10602 *J. Phys. Chem. A* **2004,** *108,* 10602−10608

Theoretical Study on Structures and Stabilities of $[H_3,Si,C,N]$ Isomers

Qiang Wang, Yi-hong Ding,* and Chia-chung Sun

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

Received: July 11, 2004; In Final Form: September 3, 2004

A detailed theoretical investigation of the singlet $[H_3,Si,C,N]$ potential energy surfaces including 26 minimum isomers and 45 interconversion transition states is reported at the Gaussian-3//B3LYP/6-31G(d) level. The three lowest-lying isomers H_3SiCN **1** (0.0 kcal/mol), H_3SiNC **2** (4.9 kcal/mol), and H_3CNSi **3** (7.4 kcal/mol) are also kinetically stable with the least conversion barriers of 23.4−46.5 kcal/mol, whereas the high-lying H_3CSiN **4** (55.9 kcal/mol) is metastable with a barrier of 14.7 kcal/mol. This is consistent with available matrix spectroscopic identifications from the parent compound $H_3CSi(N_3)_3$. Additionally, 14 new isomers with considerable kinetic stability are predicted. Among these, 7 chainlike isomers, $SiCNH_3$ **5** (85.3 kcal/mol), H_2CNSiH **8** (27.2 kcal/mol), H_2CSiNH **9** (49.4 kcal/mol), H_2NCSiH **10** (56.5 kcal/mol), H_2NCHSi **11** (55.0 kcal/mol), $H_2N-c\text{-}CHSi$ **12** (55.0 kcal/mol), and H_2NSiCH **13** (62.6 kcal/mol), and 4 three-membered ring isomers $c\text{-}CH_2SiNH$ **22** (29.0 kcal/mol), $c\text{-}NH_2SiCH$ **23** (49.6 kcal/mol), $c\text{-}SiH_2NCH$ **25** (34.2 kcal/mol), and $c\text{-}SiHCHNH$ **26** (50.6 kcal/mol) each have the conversion barriers of 18−37 kcal/mol. In particular, the 4 species **10**, **11**, **12**, and **23** can be easily converted to each other, and all of them could coexist. The remaining 3 isomers H_2SiCNH **15** (45.7 kcal/mol), H_2SiNCH **17** (45.2 kcal/mol), and $c\text{-}SiH_2CNH$ **24** (61.0) have lower conversion barriers of 11−13 kcal/mol and can be considered as metastable species. All of the predicted 14 new isomers could exist as stable or metastable intermediates under various conditions, such as the irradiation of Si,C,N-containing compounds or the $SiH_2 + HCN/HNC$, $Si + H_2CNH$, and $SiC + NH_3$ reactions. Finally, the structural and bonding analysis indicate that the newly found isomers contain various properties that are of chemical interest (e.g., silylene, $Si\equiv C$ triple bonding, intra- or interdonor−acceptor bonding, and cumulenic Si bonding). This is the first detailed theoretical study on the potential energy surfaces of the series of hydrogenated Si,C,N-containing molecules. The knowledge of the present trihydrogenated SiCN isomerism could provide useful information for more highly hydrogenated or larger Si,C,N-containing species.

1. Introduction

Silicon-containing chemistry has attracted continuing interest from various fields. One particular area of interest is the possible role in astrophysical chemistry. The concentration of Si in interstellar space is only slightly lower than the concentrations of C, N, and O.[1] However, because of the limitation of spectroscopic data, the number of detected Si-containing molecules is far lower than that of C,N,O-containing species. Regarding the Si,C,N-containing species, only the simplest and nonhydrogenated SiCN and SiNC radicals have been detected in space.[2] The SiCN and SiNC[3] radicals, as well as the monohydrogenated chainlike molecules HSiCN and HSiNC,[4] have also been detected in the laboratory. Also, the existence of these four Si,C,N-containing species and another form, HCNSi, has been confirmed by combined IR spectra and theoretical calculations.[5] At the same time, three highly hydrogenated species H_3CNSi, H_3SiCN, and H_3SiNC were tentatively characterized by IR spectra.[5] Note that no theoretical studies have been reported on H_3CNSi, H_3SiCN, and H_3SiNC.

Although silicon and carbon have iso-valence electrons, their chemical properties are rather different from each other. Silicon is usually reluctant to form multiple bonding, whereas carbon prefers it. We have been interested in the structures, stabilities, and bonding properties of a series of $[H_x,Si,C,N]$ species. Despite the iso-valence, the $[H_x,Si,C,N]$ isomers should have distinct features from the analogous $[H_x,C,C,N]$ ones. In fact, the monohydrogenated HSiCN and HSiNC isomers each have singlet ground states, whereas HCCN and HCNC have triplet ground states. It is of great interest to investigate the structures and stabilities of the $Si\equiv C$ and $Si\equiv N$ triple-bonded silylene or carbene-involving isomers ranging from chainlike to cyclic forms. In dense interstellar space, the environmental temperature is very low, and molecules with high kinetic stability can exist once generated. Unfortunately, the detailed potential energy surface information of even the simplest hydrogenated Si,C,N-molecule, [H,Si,C,N], has not been reported yet.

On the other hand, hydrogenated Si,C,N-containing species $[H_x,Si,C,N]$ also play important roles in the coating of microelectronic and photoelectronic materials. Knowledge of the structural, stability, and bonding properties of $[H_x,Si,C,N]$ is very useful for understanding the chemical vaporization processes of SiCN films and gaining insight into the atomic or radical interaction with substrates (i.e., $SiH_m + H_nCN$ ($m + n = x$)).

In this paper, we report our detailed computational work on the trihydrogenated Si,C,N-molecule, $[H_3,Si,C,N]$. At the reliable Gaussian-3//B3LYP/6-31G(d) level,[6,7] in addition to the experimentally known isomers H_3SiCN, H_3SiNC, and H_3CNSi, various new isomers are found to possess very high or moderate kinetic stabilities toward isomerization or dissociation. Attractively, these new isomers contain the silylene $Si\equiv C$ triple-bonding, intra- or intermolecular donor−acceptor bonding, and cumulenic Si-bonding.

