SiCNN—A New Stable Isomer with Si≡C Triple Bonding

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Abstract: To predict potentially stable molecules with Si≡C triple bonding, theoretical calculations at the B3LYP/6-311G(d) and CCSD(T)/6-311G(2df) (single-point) levels were employed to study the structures, energetics, and isomerization of various $SiCN_2$ isomers. A schematic potential energy surface (PES) of $SiCN_2$ was established to discuss the kinetic stability of the isomers. A new isomer SiCNN was found to possess a typical Si≡C triple bond, as confirmed by comparative calculations at the B3LYP, QCISD, QCISD(T), CCSD, and CCSD(T) levels on the bond lengths of SiCNN and other experimentally or theoretically known species of RSiCH (R = H, F, Cl, OH). Moreover, SiCNN resides in a very deep potential; the stabilization barrier is at least 53.2 kcal mol^{-1}. Thus, SiCNN may be considered as the most kinetically stable isomer with Si≡C triple bonding known to date, and it may represent a very promising molecule for future experimental characterization. In addition, the stability of the other isomers, such as the four linear species SiNCN, SiNNC, NSiCN and NSiNC, a three-membered NNC ring isomer with exocyclic C−Si bonding, and a four-membered SiCNN ring isomer is discussed and compared with SiCNN.

Keywords: ab initio calculations · isomerization · multiple bonds · silicon

Introduction

The synthesis and characterization of multiply bonded silicon compounds have remained a continuous challenge to organic chemists.[1] The first double-bonded silicon species was synthesized in 1981,[2] and since then, numerous experimental[3] and theoretical[4] studies have followed. In sharp contrast, species with triply bonded silicon are still much less known with very few exceptions. In 1994, the stable isomer HSi≡N was characterized by matrix isolation spectroscopy.[5] The first firm evidence for the existence of two new species, FSiCH and ClSiCH, with formal Si≡C triple bonding was presented by means of neutralization–reionization mass spectrometry in 1999.[6] It has been recognized[7, 8] that the difficulty in obtaining triply bonded silicon compounds generally results from their lower kinetic stability towards conversion to more stable doubly bonded silicon species. For the well-known [Si, C, H_2] system, the HSi≡CH isomer can easily rearrange to the much lower energy isomer Si=CH_2, as the barrier is just a few kcal mol^{-1}.[7a, 9] As a result, only the Si=CH_2 isomer has been detected and characterized spectroscopically in the gas phase.[9h, 10] Theoretical calculations[6, 7a, 9b, 9d] have been undertaken on many substituent molecules of the parent HSi≡CH in order to predict potentially detectable isomers with considerable kinetic stability. However, to our knowledge, the previously predicted conversion barriers of the isomers that contain Si≡C are all less than 30 kcal mol^{-1}. The promising candidates RSi≡CH with R = F, Cl, and OH, have been predicted to be separated from their corresponding Si=C(H)R species by the barriers 24.9, 15.1, and 24.5 kcal mol^{-1}, respectively at the QCISD(T)/6-31G(d,p)//QCISD/6-31G(d,p) + ZPE level.[6, 7a] Although bulky substitutions may protect the Si≡C triple bond from isomerization to the Si=C double bond, the rotation of the bulky substitutions may, on the other hand, minimize the steric stabilization. Thus the search is continuing for other candidates containing Si≡C triple bonding with higher kinetic stability.

Recently, the last linear CCNN (diazodicarbon) isomer [11] of the analogous C_2N_2 family has attracted attention; the other three linear isomers NCCN (dicyanogen), CNCN (isocyanogen), and CNNC (diisocyanogen) have been well studied. It has been shown that CCNN may be described as a species containing C≡C and N≡N triple bonding, and despite its high energy, CCNN may be considered as the second kinetically stable isomer of the C_2N_2 family.[11b] Therefore, one of our objectives was to establish whether SiCNN, the silicon analogue of CCNN, contained Si≡C and N≡N triple bonding and whether it is kinetically very stable.

In addition to SiCNN, other isomers of $SiCN_2$ may also be of interest. Intuitively, four linear isomers can be proposed: NSiCN (analogue of NCCN), SiNCN, NSiNC (analogues of CNCN), and SiNNC (analogue of CNNC), and indeed,

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Ignatyev and Schaefer[12] calculated the structures, vibrational frequencies, and energetics of the four isomers to aid future identification. However, the kinetic stability of the four isomers towards isomerization and dissociation is still uncertain, although the three analogous C_2N_2 isomers are all kinetically very stable. The second objective of the present paper is an attempt to determine the kinetic stability of these four linear isomers. Furthermore, from a theoretical viewpoint, it is desirable to see if other nonlinear isomers of $SiCN_2$ exist and if they are thermodynamically or kinetically stable. This is the third objective of our paper.

