)	−419.3461712 (148.5)
SiC($^3\Pi$)+CN($^2\Sigma$)	−420.1415030 (141.9)	−419.3703687 (133.3)
SiN($^2\Sigma$)+C_2($^1\Sigma_g$)	−420.0569146 (200.2)	−419.3249969 (161.8)
SiN($^2\Sigma$)+C_2($^3\Pi_u$)	−420.0930361 (177.5)	−419.3212818 (164.1)
TS1/3 ($^2A'$)	−420.2621631 (71.4)	−419.4871931 (60.0)
TS1/4 ($^2A'$)	−420.2345383 (88.7)	−419.4591622 (77.6)
TS1/7 ($^2A''$)	−420.2694109 (66.8)	−419.4875928 (59.8)
TS1/9 ($^2A''$)	−420.3219677 (33.8)	−419.5369996 (28.8)
TS1/13 ($^2A''$)	−420.2735672 (64.2)	−419.4892525 (58.7)
TS1/13* ($^2A''$)	−420.2433437 (83.2)	−419.4612765 (76.3)
TS2/4 ($^2A'$)	−420.2428883 (83.5)	−419.4629460 (75.3)
TS2/4′ ($^2A''$)	−420.2473772 (80.7)	−419.4740710 (68.3)
TS2/13 ($^2A''$)	−420.2878610 (55.2)	−419.5020660 (50.7)
TS3/4 (^2A)	−420.2223787 (96.3)	−419.4484533 (84.3)
TS5/9 ($^2A''$)	−420.2883576 (54.9)	−419.4999173 (52.1)
TS5/13 ($^2A''$)	−420.2540216 (76.5)	−419.4642119 (74.5)
TS6/9 ($^2A'$)	−420.1889988 (117.3)	−419.4063330 (110.8)
TS6/11 ($^2A'$)	−420.2271895 (93.3)	−419.4450250 (86.5)
TS7/13 ($^2A''$)	−420.2990793 (48.2)	−419.5127946 (44.0)
TS9/10 ($^2A''$)	−420.2675707 (68.0)	−419.4835850 (62.3)
TS9/11 ($^2A''$)	−420.2014099 (109.5)	−419.4202734 (102.0)
TS10/13 (^2A)	−420.2645936 (69.8)	−419.4827766 (62.8)
TS10/13* ($^2A''$)	−420.2675956 (68.0)	−419.4809534 (64.0)
TS13/13 ($^2A''$)	−420.2563659 (75.0)	−419.4653739 (73.7)

[a] The CCSD(T) energies of **1**, **1′**, **2**, **2′**, **5**, **5′**, and **9** are based on QCISD geometries. [b] **1′** and **2′** cannot be optimized at the B3LYP level. [c] **5** and **5′** are linear with $^2\Pi$ and $^2\Sigma$ state, respectively at the B3LYP level, whereas they are bent at the QCISD level with $^2A'$ state. [d] **8** and **12** are not energy minima, so their single-point energies are not calculated.

contain single bonding of Si. It should also be pointed out that the species **1′**, **2′**, **4′**, and **5′** may be considered as the first excited states of **1**, **2**, **4**, and **5**, respectively. Then the corresponding excitation energies of **1**, **2**, **4**, and **5** are calculated to be 35.3, 64.8, 3.5, and 8.8 kcal/mol.

3.2. Kinetic Stability. Let us turn to the kinetic stability of various SiC_2N isomers. The isomerization process of these SiC_2N isomers on potential energy surface is depicted in Figure 3. For simplicity, the details of the obtained twenty transition states are omitted. From Figure 3 we can see that most of the high-lying isomers can convert to the lowest-energy isomer SiCCN **1** via one or more pathways. The energies of the dissociation products SiC+CN and SiN+C_2 are rather high-lying above all the SiC_2N isomers and interconversion transition states, as shown in Table 3. Then, the isomerization process governs the kinetic stability of SiC_2N isomers. It may be reasonable that the most favorable isomerization process of a SiC_2N isomer determines its kinetic stability. Then, the kinetic stability ordering of various SiC_2N isomers can be obtained as **1** (28.8, **1→9**) > **2** (27.5, **2→13**) > **5** (22.6, **5→9**) > **4** (9.2, **4→2**) > **11** (7.6, **11→6**) > **7** (5.9, **7→13**) > **3** (2.5, **1→3**) > **9** (0.8, **9→1**) > **13** (0.2, **13→7**) > **10** (0.1, **10→9**) > **4′** (−1.3, **4′→2**) > **6** (−1.9, **6→11**). The values in parentheses mean the smallest conversion barriers in kcal/mol of SiC_2N isomers at the CCSD(T)/6-311G(2d) level. The negative sign of the conversion barriers results from the single-point calculations for the very small-barrier conversion process. Therefore, only the three chainlike isomers SiCCN **1**, SiCNC **2**, and SiNCC **5** have considerable kinetic stability (more than 20 kcal/mol) and may be observable in laboratory or in interstellar space. The observation of the remaining isomers may be much less likely due to their high energy and very small conversion energies (less than 10 kcal/mol). It is worth mentioning that although the cyclic isomer **9** is 1.5 kcal/mol lower than the isomer SiNCC **5**, it is rather unstable toward isomerization to the most stable isomer SiCCN **1** with only 0.8 kcal/mol. Therefore, the molecule SiC_2N has no cyclic isomers that could be kinetically stabilized, despite that several cyclic forms are located as energy minima. For the well-known C_3N radical, no cyclic forms have been investigated previously in addition to the linear isomers CCCN and CCNC. It should be pointed out that we could not locate any transition states connecting the species **1′**, **2′**, and **5′**. In section 3.1, we know that they are the respective first excited states of **1**, **2**, and **5**. Under normal conditions, formation of **1′**, **2′**, and **5′** may be difficult, and even if produced, they may quench to their ground states **1**, **2**, and **5**. So, we decided not to work on them further.