10.1021/jp046933p CCC: $27.50

2. Computational Methods

All of the calculations were carried out using the *Gaussian 98* program package.[8] The geometries of the [H_3,Si,C,N] isomers and the interconversion transition states were fully optimized at the B3LYP/6-31G(d) level. Harmonic vibrational frequencies were calculated at the same level to check whether the obtained structure is a minimum or a saddle point. To get more accurate energies, Gaussian-3 calculations were performed at the B3LYP/6-31G(d) geometries. Intrinsic reaction coordinate (IRC) calculations were also carried out to test whether the transition state connects the right isomers at the B3LYP/6-31G(d) level.

3. Results and Discussions

For the singlet [H_3,Si,C,N] system, various isomeric forms were searched as many ways as possible following the SiCN chain, SiNC chain, and *c*-SiCN three-membered-ring procedures. A total of 26 isomers and 45 interconversion transition states are located. The optimized structures of the isomers and the transition states are shown in Figures 1 and 2, respectively, while the vibrational frequencies of the isomers is given in Table 1. The energetics of all the species are listed in Table 2. Finally, a schematic singlet potential energy surface (PES) of [H_3,Si,C,N] is plotted in Figure 3. In the following discussions, the term "thermodynamical stability" is referring to the relative energy order. An isomer with low relative energy is considered to have high thermodynamical stability. On the other hand, kinetic stability is judged by its least conversion barrier. The lower the least conversion barrier the isomer has, the higher the kinetic stability it possesses.

3.1. H_3SiCN 1, H_3SiNC 2, and H_3CNSi 3. On the singlet [H_3,Si,C,N] PES, the two lowest-lying isomers are silylcyanide H_3SiCN **1** (0.0) and silylisocyanide H_3SiNC **2** (4.9), each of which has C_{3v} symmetry. The values in parentheses are relative energies in kcal/mol calculated at the G3//B3 level. Structurally (in Figure 1), **1** and **2** can be viewed as the combination between SiH_3 and C≡N radicals. Because, for the CN radical, the C-atom has much higher spin density (0.841 e) than the N-atom (0.159 e), the SiH_3 attack at the C-site should be more favored than at the N-site. Both **1** and **2** are kinetically stabilized by **ts1/2** with the barriers 28.3 and 23.4 kcal/mol, respectively.

The third low-lying isomer, silaisonitrile H_3CNSi **3** (7.4) and another high-lying isomer H_3CSiN **4** (55.9) are C_{3v}-symmetrized adducts between CH_3 and SiN radicals. In contrast to the situation of the CN radical, the N-atom of the SiN radical has much larger spin density (0.859 e) than the Si-atom (0.141 e). This renders isomer **3** to be energetically more stable than **4**. Isomer **3** has a very high kinetic stability, 46.5 kcal/mol, governed by **ts3/8**. However, isomer **4** has a much lower kinetic stability at 14.7 kcal/mol (**ts3/4**). It is a metastable species as a reaction intermediate. Interestingly, the Si≡N triple bond distances within **3** (1.5644 Å) and **4** (1.5677 Å) are very close.

Isomer **1** is already well-known.[9] Isomers **2** and **3** were generated recently by Maier et. al. from the parent compound triazidomethylsilane $H_3CSi(N_3)_3$.[5] A possible route was suggested: $H_3CSi(N_3)_3$ → H_3CSiN **4** → H_3CNSi **3** → H_3SiNC **2** ↔ H_3SiCN **1**. Because it is different from the direct and relatively easier **4** → **3** and **1** ↔ **2** conversions, the isomerization from **3** to **2** is very complicated and difficult. The most feasible pathway is H_3CNSi **3** → *c*-CH_2SiNH **22** → *c*-CHNHSiH **26** → HNCHSiH **21** → *c*-SiH_2NCH **25** → H_3SiNC **2**, among which two three-membered-ring isomers **25** and **26** are involved (the highest energy transition state is **ts22/26** at 68.7 kcal/mol). However, the successive H-hopping pathway H_3CNSi **3** → H_2CNSiH **8** → HCNHSiH **19** → H_2SiNHC **18** → H_3SiNC **2** cannot compete because of the rather high energy of **ts8/18** at 110.4 kcal/mol. As listed in Table 1, the characteristic vibrational

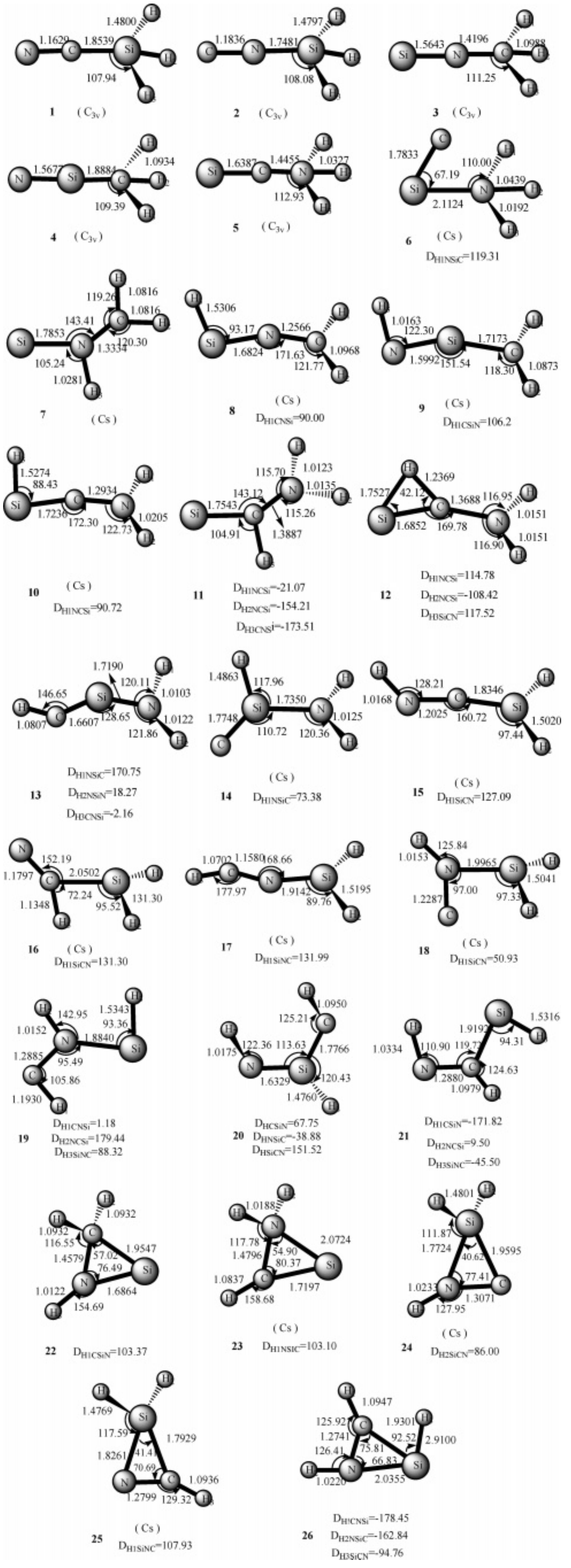


Figure 1. Optimized geometries of singlet [H_3,Si,C,N] isomers at the B3LYP/6-31G(d) level. Bond lengths are in angstroms and angles in degrees.