Computational Methods

The fully optimized geometries and vibrational frequencies of various $SiCN_2$ isomers and their interconversion transition states were obtained at the B3LYP/6-311G(d) level. The reliable energetics were evaluated at the single-point CCSD(T)/6-311G(2df) level. To test whether the transition state corresponds to the right isomers, the intrinsic reaction coordinate (IRC) calculations were also carried out at the B3LYP/6-311G(d) level. Further calculations at the QCISD, QCISD(T), CCSD, and CCSD(T) levels were performed on the structures of SiCNN (with the 6-311G(d) basis set) and other related species, namely RSi≡CH and Si=C(H)R (R = H, F, Cl, OH) for comparison (with the 6-311G(d,p) basis set). All these calculations were carried out with the Gaussian98 program package.[13]

Results and Discussion

For the $SiCN_2$ system, we searched the possible isomeric forms. Yet, we only located seven isomers as minima with real frequencies. They are denoted as linear SiNCN (**1**), linear SiNNC (**2**), linear NSiCN (**3**), linear NSiNC (**4**), linear SiCNN (**5**), a four-membered SiNCN ring (**6**), and a three-membered NNC ring with exocyclic C–Si bonding (**7**) (Figure 1). To inspect the isomerization processes of various isomers, thirteen transition states (**TS**) were located, which are denoted as **TS*m*/*n*** with ***m*** and ***n*** being the corresponding isomers (Figure 2). The discussions are organized as follows. In the first section, the structure and bonding nature of SiCNN is described and compared with other related species.

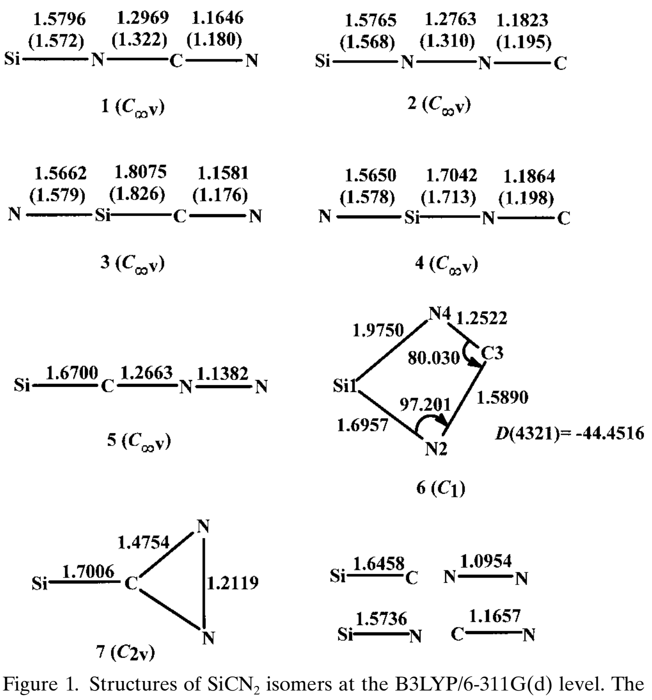

Figure 1. Structures of $SiCN_2$ isomers at the B3LYP/6-311G(d) level. The values in parentheses are CCSD/DZP values taken from ref. [12].