3.3. Structural Properties of the Relevant Species. From section 3.2, we know that among various isomeric forms, only three chainlike species SiCCN **1**, SiCNC **2**, and SiNCC **5** possess considerable kinetic stability. The SiC and CN bond lengths of SiCCN **1** are 1.6877 and 1.1749 Å, whereas those of SiCNC **2** are 1.6907 and 1.1932 Å, as shown in Figure 1. Compared to the values shown in Figure 2 of the separate species SiC (1.7245 Å for $^3\Pi$ state and 1.6536 Å for $^1\Sigma$ state) and CN (1.1748 Å), both isomers can principally be considered as the addition products between SiC (triplet or singlet) and doublet CN species. The bond lengths of SiC (about 1.69 Å) in both the isomers **1** and **2** seem to be closer to the Si≡C value in RSi≡CH (1.6701, 1.6872, 1.6835, and 1.6803 Å for R=H, F, Cl, and OH, respectively) than to the Si=C value in Si=

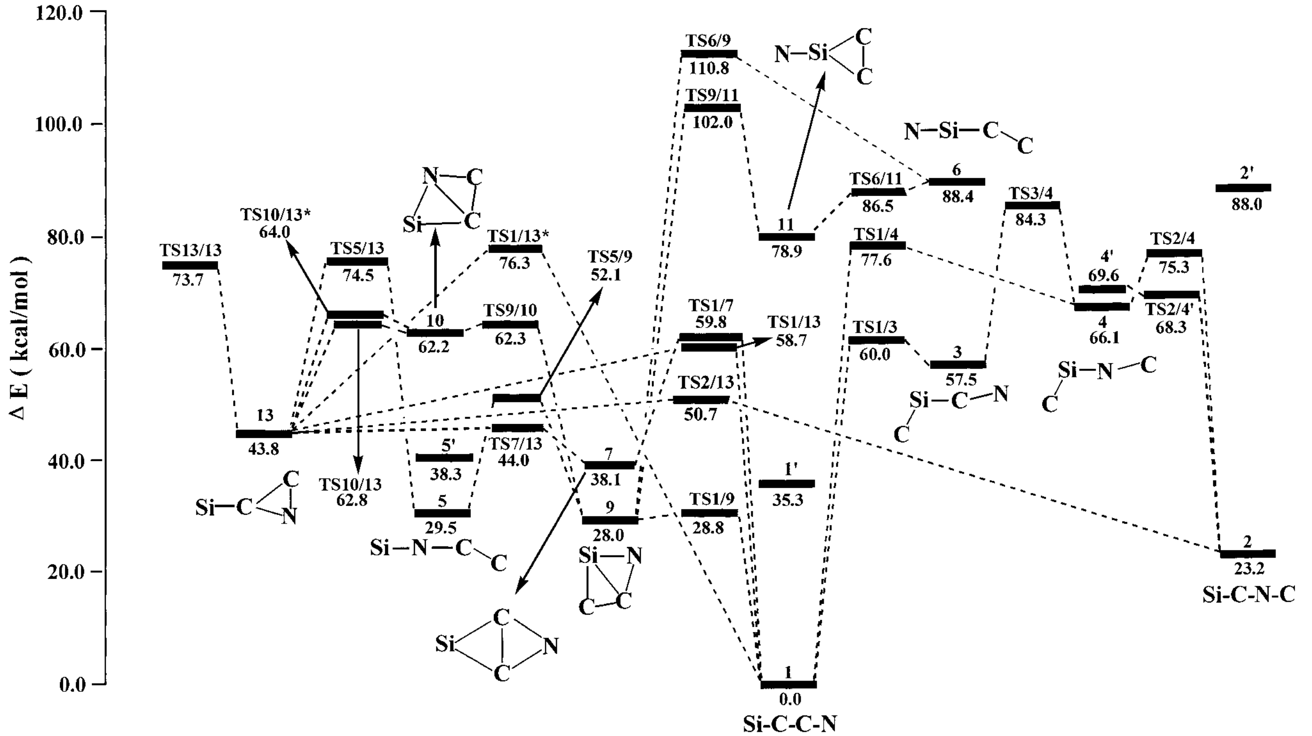

Figure 3. Schematic potential energy surface of SiC_2N at the CCSD(T)/6-311G(2d) single-point level. The energies of the species **1**, **1′**, **2**, **2′**, **5**, **5′**, and **9** are calculated using the QCISD/6-311G(d) geometries, whereas those of the remaining species and transition states are obtained using the B3LYP/6-311G(d) geometries.

TABLE 4: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in parentheses), Dipole Moment (Debye), and Rotational Constant (GHz) of the Relevant SiC_2N Isomers at the QCISD/6-311G(d) Level

species	frequencies (infrared intensity)	dipole moment	rotational constant
SiCCN **1** ($^2\Pi$)	145 (0) 162 (1) 473 (9) 545 (27) 611 (9) 1430 (13) 2129 (1)	4.0923	2.619367
SiCCN **1′** ($^2\Sigma$)	208 (5) 558 (41) 676 (0) 1532 (1) 2230 (23)	6.1847	2.710426
SiCNC **2** ($^2\Pi$)	153 (0) 174 (1) 371 (2) 430 (11) 630 (19) 1459 (0) 2077 (259)	2.9575	2.808544
SiCNC **2′** ($^2\Sigma$)	164 (17) 542 (3) 659 (0) 1411 (7) 1909 (115)	1.9575	2.894348
SiNCC **5** ($^2A'$)	149 (10) 355 (112) 411 (10) 725 (22) 1363 (54) 1692 (357)	5.4374	2776.56902, 2.97031, 2.96714