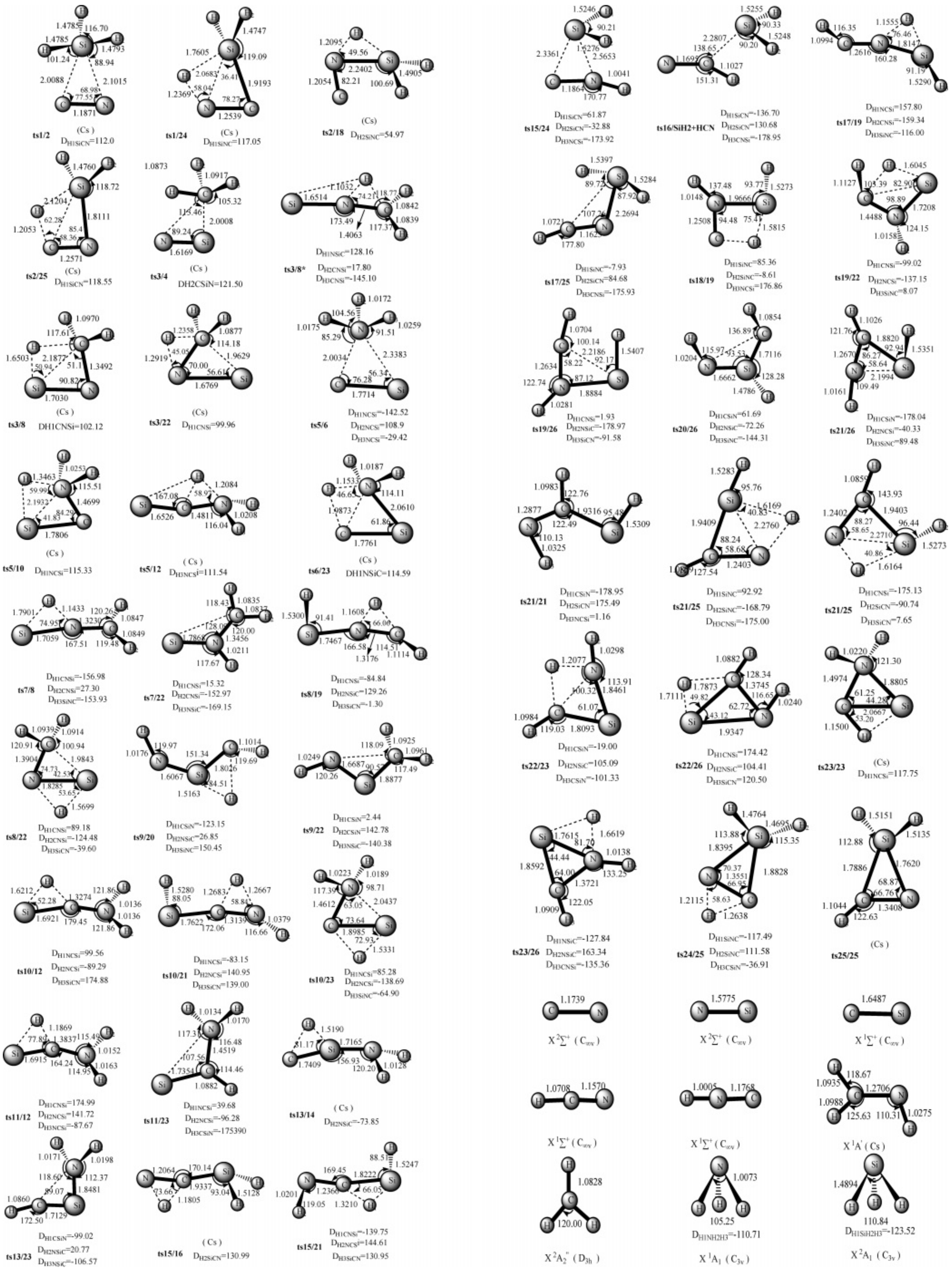


Figure 2. Optimized geometries of interconversion transition states and dissociation products between singlet [H_3,Si,C,N] isomers. Bond lengths are in angstroms and angles in degrees.

TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), IR Intensities (km/mol) (in parentheses), Dipole Moment (Debye), and Rotational Constants (GHz) of Singlet [H_3,Si,C,N] Structures at the B3LYP/6-31G(d) Level