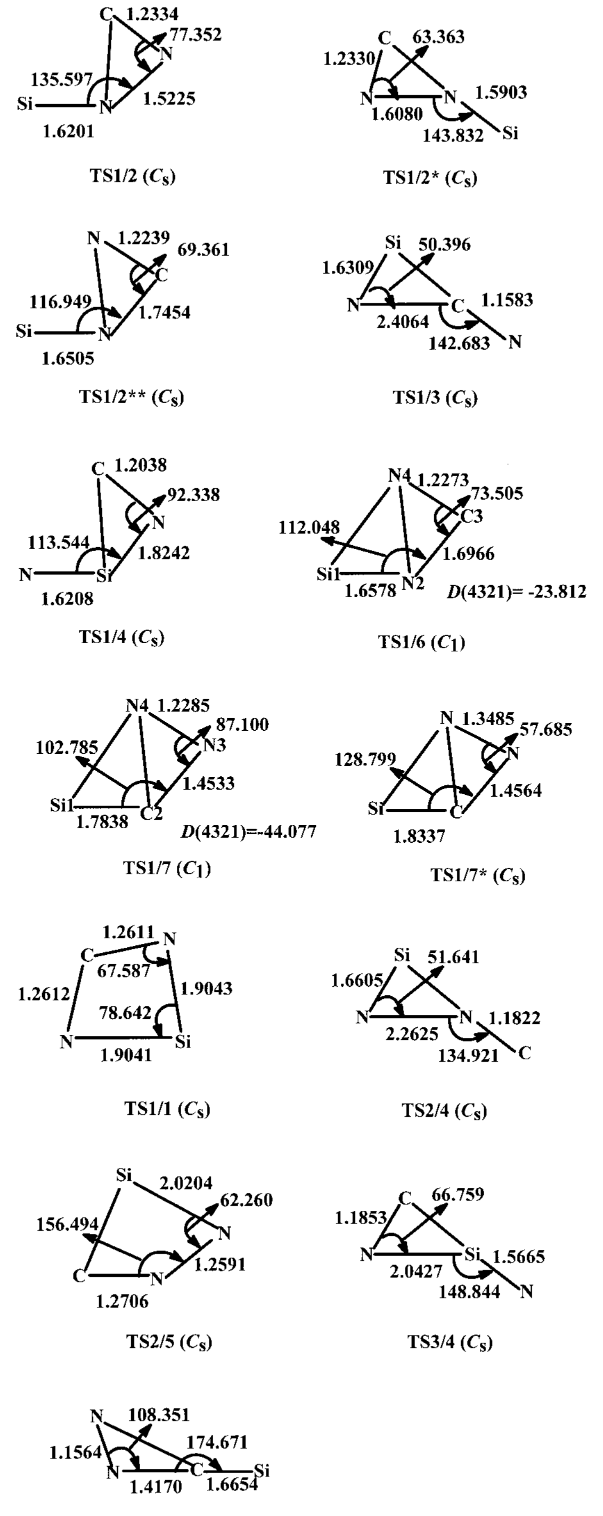

Figure 2. Structures of $SiCN_2$ interconversion transition states at the B3LYP/6-311G(d) level.

In the second section, the stability of SiCNN is discussed, and in the third section, the structure and stability of the other $SiCN_2$ isomers are briefly discussed and compared with SiCNN.

It should be pointed out that the structures, energetics and spectroscopies of the isomers **1**, **2**, **3**, and **4** have been previously discussed by Ignatyev and Schaefer.[12] As can be seen from Figure 1 and Table 3, our B3LYP/6-311G(d) bond lengths and vibrational frequencies are in good agreement with the respective CCSD/DZP and B3LYP/DZP values calculated by Ignatyev and Schaefer[12] (they did not calculate the CCSD/DZP frequencies). Also, Table 5 shows that the relative energies of the four isomers at our CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) and their CCSD(T)/TZP2f//CCSD/DZP levels are very close.

Structure and bonding of SiCNN: The optimized bond lengths of SiCNN and the separate species SiC, SiC^-, N_2, and N_2^+ are given in Table 1. At all the levels considered, the Si–C bond length in SiCNN is very close to that in the singlet SiC molecule, while the N–N bond length in SiCNN is somewhat longer than that in the singlet N_2 molecule. At the 6-311G(d) B3LYP, QCISD and QCISD(T) levels, the central C–N bond length of SiCNN is shorter than that of CCNN (within 0.003 Å) and the terminal N–N bond length of SiCNN is ≈0.01 Å longer than that of CCNN. Also, we can see from Table 2 that at all the levels considered, the Si–C bond length in SiCNN is very close to that in $RSi{\equiv}CH$ and significantly shorter than that in $Si{=}C(H)R$. At the CCSD(T) level, the Si–C bond length in SiCNN is much closer to that in $RSi{\equiv}CH$ (R = H 0.011 Å longer, R = OH 0.001 Å longer; R = F 0.005 Å shorter; R = Cl 0.002 Å shorter). The natural bond order analysis indicates that both Si–C and N–N within SiCNN possess triple-bonding character similar to the situation in CCNN. Therefore, from both the structural and bonding analyses, SiCNN can be classified as an isomer that contains a typical $Si{\equiv}C$ triple bond.

The interatomic overlap density plots of the species SiCNN, SiC, and N_2 at the QCISD/6-31G(d) level are given in Figure 3. It can be seen that the electrons are transferred from N_2 to SiC. This may lead to an ionic structure $(SiC)^-(N_2)^+$. Actually, both the Si–C and N–N bond lengths are much closer to the values of SiC^- and N_2^+ than to those of SiC^+ and N_2^-, respectively.