SiNCC **5′** ($^2A'$)	162 (13) 265 (74) 417 (262) 748 (34) 1505 (4) 1976 (2989)	3.3906	2300.98870, 3.03719, 3.03319
cSiCCN **9** ($^2A''$)	251 (9) 389 (45) 550 (37) 874 (51) 1174 (3) 1482 (23)	2.6921	12.35615, 11.45512, 5.94429

C(H)R (1.7478, 1.7527, 1.7388, and 1.7473 Å for R=H, F, Cl, and OH, respectively).[9] However, the SiC values in **1** and **2** are almost the same as the Si=C double bond value (1.6925 Å) in the ground state of the SiCH doublet radical, and are significantly longer than the Si≡C triple bond value (1.6118 Å) in the excited state of SiCH.[10] The Mulliken population analysis is also indicative of a Si=C double bond instead of a Si≡C triple bonding within the isomers **1** and **2**. For isomer **1**, the spin density of Si, C, C, and N is 0.061, 0.810, −0.219, and 0.348, respectively, suggesting a valence structure |Si=C−C≡N|, where "|" denotes the lone electron pair. For isomer **2**, the spin density (0.119, 0.759, −0.074, and 0.205 for Si, C, N, and C, respectively) suggests a main structure |Si=C−N≡C|. In all, we would like to consider both **1** and **2** as containing Si=C double and C≡N triple bonding with the lone electron positioned at the C-atom neighboring to Si-atom. Such valence structures are confirmed by the natural bond order (NBO) analysis.

The excited structures SiCCN **1′** and SiCNC **2′** each have a $^2\Sigma$ electronic state. Their SiC bond lengths are 1.6136 and 1.6702 Å, respectively. When compared to the experimentally determined bond length in SiCH (triple bond value is 1.6118 and double bond value is 1.6925 Å),[10] **1′** is suggested to have a Si≡C−C≡N| valence structure with the respective spin densities of Si, C, C, and N being 0.908, 0.081, −0.001, and 0.013. However, the spin density of **2′** is −0.507, 0.227, −0.252, and 1.532 for Si, C, N, and C, respectively, indicating a |Si=C−N≡C structure with the unpaired electron mainly positioned at the terminal C atom.