species	frequencies (IR intensity)	dipole moment (Debye)	rotational constant (GHz)		
H_3SiCN **1**	272 (4) 272 (4) 604 (37) 689 (42) 689 (42) 936 (251) 946 (53) 946 (53) 2284 (49) 2300 (106) 2300 (106) 2326 (10)	3.3288	84.311 61	4.933 63	4.933 63
H_3SiNC **2**	206 (0) 206 (0) 676 (67) 714 (55) 714 (55) 953 (68) 953 (68) 966 (316) 2176 (294) 2287 (35) 2299 (131) 2299 (131)	2.9125	84.479 34	5.615 76	5.615 76
H_3CNSi **3**	265 (23) 265 (23) 778 (0) 1142 (1) 1142 (1) 1466 (70) 1513 (5) 1513 (5) 1516 (20) 3013 (79) 3069 (29) 3069 (29)	0.7560	159.391 17	5.247 37	5.247 37
H_3CSiN **4**	110 (4) 110 (4) 612 (6) 796 (2) 796 (2) 1270 (1) 1303 (3) 1477 (14) 1477 (14) 3071 (0) 3165 (0) 3165 (0)	5.7411	157.129 79	5.425 48	5.425 48
H_3NCSi **5**	238 (80) 238 (80) 656 (0) 1043 (5) 1043 (5) 1396 (49) 1523 (0) 1679 (30) 1679 (30) 3261 (73) 3288 (22) 3288 (22)	8.1860	184.762 36	4.634 54	4.634 54
H_3NSiC **6**	281 (28) 337 (0) 386 (0) 688 (37) 706 (28) 908 (3) 1242 (196) 1631 (41) 1665 (40) 3133 (45) 3502 (32) 3584 (48)	4.5506	17.900 88	9.709 47	6.523 47
H_2CNHSi **7**	286 (6) 460 (74) 575 (17) 591 (18) 780 (52) 1096 (4) 1354 (240) 1436 (33) 1540 (73) 3200 (5) 3309 (11) 3401 (17)	1.8865	86.326 07	5.466 28	5.140 76
H_2CNSiH **8**	224 (20) 298 (8) 685 (7) 718 (11) 848 (100) 1023 (19) 1179 (11) 1526 (1) 1805 (12) 2025 (303) 3046 (36) 3114 (34)	2.0547	124.316 45	5.390 27	5.358 23
H_2CSiNH **9**	188 (3) 229 (2) 590 (59) 597 (64) 643 (200) 738 (3) 842 (22) 1199 (28) 1391 (11) 3161 (3) 3251 (0) 3582 (39)	2.0625	121.341 55	6.021 00	5.967 15
H_2NCSiH **10**	255 (40) 270 (5) 655 (231) 668 (10) 734 (22) 735 (7) 1168 (0) 1640 (69) 1696 (61) 2044 (168) 3424 (2) 3488 (17)	4.4988	132.755 87	4.873 42	4.834 44
H_2NCHSi **11**	235 (1) 367 (89) 591 (343) 651 (66) 682 (19) 1075 (9) 1275 (102) 1438 (72) 1698 (32) 2995 (15) 3535 (15) 3635 (8)	2.6276	84.725 38	5.155 55	4.880 67
H_2N−*c*-SiHC **12**	227 (35) 279 (75) 431 (6) 488 (315) 722 (30) 1152 (63) 1173 (3) 1508 (84) 1668 (15) 2004 (44) 3503 (7) 3587 (16)	2.2811	158.009 92	4.913 15	4.896 63
H_2NSiCH **13**	101 (54) 211 (22) 231 (198) 458 (81) 741 (62) 807 (55) 841 (22) 1101 (45) 1605 (39) 3310 (2) 3582 (47) 3685 (45)	2.4552	55.623 23	6.700 27	5.990 16
H_2NSiHC **14**	55 (18) 127 (23) 319 (3) 360 (201) 742 (37) 817 (9) 830 (33) 953 (11) 1621 (33) 2239 (109) 3569 (39) 3662 (51)	2.8376	24.897 53	8.261 94	6.426 28
H_2SiCNH **15**	286 (0) 319 (65) 425 (338) 604 (18) 644 (109) 743 (56) 797 (283) 952 (105) 1999 (507) 2157 (71) 2172 (171) 3559 (98)	2.9202	101.346 43	4.885 65	4.852 67
H_2SiCHN **16**	163 (6) 221 (27) 325 (4) 548 (3) 641 (18) 716 (24) 972 (84) 1006 (54) 2056 (57) 2111 (141) 2125 (237) 2672 (84)	2.2589	74.209 59	4.659 79	4.590 11
H_2SiNCH **17**	236 (10) 280 (32) 375 (2) 467 (48) 747 (28) 761 (48) 761 (24) 972 (74) 2070 (201) 2077 (297) 2181 (140) 3478 (317)	5.3015	108.251 90	4.922 25	4.899 66
H_2SiNHC **18**	239 (7) 243 (4) 243 (4) 549 (110) 694 (3) 712 (4) 919 (66) 1021 (57) 1783 (29) 2140 (100) 2165 (222) 3571 (122)‘	2.7078	33.473 51	7.288 06	6.394 47
HCNHSiH**19**	372 (33) 533 (6) 547 (19) 573 (14) 844 (32) 1022 (100) 1080 (56) 1285 (1) 1555 (32) 2010 (394) 2228 (107) 3559 (40)	1.8393	33.361 69	8.072 05	6.903 28
HCSiHNH **20**	123 (27) 395 (33) 492 (65) 521 (10) 656 (82) 675 (156) 860 (70) 877 (14) 1028 (19) 2310 (86) 3151 (8) 3567 (15)	2.5188	26.199 45	8.549 79	6.596 59
HNCHSiH**21**	102 (5) 262 (14) 565 (39) 632 (16) 855 (75) 1168 (53) 1227 (83) 1421 (68) 1605 (7) 2043 (285) 3065 (62) 3298 (14)	1.2672	45.529 17	5.890 48	5.307 36
c-CH_2SiNH **22**	387 (134) 549 (37) 821 (0) 842 (45) 987 (14) 1097 (21) 1150 (27) 1153 (0) 1539 (7) 3067 (57) 3134 (45) 3578 (14)	1.1683	26.022 01	11.070 44	8.187 58
c-NH_2SiCH **23**	357 (36) 632 (98) 747 (8) 847 (149) 913 (6) 1018 (14) 1127 (3) 1198 (4) 1689 (1) 3232 (11) 3443 (1) 3515 (7)	2.7257	27.753 78	9.689 48	7.481 58
c-SiH_2CNH**24**	451 (23) 465 (0) 658 (32) 662 (9) 749 (151) 755 (5) 953 (67) 1176 (27) 1447 (59) 2271 (55) 2298 (149) 3405 (1)	2.4411	31.693 80	9.895 17	8.315 13
c-SiH_2NCH **25**	489 (19) 571 (0) 652 (19) 656 (38) 818 (21) 820 (35) 974 (81) 1167 (31) 1630 (53) 2285 (54) 2308 (134) 3117 (30)	1.8774	32.323 03	10.076 35	8.488 97
c-NHCHSiH **26**	311 (96) 401 (55) 596 (46) 667 (42) 843 (85) 1025 (16) 1044 (8) 1271 (82) 1653 (38) 1975 (415) 3110 (34) 3449 (8)	3.5016	31.856 11	8.732 36	7.306 87

frequencies (unscaled) of the three species calculated at the B3LYP/6-31G(d) level are 2326 cm^{-1} ($-C\equiv N$ stretch) for **1**, 2176 cm^{-1} ($-N\equiv C$ stretch) for **2**, and 1516, 1466 cm^{-1} ($C-N\equiv Si$ stretch) for **3**. To compare with the experimental values, a scale factor of 0.96 is used[7] to place these vibrational bands at 2233, 2089, 1455, and 1407 cm^{-1}, in excellent agreement with the corresponding experimental values 2200, 2098, 1467, and 1410 cm^{-1}.[5] Isomers **1** and **2** have very large dipole moments at 3.3288 and 2.9125 D, respectively, making their detection via microwave technique very easy. The dipole moment of **3** is as small at 0.7560 D.