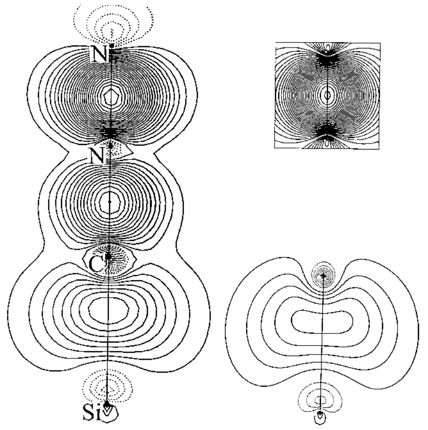

Figure 3. Interatomic overlap density plots of the species SiCNN, SiC, and N_2 at the QCISD/6-31G(d) level.

This Lewis description is also consistent with the natural atomic charge distribution of SiCNN; however, it is in contrast to the Mulliken charge distribution of SiCNN. At the QCISD/6-311G(d) level, the natural charges of Si, C, N, and N are 0.8012, −0.9080, 0.0827, and 0.0241 *c*, respectively, whereas the corresponding Mulliken charges are 0.4225, −0.3895, 0.0566, and −0.0896 *c*. At the QCISD/6-311G(d) level, SiCNN has two intense vibrational bands at 2160 and 1575 cm^{-1} with the corresponding IR intensities 1024 and 316 $km\,mol^{-1}$ (Table 3). However, the dipole moment of SiCNN, 0.8525 Debye, is much smaller than that of CCNN at the same level (3.349 Debye[11b]). Therefore, SiCNN is much less polar than CCNN. The direction of the dipole moment points to the terminal Si atom. Interestingly, this direction is contrary to the above description of SiCNN as an ionic structure $(SiC)^-(N_2)^+$, although it is consistent with the simple idea of dipole moments based on atomic electronegativity and consistent with the Mulliken charge distribution. It is worthy of note that for CCNN, the direction of the dipole moment points to the terminal N atom, which is consistent with both the ionic description $(C_2)^-(N_2)^+$ and the natural atomic charge distribution.[11b]

Table 1. Bond lengths [Å] of SiCNN, SiC, N_2, SiC^-, and N_2^+ at various levels.

Levels	SiCNN			SiC	N_2	SiC^-	N_2^+
	Si–C	C–N	N–N	Si–C	N–N	Si–C	N–N
B3LYP6-311G(d)	1.6700	1.2663	1.1382	1.6458	1.0954	1.6767	1.1086
QCISD/6-311G(d)	1.6634	1.2789	1.1371	1.6536	1.1041	1.6872	1.1240
QCISD(T)/6-311G(d)	1.6811	1.2763	1.1521	1.6634	1.1099	1.6958	1.1304
CCSD/6-311G(d)	1.6614	1.2789	1.1357	1.6554	1.1029	1.6877	1.1214
CCSD(T)/6-311G(d)	1.6794	1.2761	1.1509	1.6647	1.1093	1.6989	1.1291

Table 2. Si–C bond lengths [Å] of SiCNN, $RSi{\equiv}CH$, and $Si{=}C(H)R$ at the B3LYP, QCISD, QCISD(T), CCSD, and CCSD(T) levels calculated with the 6-311G(d,p) basis set.[a]

Levels	SiCNN	$RSi{\equiv}CH$				$Si{=}C(H)R$			
		R = H	R = F	R = Cl	R = OH	R = H	R = F	R = Cl	R = OH
B3LYP	1.6700	1.6474	1.6733	1.6664	1.6655	1.7130	1.7478	1.7350	1.7444
QCISD	1.6634	1.6701	1.6872	1.6835	1.6803	1.7478	1.7527	1.7388	1.7473
QCISD(T)	1.6811	1.6747	1.6909	1.6889	1.6837	1.7257	1.7614	1.7475	1.7535
CCSD	1.6614	1.6531	1.6739	1.6678	1.6680	1.7182	1.7513	1.7376	1.7455
CCSD(T)	1.6794	1.6685	1.6841	1.6809	1.6789	1.7257	1.7611	1.7469	1.7533

[a] The 6-311G(d) basis set was used in the calculations of SiCNN.

Stability of SiCNN: To inspect the kinetic stability of SiCNN,

Table 3. Calculated vibrational frequencies [cm^{-1}] with infrared intensities in parentheses [km mol^{-1}], dipole moments [Debye], and rotational constants [GHz] of $SiCN_2$ isomers.