The $^2A'$ state structure SiNCC **5** contains an SiN bond of slightly longer value (1.5932 Å) than the separate doublet SiN radical (1.5787 Å), and a CC bond of shorter value (1.2952 Å) than the separate triplet C_2 radical (1.3233 Å) or of longer value than the singlet C_2 (1.2594 Å). The single unpaired electron is highly delocalized between the terminal Si atom and the two C atoms (the spin densities are 0.217, −0.020, 0.389, and 0.415 for Si, N, C, and C, respectively). Thus, isomer **5** can be viewed as a resonant structure between three forms: (1) |Si=N−C≡C, (2) |Si=N−C=C|, and (3) Si≡N−C=C|, with form (1) having most weight, (2) less than (1), and (3) the least. The SiN bond (1.5655 Å) of the excited structure **5′** is a bit shorter than that (1.5787 Å) of the SiN radical, and the CC value (1.2302 Å) is smaller than that (1.2594 Å) of singlet C_2. Thus, **5′** (also with $^2A'$ state) can be seen as mainly having Si≡N and C≡C triple bonding with the lone electron located at the terminal C atom (|Si≡N−C≡C), as shown by NBO analysis. The spin densities of Si, N, C, and C are −0.045, 0.035, −0.121, and 1.132, respectively.

Now it is clear that for the three chainlike forms (SiCCN, SiCNC, and SiNCC) the ground-state structure possesses double bonding character of Si with $^3\Pi$ or $^2A'$ state, whereas that with Si triple bonding does not exist or lies energetically higher. This is in sharp contrast to the well-known analogous C_3N radical. Previous calculations[3b] have shown that the ground state of the two isomers CCCN and CCNC is $^2\Sigma$ with terminal C≡C triple bonding. The unpaired electron is mainly located at the terminal C atom away from the N atom. Then, the present calculations again manifest that Si≡C triple bonding is much less stable than C≡C triple bonding. We can expect that when a hydrogen atom is added to SiCCN, SiCNC, and SiNCC, the species SiC(H)CN, SiC(H)NC, and SiNCCH should be energetically more preferable than other forms. On the other hand, there indeed exist some cyclic forms located as energy minima on the SiC_2N potential energy surface, and the four-membered ring isomer cSiCCN **9** is even 1.5 kcal/mol lower than the chainlike isomer SiNCC **5**. However, kinetic analysis shows that none of these cyclic isomers may be experimentally observable due to their very easy conversion to other isomers. In this point, SiC_2N is similar to C_3N.

To aid future identification of the three SiC_2N isomers, either in laboratory or in interstellar space, the calculated vibrational frequencies, dipole moments, and rotational constants at the QCISD/6-311G(d) level are presented in Table 4. The properties of the species **1′**, **2′**, and **5′** with high-energy electronic state and the low-lying cyclic isomer **9** are also presented. We can easily see that the dominant frequencies of the isomers **1**, **2**, and **5** are 545, 2077, and 1692 cm^{-1}, respectively. Interestingly, all three isomers have very large dipole moments, i.e., 4.0923, 2.9575, and 5.4374 D for **1**, **2**, and **5**, respectively, making their interstellar detection very promising via radio astronomy techniques. The direction of these dipole moments all points to the terminal Si atom. because the separate species SiC, CN, SiN, and C_2 have all been detected in interstellar space, the formation of the isomers SiCCN **1**, SiCNC **2** and SiNCC **5** is also probable. The calculated CCSD(T)/6-311G(2d)//QCISD/6-311G(d) first excited energies of **1**, **2**, and **5** (35.3, 64.8, and 8.8 kcal/mol, respectively) may also be helpful for their experimental characterization.

4. Conclusions

B3LYP/6-311G(d), QCISD/6-311G(d), and CCSD(T)/6-311G(2d) (single-point) methods are employed to study the potential energy surface of the unknown interstellar molecule SiC_2N. Among the obtained eleven minimum isomers, only three isomers, i.e., linear SiCCN **1**, linear SiCNC **2** (at 23.2 kcal/mol), and bent SiNCC **5** (at 29.5 kcal/mol) that contain Si═C and Si═N double bonding, may be kinetically stable. Although several cyclic forms are identified as energy minima on potential energy surface, they are kinetically unstable toward isomerization. The Si≡C and Si≡N triply bonded structures of SiCCN **1′**, SiCNC **2′**, and SiNCC **5′** are found to either not exist or be energetically higher than the corresponding Si═C and Si═N doubly bonded species **1**, **2**, and **5**, in sharp contrast to the situation of C_3N. The calculated geometries, harmonic vibrational frequencies, dipole moments, rotational constants, and the first excitation energies may be helpful for future identification of the three kinetically stable isomers **1**, **2** and **5** in both laboratory and interstellar space.

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