3.2. Newly Predicted [H_3,Si,C,N] Isomers. *3.2.1. Kinetically Stable Isomers.* In addition to the already observed isomers **1**, **2**, and **3** and the suggested intermediate **4** in the experiment of Maier et al.,[5] we obtained various new species that are kinetically stable or metastable. We will first discuss the kinetically stable species. There are seven chainlike isomers: $SiCNH_3$ **5** (85.3), H_2CNSiH **8** (27.2), H_2CSiNH **9** (49.4), H_2NCSiH **10** (56.5), H_2NCHSi **11** (55.0), H_2N−*c*-CHSi **12** (55.0), and H_2NSiCH **13** (62.6) with their possible valence structures shown in Scheme 1 (deduced from the structures and natural bond order (NBO) analysis). Among these, despite the fact that it has the highest energy, the C_{3v} isomer $SiCNH_3$ **5** still has high kinetic stability at 24.7 kcal/mol (**ts5/12**). It possesses an interesting $Si\equiv C$ triple bond, whose bond length of 1.6387 Å is slightly shorter than the typical value of 1.6519 Å in HSiCH.[14] The CN distance of 1.4455 Å is very close to the typical C−N single bond value (1.4651 Å) in H_3CNH_2. This

TABLE 2: Total (a.u.) and Relative (kcal/mol) Energies of the Singlet [H_3,Si,C,N] Isomers, Transition States, and Dissociation Products at the G3//B3LYP/6-31G(d) Levels

species	B3LYP	G3//B3LYP
H_3SiCN **1**	−384.13671 (0.00)	−383.93470 (0.00)
H_3SiNC **2**	−384.12724 (5.94)	−383.92685 (4.93)
H_3CNSi **3**	−384.13746 (−0.47)	−383.92295 (7.38)
H_3CSiN **4**	−384.04649 (56.61)	−383.84554 (55.95)
H_3NCSi **5**	−384.00228 (84.36)	−383.79880 (85.28)
H_3NSiC **6**	−383.94214 (122.09)	−383.74179 (121.06)
H_2CNHSi **7**	−384.03751 (62.25)	−383.82614 (68.12)
H_2CNSiH **8**	−384.10590 (19.33)	−383.89140 (27.17)
H_2CSiNH**9**	−384.04912 (54.96)	−383.85602 (49.38)
H_2NCSiH**10**	−384.05496 (51.30)	−383.84466 (56.50)
H_2NCHSi **11**	−384.05677 (50.16)	−383.84710 (54.97)
H_2N-cCHSi **12**	−384.04855 (55.32)	−383.84708 (54.98)
H_2NSiCH **13**	−384.02065 (72.83)	−383.83492 (62.61)
H_2NSiHC**14**	−383.94708 (118.99)	−383.75481 (112.88)
H_2SiCNH**15**	−384.07150 (40.92)	−383.86195 (45.65)
H_2SiCHN **16**	−384.03262 (65.31)	−383.82929 (66.15)
H_2SiNCH **17**	−384.06993 (41.90)	−383.86266 (45.21)
H_2SiNHC **18**	−384.02585 (69.56)	−383.81934 (72.39)
HCNHSiH **19**	−384.02726 (68.80)	−383.82403 (69.45)
HCSiHNH**20**	−383.95921 (111.38)	−383.77496 (100.24)
HNCHSiH**21**	−384.05418 (51.79)	−383.84562 (55.90)
cCH_2SiNH **22**	−384.09681 (25.03)	−383.88855 (28.96)
cNH_2SiCH**23**	−384.06437 (45.39)	−383.85573 (49.55)
$cSiH_2CNH$**24**	−384.03976 (60.83)	−383.83757 (60.95)
$cSiH_2NCH$**25**	−384.08569 (32.02)	−383.88019 (34.21)
cNHCHSiH **26**	−384.06363 (45.86)	−383.85405 (50.61)
ts1/2	−384.08989 (29.38)	−383.88968 (28.25)
ts1/24	−383.99523 (88.78)	−383.79888 (85.23)
ts2/18	−383.99727 (87.50)	−383.79942 (84.89)
ts2/25	−384.02243 71.71)	−383.82547 (68.55)
ts3/4	−384.01948 (73.56)	−383.82218 (70.62)
ts3/8	−384.05606 (50.61)	−383.84877 (53.92)
ts3/8*	−383.99831 (86.85)	−383.80029 (84.35)
ts3/22	−384.02183 (72.08)	−383.81971 (72.16)
ts5/6	−383.93627 (125.77)	−383.73660 (124.32)
ts5/10	−383.92342 (133.84)	−383.72746 (130.05)
ts5/12	−383.95945 (111.23)	−383.75939 (110.01)
ts5/16	−384.00433 (83.07)	−383.80103 (83.88)
ts6/23	−383.93977 (123.58)	−383.74179 (121.05)
ts7/8	−384.02168 (72.18)	−383.81897 (72.62)
ts7/22	−384.03493 (63.86)	−383.82985 (65.80)
ts8/19	−383.96126 (110.10)	−383.75873 (110.42)
ts8/22	−384.01483 (76.48)	−383.81028 (78.08)
ts9/20	−383.95268 (115.48)	−383.76285 (107.84)
ts9/22	−384.00030 (85.60)	−383.80964 (78.48)
ts10/12	−384.04769 (55.86)	−383.84564 (55.89)
ts10/21	−383.96280 (109.13)	−383.76009 (109.58)
ts10/23	−383.96746 (106.20)	−383.76479 (106.62)
ts11/12	−384.04822 (55.52)	−383.84632 (55.46)
ts11/22	−384.04725 (56.13)	−383.84028 (59.25)
ts12/25	−384.03087 (66.41)	−383.82591 (68.27)
ts13/14	−383.94308 (121.50)	−383.75318 (113.91)
ts13/23	−383.99800 (87.04)	−383.80152 (83.57)
ts15/21	−384.04641 (56.66)	−383.84196 (58.20)
ts15/24	−384.02172 (72.16)	−383.81909 (72.55)
ts16/SiH_2 + HCN	−384.03199 (65.71)	−383.82912 (66.26)
ts17/19	−383.99870 (86.60)	−383.79447 (88.00)
ts17/25	−384.04964 (54.63)	−383.84583 (55.77)
ts18/19	−384.01960 (73.49)	−383.81578 (74.63)
ts19/22	−383.98382 (95.94)	−383.78490 (94.00)
ts19/26	−384.00218 (84.42)	−383.79576 (87.19)
ts20/26	−383.95813 (112.06)	−383.77884 (97.80)
ts21/21	−384.05396 (51.92)	−383.84506 (56.25)
ts21/25	−384.03087 (64.41)	−383.82591 (68.27)
ts21/26	−384.02837 (67.99)	−383.82073 (71.52)
ts22/23	−383.98401 (95.82)	−383.78969 (91.00)
ts22/26	−384.02785 (68.31)	−383.82514 (68.75)
ts23/23	−383.96017 (110.78)	−383.76885 (104.07)
ts23/26	−383.94804 (118.39)	−383.75366 (113.60)
ts24/25	−383.96099 (110.26)	−383.76804 (104.58)
ts25/25	−384.00326 (83.74)	−383.80044 (85.25)
$^2SiH_3 + {}^2CN$	−383.94400 (120.93)	−383.74430 (119.48)
$^2CH_3 + {}^2SiN$	−383.95660 (113.02)	−383.75390 (113.46)
$^1NH_3 + {}^1CSi$	−383.87760 (162.59)	−383.70360 (145.02)
$^1SiH_2 + {}^1HCN$	−384.03577 (63.34)	−383.83670 (61.50)
$^1SiH_2 + {}^1HNC$	−384.00930 (79.95)	−383.81330 (76.18)
$^1Si + {}^1H_2CNH$	−383.95612 (113.32)	−383.75280 (114.14)
$^3Si + {}^1H_2CNH$	−383.99895 (86.44)	−383.78027 (96.91)