Species	Levels	Frequencies and IR intensities												Dipole moment	Rotational constant
		ω_1	A	ω_2	A	ω_3	A	ω_4	A	ω_5	A	ω_6	A		
SiNCN (**1**)	B3LYP/6-311G(d)	2292	62	1502	81	724	14	559	26	176	1			5.3267	2.899035
	B3LYP/DZP[a]	2280	78	1506	87	725	13	552	21	193	1				
SiNNC (**2**)	B3LYP/6-311G(d)	2148	102	1495	57	722	15	423	11	182	1			4.4331	3.068038
	B3LYP/DZP[a]	2136	88	1493	59	721	14	471	14	182	2				
NSiCN (**3**)	B3LYP/6-311G(d)	2275	21	1266	0	565	24	274	4	86	23			1.6838	2.944567
	B3LYP/DZP[a]	2249	19	1254	0	565	25	276	3	70	21				
NSiNC (**4**)	B3LYP/6-311G(d)	2091	418	1275	8	636	50	192	0	93	18			2.2040	3.250271
	B3LYP/DZP[a]	2081	413	1262	7	638	47	240	0	74	18				
SiCNN (**5**)[a]	B3LYP/6-311G(d)	2184	805	1590	189	671	19	587	21	158	4			1.5055	2.790250
	QCISD/6-311G(d)	2160	1024	1575	316	675	4	577	25	146	7			0.8525	2.782081
6[b]	B3LYP/6-311G(d)	1573	13	903	37	532	16	412	24	318	18	193	0	3.2324	19.44409, 7.58110, 5.92383
7[c]	B3LYP/6-311G(d)	1783	27	1128	49	592	11	532	3	303	13	164	1	0.5739	49.14590, 3.88301, 3.59868

[a] From ref. [12]. [b] Species **6** denotes the four-membered SiNCN ring isomer. [c] Species **7** denotes the three-membered NNC ring isomer with exocyclic C–Si bonding.

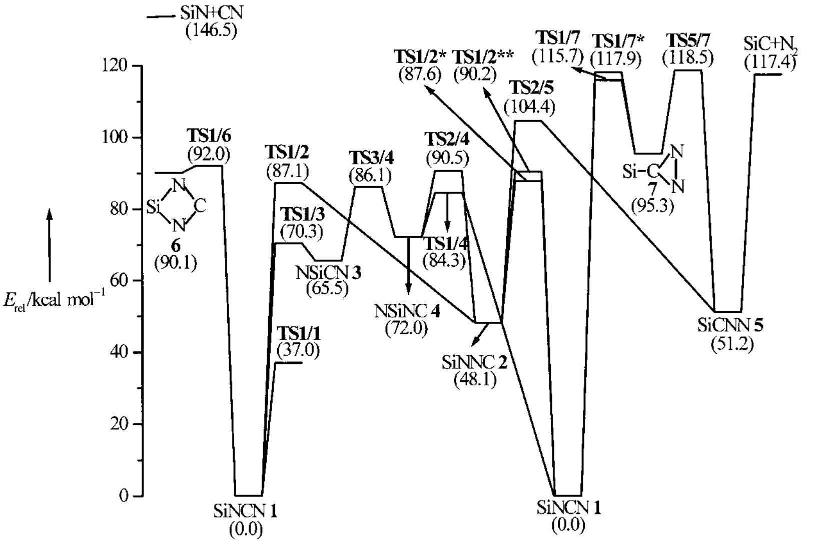

Figure 4. Schematic plot of the potential energy surface of $SiCN_2$ at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) level.

the whole potential energy surface (PES) of the $SiCN_2$ system involving the seven minimum isomers **1**–**7** was constructed (Figure 4). The structures of all the obtained $SiCN_2$ isomers and interconversion transition states are depicted in Figure 1 and Figure 2, respectively, and their corresponding vibrational frequencies are listed in Table 3 and Table 4. From Table 5 and Figure 4, we can see that the order of thermodynamic stability of the seven $SiCN_2$ isomers is **1** (0.0) > **2** (48.1) > **5** (51.2) > **3** (65.5) > **4** (72.0) > **6** (90.1) > **7** (95.3). The values in parentheses are relative energies in kcal mol^{-1} with reference to the lowest energy isomer **1** at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) level. The thermodynamic stability order **1** > **2** > **3** > **4** is quite different from that of the corresponding C_2N_2 isomers, which is NCCN > CNCN > CNNC. This discrepancy was rationalized by Ignatyev and Schaefer[12] as follows: the unpaired electron is mainly localized on the carbon center in the CN radical, while it is localized on the nitrogen center in the SiN radical, this means that for the CN

Table 4. Calculated B3LYP/6-311G(d) vibrational frequencies [cm^{-1}] and infrared intensities in parentheses [km mol^{-1}] of interconversion transition states of $SiCN_2$.