C−N single bond is formed when the lone pair orbital of NH_3 interacts with the SiC vacant orbital. Surely, isomer **5** can be viewed as a kinetically stable species formed between two closed-shell molecules SiC and NH_3 via an intermolecular donor−acceptor interaction. Note that the arrow in Scheme 1 denotes the donor−acceptor bonding.

The three isomers H_2CNSiH **8**, H_2CSiNH **9**, and H_2NCSiH **10** can each generally be considered as having a cumulenic structure HX═Y═ZH_2, with X, Y, and Z being either Si, C, or N. The monohydrogenated X-atom contains a lone pair of electrons. The internal Y-atom is sp-hybridized. The terminal Si-atom of **8** and **10** is sp^3-hybridized. Note that the SiN bond distance of 1.6824 Å in **8** is somewhat longer than the typical Si═N value of 1.6076 Å, which is rationalized by the fact that the large electron withdrawal ability of C and N reduces the extent of the electron lone pair donation from the N- to the Si-atom. H_2CNSiH **8** is also the fourth lowest-lying [H_3,Si,C,N] isomer. Isomer H_2NCHSi **11** has a silylene structure with Si═C double bonding. Besides the Si═C bonding, isomer H_2N−*c*-CHSi **12** has a $3c-2e$ bridged Si−H−C bond with the density greatly located between Si- and C-atoms, which leads to a nonclassical structure. Such an additional silylene structure contains Si═C double bonding. Both **11** and **12** have a lone pair of electrons at Si- and N-sites. Their greatly strengthened C−N single bond (1.3887 and 1.3688 Å, respectively) could be ascribed to the significant overlap between the lone pair orbital and the π-orbital of SiC. Isomer H_2NSiCH **13** possess a normal Si≡C triple bond (1.6607 Å) that is very close to the typical value of 1.6519 Å. Interestingly, although isomers **10** and **13** have just the opposite Si- and C-atom positions, the nature of the SiC bond is markedly different (i.e., Si═C in **10** and Si≡C in **13**). Surely, strong electron withdrawal groups or atoms at the Si-site favor the Si≡C bonding.

There are four kinetically stable isomers *c*-CH_2SiNH **22** (29.0), *c*-NH_2SiCH **23** (49.6), *c*-SiH_2NCH **25** (34.2), and *c*-SiHCHNH **26** (50.6) with SiNC three-membered rings. Isomers **22** (29.0) and *c*-SiH_2NCH **25** (34.2) are the fifth and sixth lowest-lying isomers, respectively, on the [H_3,Si,C,N] PES. Isomer **25** has the normal structure with SiH_2 taking a side-addition to the C≡N bond of HCN (Scheme 2). Formally, isomers **22**, **23**, and **26** have silylene structures. The lone pair of electrons on the N-atom can effectively donate to the vacant orbital of the Si-atom, which greatly suppresses the silylene reactivity and increases stability. Interestingly, isomer **22** is slightly lower in energy than **25**. It contains the intramolecular donor−acceptor interaction between the N-lone pair and the vacant orbital of carbene or silylene. The intramolecular donor−acceptor bonding mechanism should contribute to the unusual stability of **22**, **23**, and **26**.

As shown in Figure 3, the isomers H_2CNSiH **8**, H_2CSiNH **9**, and H_2NSiCH **13** all possess high kinetic stability with corresponding least conversion barriers of 26.7 (**8** → **3**), 29.1 (**9** → **22**), and 21.0 (**13** → **23**) kcal/mol. Notice that the **8** → **3** conversion has two transition states **ts3/8** (53.9) and **ts3/8*** (84.3). The lower-energy **ts3/8** that governs the kinetic stability of isomer **8** is three-membered-ring-like. The high-energy **ts3/**

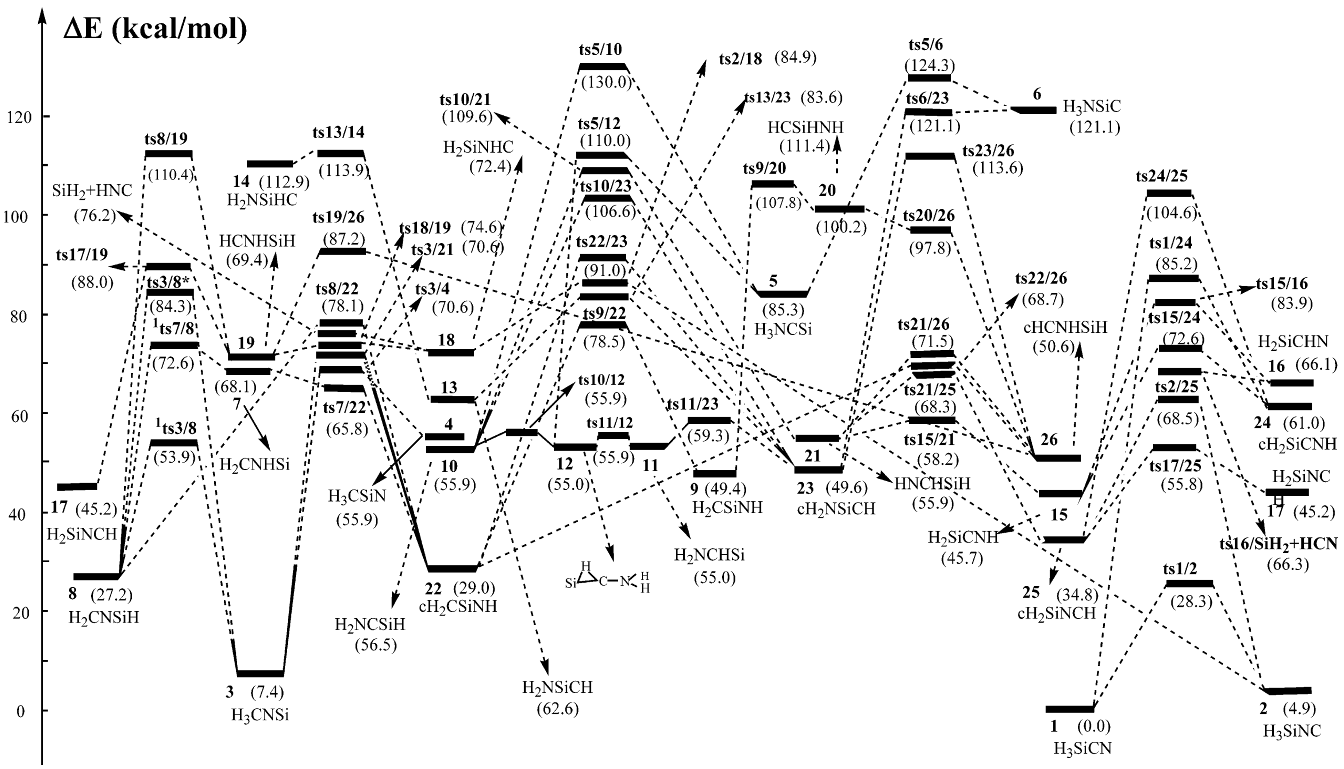
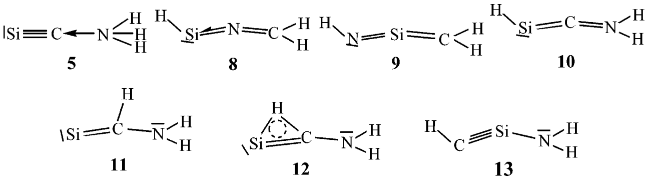
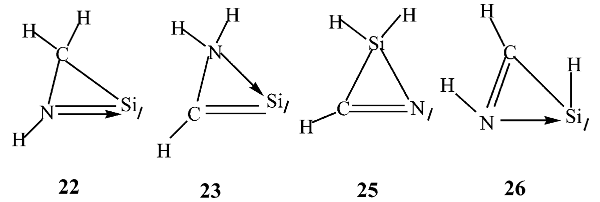


Figure 3. Schematic potential energy surface of singlet [H$_3$,Si,C,N] at the G3//B3LYP/6-31G(d) level.

SCHEME 1

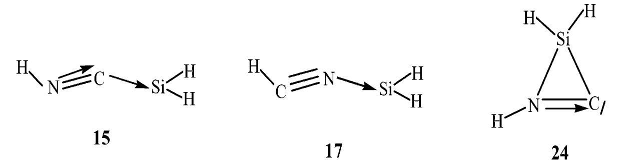


SCHEME 2



8* is an anti-Hammond transition state with SiNC almost linear (∠SiNC = 173.49°), confirmed by IRC calculations. The **ts** structural parameters are closer to those of the low-lying isomer **3** rather than the high-lying **8**. Interestingly, the three isomers H$_2$NCSiH **10**, H$_2$NCHSi **11**, and H$_2$N−*c*-CHSi **12** lie not only energetically very close (within 1.5 kcal/mol) but also can be converted to each other very easily (the barrier is within 1 kcal/mol). Moreover, they can easily rearrange to the cyclic isomer *c*-NH$_2$SiCH **23** with the highest barrier of 4.3 kcal/mol (**11** → **23**). However, despite the easy interconversions among them, the four isomers **10**, **11**, **12**, and **23** are subject to high barriers toward isomerization to other isomers. The lowest-energy transition state related to them is **ts13/23** (83.6), with which the kinetic stabilities of **10**, **11**, **12**, and **23** are deduced to be 27.1, 28.6, 28.6, and 34.0 kcal/mol, respectively. The four species can coexist as floppy isomers. The kinetic stabilities of the forms **22**, **25**, and **26** are as high as 36.8, 21.0, and 18.1 kcal/mol, respectively. The harmonic vibrational frequencies, dipole moments, and rotational constants given in Table 1 can be useful for future experimental characterization or astrophysical detection.