Species	Frequencies and IR intensities											
	ω_1	A	ω_2	A	ω_3	A	ω_4	A	ω_5	A	ω_6	A
TS1/2	1785	6	1119	11	616	28	428	30	258	7	206*i*	5
TS1/2*	1773	4	1194	74	580	6	256	10	218	6	194*i*	6
TS1/2**	1798	51	1017	55	533	1	312	4	105	2	106*i*	18
TS1/3	2265	3	1037	11	572	15	289	2	267	7	264*i*	19
TS1/4	1900	6	1052	8	629	58	291	6	224	6	264*i*	17
TS1/6	1751	29	988	54	508	2	339	7	145	20	121*i*	2
TS1/7	1556	70	809	93	675	49	596	56	401	14	400*i*	63
TS1/7*	1418	26	1055	103	616	37	400	1	298	16	1108*i*	182
TS1/1	1671	243	1276	0	951	38	617	18	552	57	330*i*	4
TS2/4	2096	235	951	9	588	25	196	0	171	1	304*i*	14
TS2/5	1424	310	1148	52	819	69	556	7	518	31	615*i*	60
TS3/4	2019	4	1244	4	541	56	117	11	114	11	248*i*	20
TS5/7	1833	371	1226	199	591	25	201	23	167	15	843*i*	360

Table 5. Total [a.u.] and relative [kcal mol^{-1}, in parentheses] energies of $SiCN_2$ isomers and interconversion transition states. The values given in italics in the parentheses are at the CCSD(T)/TZ2Pf//CCSD/DZP level from ref. [12].

Species	B3LYP/6-311G(d)	CCSD(T)/6-311G(2df) //B3LYP/6-311G(d)
SiNCN (**1**)	– 437.1331271 (0.0)	– 436.3846695 (0.0)
SiNNC (**2**)	– 437.0572242 (47.6)	– 436.3079883 (48.1, *48.5*)
NSiCN (**3**)	– 437.0136792 (75.0)	– 436.2803265 (65.5, *64.1*)
NSiNC (**4**)	– 437.0037442 (81.2)	– 436.2700080 (72.0, *70.2*)
SiCNN (**5**)	– 437.0557233 (48.6)	– 436.3030121 (51.2)
6[a]	– 436.9805232 (95.8)	– 436.2411013 (90.1)
7[b]	– 436.9772466 (97.8)	– 436.2328384 (95.3)
SiN + CN	– 436.8932347 (150.5)	– 436.1511874 (146.5, *144.4*)
SiC + N_2	– 436.9180380 (135.0)	– 436.1975155 (117.4)
TS1/2	– 436.9875112 (91.4)	– 436.2458214 (87.1)
TS1/2*	– 436.9929493 (88.0)	– 436.2450473 (87.6)
TS1/2**	– 436.9794064 (96.5)	– 436.2409789 (90.2)
TS1/3	– 436.9944032 (87.1)	– 436.2726086 (70.3)
TS1/4	– 436.9706456 (102.0)	– 436.2503602 (84.3)
TS1/6	– 436.9790391 (96.7)	– 436.2380712 (92.0)
TS1/7	– 436.9371732 (123.0)	– 436.2003682 (115.7)
TS1/7*	– 436.9334637 (125.3)	– 436.1968306 (117.9)
TS1/1	– 437.0652551 (42.6)	– 436.3257529 (37.0)
TS2/4	– 436.9711022 (101.7)	– 436.2404432 (90.5)
TS2/5	– 436.9565378 (110.8)	– 436.2183434 (104.4)
TS3/4	– 436.9754104 (99.0)	– 436.2474928 (86.1)
TS5/7	– 436.9470117 (116.8)	– 436.1958092 (118.5)

[a] Species **6** denotes the four-membered SiNCN ring isomer. [b] Species **7** denotes the three-membered NNC ring isomer with exocyclic C–Si bonding.

radical the structure $^{\bullet}$C≡N: is "good", while :C=N$^{\bullet}$ is "bad", and for the SiN radical the structure $^{\bullet}$Si≡N: is "bad", while :Si=N$^{\bullet}$ is "good". Notably, **1** and **2** are 51.2 and 3.1 kcal mol^{-1}, respectively, lower than **5**, whereas the isomers **3** and **4** are 14.3 and 20.8 kcal mol^{-1}, respectively, higher than **5**. The high thermodynamic stability of **5** relative to **3** and **4** may be ascribed to the inherent strong N=N bonding in **5** and the unfavorable N=Si bonding in **3** and **4**.

Compound **5** lies in a moderately deep potential well (Figure 4); its dissociation energy to give two singlet molecules SiC and N_2 is at least 66.2 kcal mol^{-1}. Two isomerization pathways of **5** may take place: migration of the Si atom to the opposite end gives the lower energy isomer **2**, while a simple NNC ring closure gives the high-energy three-membered ring **7**. The conversion barriers for **5** → **2** and **5** → **7** are 53.2 and 67.3 kcal mol^{-1}, respectively. In spite of numerous attempts, the search for the direct isomerization pathways of **5** to the linear isomers SiNCN (**1**), NSiCN (**3**), and NSiNC (**4**) was unsuccessful. However, these conversion processes may either involve very complicated atomic rearrangements or concerted cleavage and formation of strong multiple bonds. Thus, direct conversion of **5** to these isomers is expected to overcome much higher barriers than those for the **5** → **2** and **5** → **7** conversions.

Usually, the smallest isomerization or dissociation barrier governs the kinetic stability of an isomer. Thus, given the smallest isomerization barrier of 53.2 kcal mol^{-1}, the linear isomer SiCNN (**5**) possesses very high kinetic stability. This finding is interesting since SiCNN bears a typical Si≡C triple bond and a very short N=N bond that is close to the N≡N triple bond. This indicates that when the two singlet molecules SiC and N_2 approach one another, they are able to form a very stable molecule in which the strong Si≡C and N≡N triple bonding is almost retained rather than the formation of a weakly bound van der Waals species. Thus, a comparison of the kinetic stability with other species that contain Si≡C triple bonding may be useful. The isomerization barriers from RSi≡CH to Si=C(H)R for R = H, F, Cl, OH, CH_3, and SiH_3 have been calculated to be 9.0 (6.0), 22.5 (24.9), (15.1), 25.0 (24.5), 17.5, and 3.2 kcal mol^{-1}, respectively.[6, 7a] Note that the energetic values without parentheses are at the MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) + ZPE level, while those in parentheses are at the QCISD(T)/6-31G(d,p)//QCISD/6-31G(d,p) + ZPE level. Our calculated barriers for SiCNN for both the isomerization and the dissociation are significantly higher than those of RSi≡CH with all substituents R. It seems that bulkier R substituents, such as *t*Bu$(CH_3)_2$C and 2,4,6-tri-*tert*-butylphenyl or 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl may increase the thermodynamic stability of RSi≡CR′ relative to Si=C(R′)R, and may even prevent their interconversion by large barriers as a result of steric hindrance. However, the bulky substituents may, on the other hand, rotate to minimize such steric stabilization. To our knowledge, no detailed calculations on the barriers for RSi≡CR′ → Si=C(R′)R conversion with bulky substituents have been reported. Therefore, SiCNN may be considered as the most kinetically stable isomer with typical Si≡C triple bonding known to date. We hope that the synthesis of such an interesting isomer may open a new pathway to the issue of stable Si≡C triple bonding. Since HSi≡N was characterized by matrix-isolation spectroscopy from a silyl azide precursor[5] and RSi≡CH (R = F, Cl) by neutralization–reionization mass spectrometry with a 1,1-dihalosilacyclobutanes precursor,[6] we suggest that SiCNN may be identified under similar conditions from precursors which contain Si, C, and N components. For the cationic system $[SiCN_2]^+$, $SiCNN^+$ is the second stable isomer both thermodynamically and kinetically,[14] which makes its detection by mass spectrometry very promising. During the vaporization of silicon carbide[15] in the presence of N_2 at high temperatures, the formation of SiCNN may also be possible. In addition, to examine the possibility of the formation SiCNN by the direct addition of SiC and N_2 (both have been detected in interstellar space), we calculated the dissociation curve of SiCNN to SiC and N_2 at both the 6-311G(d) B3LYP and MP2 levels. These two methods were chosen since B3LYP usually underestimates the association barrier, whereas MP2 may overestimate it. The dissociation curves in Figure 5 and Figure 6 clearly show that SiC and N_2 can associate without a barrier to give SiCNN, especially in dark interstellar clouds in which the temperature is very low and much collisional stabilization occurs. This is in sharp contrast to the situation for CCNN where there is a distinct barrier of 5.5 kcal mol^{-1} for the association of C_2 and N_2 to form CCNN at all the ab initio levels employed.[11b] Therefore, the observation of SiCNN under laboratory and interstellar conditions appears very promising.