SCHEME 3



3.2.2. Kinetically Metastable Isomers. Three new isomers H$_2$SiCNH **15** (45.7), H$_2$SiNCH **17** (45.2), and *c*-SiH$_2$CNH **24** (61.0) are found to be kinetically metastable. Their respective least conversion barriers are 12.5 (**15** → **21**), 10.6 (**17** → **25**), and 11.6 (**24** → **15**) kcal/mol. Isomers **15** and **17** are adducts of the type HXY → SiH$_2$ (XY=CN or NC) between silylene SiH$_2$ and HNC/HCN via an intermolecular donor (N- or C-lone pair)−acceptor (Si-vacant orbital) interaction. Thus, the newly formed Y−Si bond is as long as 1.8346 Å for **15** and 1.9146 Å for **17**, which is close to and much longer than the Y−Si single bond, respectively. The three-membered-ring isomer **24** contains the carbene and silylene characters, respectively. It contains the intramolecular donor−acceptor interaction between the N-lone pair and the vacant orbital of carbene or silylene.

3.2.3. Kinetically Unstable Isomers. The remaining eight isomers are H$_3$NSiC **6** (121.1), H$_2$CNHSi **7** (68.1), H$_2$NSiHC **14** (112.9), H$_2$SiCHN **16** (66.1), H$_2$SiNHC **18** (72.4), HCNHSiH **19** (69.4), HCSiHNH **20** (100.2), and HNCHSiH **21** (55.9). Their respective least conversion barriers are very small at 0.0 (**6** → **23**), −2.3 (**7** → **22**), 1.0 (**14** → **13**), 0.2 (**16** → SiH$_2$ + HCN), 3.8 (**18** → SiH$_2$ + HNC), 5.2 (**19** → **18**), −2.4 (**20** → **26**), and 2.3 (**21** → **15**) kcal/mol. They could be considered as kinetically unstable. Note that the negative values are a result of the single-point calculations at a different level, indicative of zero or very small conversion barriers.

3.3. Experimental and Astrophysical Implications. In all, eleven new [H$_3$,Si,C,N] isomers are predicted to have very high kinetic stability of more than 20 kcal/mol. They contain SiCN− (**5**, **10**, **11**, **12**), SiNC− (**8**), CSiN− (**9**, **13**), and *c*-SiCN-ring (**22**, **23**, **25**, **26**) skeletons. They are expected to exist under various conditions. The successful generation of isomers **1**, **2**, **3**, and possibly **4** gives strong support to the potential characterization of these new isomers when suitable precursors are selected. Using the Si + HCN reaction, Maier et al. generated and characterized the simplest hydrogenated [H,Si,C,N] isomers (i.e., HCNSi, *c*-SiNCH, HSiNC, and HSiCN with the relative energies 22.3, 6.8, 3.2, and 0.0 kcal/mol at the BLYP/6-311G(d,p) level).[5] Using the gas mixtures of SiH_4 with C_2N_2 or HC_3N, Sanz et. al. successfully obtained microwave spectroscopy of HSiCN and HSiNC.[4] It is reasonable to expect that the reactions Si + H_2CNH, SiC + NH_3, and SiH_2 + HCN can produce various [H_3,Si,C,N] isomers, including the metastable species. The initially formed kinetically stable isomers could be **21** (Si + H_2CNH → **7** → **21**), **5**, **10**, **11**, **12**, **23**, and **13** [SiC + NH_3 → **5** → (**10**,**11**,**12**,**23**) → **13**], and **25** (SiH_2 + HCN → **17** → **25**). Subsequently, the large heat from the reactants can further lead to the three lowest-lying products **1**, **2**, and **3**. However, we must bear in mind that, in the dense interstellar clouds with very low temperature, the high kinetic stability enables the [H_3,Si,C,N] isomers to exist once they are formed. The $SiH_4/C_2N_2(HC_3N)$ reaction system is also a potential source for [H_3,Si,C,N] isomers.

From the viewpoint of basic chemistry, the newly predicted [H_3,Si,C,N] isomers contain various interesting features. It is known that, despite the iso-valence, silicon is reluctant to form multiple-bonded species because of the weak p−p π-overlap, in sharp contrast to carbon. The silicon triple-bonded species are of particular interest. Up to now, very few such species had been experimentally known.[10−12] The species $SiCNH_3$ **5**, H_2N−*c*-CHSi **12**, and H_2NSiCH **13** are such good examples that possess Si≡C triple bonding that has bond distances either shorter or close to the typical Si≡C triple bond value. Note that isomer **12** has a 3*c*−2*e* bond. Also, the isomer $HNSiCH_2$ **9** contains the sp-hybridized cumulenic silicon bonding. The examples are also very rare.[13] Finally, the intermolecular or intramolecular donor−acceptor interaction is popular in all 14 species except **9**−**13** because of the existence of carbene or silylene structures.

4. Conclusions

The detailed Gaussian-3//B3LYP/6-31G(d) calculations are performed on the potential energy surface of [H_3,Si,C,N]. The main results can be summarized as follows:

1. Eleven new kinetically stable isomers $SiCNH_3$ **5**, H_2CNSiH **8**, H_2CSiNH **9**, H_2NCSiH **10**, H_2NCHSi **11**, H_2N−*c*-CHSi **12**, H_2NSiCH **13**, *c*-CH_2SiNH **22**, *c*-NH_2SiCH **23**, *c*-SiH_2NCH **25**, and *c*-SiHCHNH **26** are predicted with the least conversion barriers of 18−37 kcal/mol. Three new kinetically metastable isomers H_2SiCNH **15**, H_2SiNCH **17**, and *c*-SiH_2CNH **24** are predicted with lower conversion barriers of 11−13 kcal/mol.

2. These 14 new species provide good examples of those containing the stable silylene, Si≡C triple-bonded, intra- or intermolecular donor−acceptor bonding, and cumulenic Si-bonding features. These interesting properties may hold for other larger hydrogenated Si,C,N-containing species. In view of the potential importance in Si,C,N-based film coatings and interstellar space, the calculated spectroscopic properties should be helpful for future identification of these [H_3,Si,C,N] isomers in both the laboratory and interstellar space.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20103003), Doctor Foundation of Educational Ministry, and Excellent Young Teacher Foundation of Ministry of Education of China.

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(14) For parallel comparison on the C−N, C−Si, N−Si, C═N, C═Si, N═Si, C≡N, C≡Si, and N≡Si bonding, additional B3LYP/6-31G(d) calculations (with frequency confirmation as stationary points) are carried out for the structures of model systems CH_3NH_2, CH_3SiH_3, NH_2SiH_3, CH_2NH, CH_2SiH_2, $NHSiH_2$, CHN, CHSiH, and NSiH. In the following, the bond length comparisons are made with the above B3LYP/6-31G(d) results.