Properties of other isomers: Other valuable information can also be obtained from the PES of $SiCN_2$ (Figure 4). Although

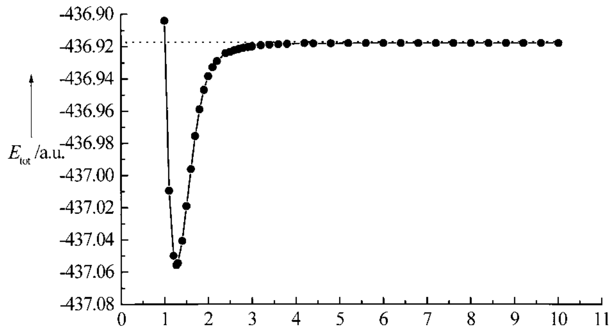

Figure 5. Dissociation curve of SiCNN at the B3LYP/6-311G(d) level. The dotted line denotes the B3LYP/6-311G(d) total energy of SiC and N$_2$.

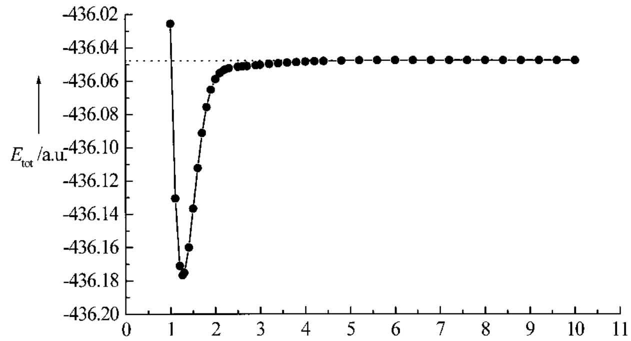

Figure 6. Dissociation curve of SiCNN at the MP2/6-311G(d) level. The dotted line denotes the MP2/6-311G(d) total energy of SiC and N$_2$.

Ignatyev and Schaefer[12] have studied the structures, energetics, and frequencies of the isomers SiNCN (**1**), SiNNC (**2**), NSiCN (**3**), and NSiNC (**4**), they did not consider the kinetic stability, which might be very important for the prediction of their possible existence. Actually, our calculations show that the isomers **3** and **4** may be kinetically unstable compared to **5**. The smallest conversion barriers for **3** and **4** are 4.8 (**3**→**1**) and 12.3 kcal mol^{-1} (**4**→**1**), respectively. Therefore, the observation of the isomers **3** and **4** seems much less likely. The lowest lying isomer **1** is also kinetically the most stable with the smallest barrier of 70.3 kcal mol^{-1} for **1**→**3** conversion. The second low-lying isomer **2** at 48.1 kcal mol^{-1} is stabilized by the smallest isomerization barrier 39.0 kcal mol^{-1} (**2**→**1**). As both **1** and **2** have high kinetic stability, they may be experimentally observable. NBO analysis indicates that both isomers still contain conjugate Si≡N and C≡N triple bonding, although for the SiN radical, the "**:**Si=N**·**" structure may have more weight than the "**·**Si≡N**:**" structure. Since both SiN and CN radicals have been observed in interstellar space, their direct addition to form SiNCN (**1**) and SiNNC (**2**) is quite feasible. Therefore, the isomers **1** and **2** may also be promising candidates with silicon multiple bonding for future detection. Interestingly, the kinetic stability of **2** is 14.2 kcal mol^{-1} less than that of **5**, although the former is 3.1 kcal mol^{-1} lower in energy than the latter. The newly found four-membered SiNCN ring isomer **6** at 90.1 kcal mol^{-1} is presumably not detectable since its barrier to the isomerization to isomer **1** is only 1.9 kcal mol^{-1}. Interestingly, another new isomer **7**, which has a three-membered NNC ring structure, resides in a moderately deep potential well stabilized by the smallest barrier 20.4 kcal mol^{-1} (**7**→**1**) even though its relative energy is rather high, 95.3 kcal mol^{-1}. If isomer **7** is converted to isomer **1**, a large exothermicity 95.3 kcal mol^{-1} will be released, which makes isomer **7** a potential high-energy-density (HED) molecule.

Conclusions

We have investigated the structures, spectroscopies, and stabilities of SiCNN and its isomers at different levels of theory. By comparison with other molecules (RSi≡CH (R = H, F, Cl, OH)), SiCNN was shown to possess a typical Si≡C triple bond. Furthermore, the potential energy surface of SiCN$_2$ indicates that SiCNN is kinetically very stable with the smallest conversion barrier of 53.2 kcal mol^{-1}. Therefore, SiCNN may be considered as the most kinetically stable isomer with Si≡C triple bonding known to date, and awaits future experimental and interstellar detection. In addition, SiCNN has a strong N≡N triple bond. We anticipate that the present theoretical study will stimulate future experimental considerations on this interesting molecule. The calculated structure, vibrational frequencies, dipole moments, and rotational constants may assist its future characterization. The properties of other SiCN$_2$ isomers are also discussed.

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