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Theoretical Study on Structures and Stability of SiC_2S Isomers

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The structures, energetics, spectroscopies, and isomerization of singlet and triplet SiC_2S isomeric species are explored at various levels. At the B3LYP/6-311G(d) level, a total of 29 minimum isomers and 37 interconversion transition states are located. At the higher CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level, the lowest lying isomer is the linear SiCCS ^{1}**1** with a resonance structure mainly between Si═C═C═S and Si≡C−C≡S. In contrast to the C_3S molecule that has no kinetically stable singlet species besides CCCS, SiC_2S has another two kinetically very stable species, i.e., the SiCC three-membered ring with exocyclic SSi bonding ^{1}**5** at 23.2 kcal/mol, and the SiCSC four-membered ring with CC cross bonding ^{1}**7** at 44.3 kcal/mol. Particularly, isomer ^{1}**5** possesses considerable Si≡S and C≡C triple bonding character and can be viewed as a charge-transfer species containing SiS^+ and C_2^-. Isomer ^{1}**7** has a very short CC crossed bond due to the existence of two sets of π-bonding orbital and the weak electron-accepting ability of silicon. The remaining singlet and all the triplet species except triplet SiCCS ^{3}**1** either have much higher energy or much lower kinetic stability and have little chance of existence. The bonding nature and possible formation strategies of ^{1}**1**, ^{1}**5**, and ^{1}**7** are discussed.

1. Introduction

Silicon and sulfur chemistry have received considerable attention from various aspects. One particular interest is their possible role in astrophysical chemistry. Up to now, several silicon- or sulfur-containing molecules, such as SiC_n ($n = 1-4$), SiN, SiO, SiS, PC, and CS have been detected in interstellar space.[1] Larger SiC_n and C_nS species have also been studied both theoretically and experimentally, and were expected to be carriers of some interstellar bands.[2−11] Among these, SiC_2[2,3] and SiC_3[4−6] have unique cyclic ground-state structures. On the other hand, SiC-related clusters play an important role in the science of the semiconducting materials. Minor sulfide species may act as useful impurities to modulate the properties of the SiC materials. The mixed SiC_nS species may present a bridge between the SiC_n and C_nS clusters. Understanding the structural, bonding, and stability properties of SiC_nS clusters may be helpful for future identification of the new Si, C, and S-containing species either in laboratory or in space and also for elucidation of the formation mechanism of the sulfide-doped SiC-materials.

Unfortunately, no theoretical, experimental, and astrophysical studies on the SiC_nS species have been reported despite their importance. In this paper, we choose to study the ternary system SiC_2S. C_3S was predicted[7] to have a singlet linear ground state, which is kinetically the most stable. All the other singlet species are higher in energy and unstable toward conversion to CCCS. For SiC_3,[6,8] the linear triplet CCCSi and singlet C_3Si four-membered ring with CC cross bonding have very close energies, another singlet four-membered ring with SiC cross bonding lies slightly higher in energy. The second-row elements were previously shown to have much less trend to form π-bonding than the first-row elements. When one C-atom of C_3S is replaced by the second-row Si-atom, the contribution of the cyclic forms with more σ-bonds may increase whereas that of the chain forms with more π-bonds may decrease. Naturally, we may raise the following questions for the unknown SiC_2S: (1) Does it have a linear or cyclic ground state? (2) Does the triplet state have significant contribution as in SiC_3 and Si_2C_2? (3) Does it have stable cyclic structures that allow for future laboratory or interstellar observation? In fact, many other Si-containing molecules have stable cyclic isomers (such as SiC_2,[2,3] Si_2C_2,[9] and SiC_2P[10] with the former two having been astrophsically detected or experimentally characterized). (4) Is there any unique bonding features for SiC_2S? These questions are answered in the present article.

2. Computational Methods

All computations are carried out using the GAUSSIAN98[12] and MOLCAS 5.2[13] (for CASSCF and CASPT2) program packages. The optimized geometries and harmonic vibrational frequencies of the local minima and transition states are initially obtained at the B3LYP/6-311G(d) level followed by CCSD(T)/6-311G(2df) single-point calculations using the B3LYP/6-311G(d)-optimized 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. Further, for most relevant species, the structures and frequencies are refined at the QCISD/6-311G(d) level and the energetics at the CCSD(T)/6-311+G(2df) level with inclusion of QCISD/6-311G(d) zero-point vibrational energies (ZPVE). Finally, CASSCF(12,12)/6-311G(2df) structural optimization followed by single-point energy CASPT2/6-311G(2df) calculation is performed for the relevant species for investigation of the multiconfigurational effect. For conciseness, the levels CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE, CCSD(T)/

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TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intersities (km/mol) (in Parentheses), Dipole Moment (Debye), and Rotational Constants (GHz) of Singlet and Triplet SiC$_2$S Structures at the B3LYP/6-311G(d) Level^{b}

species	frequencies (infrared intensity)	dipole moment	rotational constant		
SiCCS ^{1}**1** ($^{1}\Sigma$)	123 (4), 123 (5), 476 (3), 476 (3), 538 (42), 1169 (8), 1937 (1603)	1.7041	1.591561		
SiCCS ^{1}**1**^{a} ($^{1}\Sigma$)	98 (7), 98 (7), 424 (4), 424 (4), 543 (34), 1183 (19), 1920 (1880)	1.4411	1.588884		
SSiCC ^{1}**2** (^{1}A′)	60 (4), 192 (28), 193 (28), 560 (3), 969 (125), 1957 (790)	3.1802			
SSiCC ^{1}**2′** ($^{1}\Sigma$)	55 (3), 55(3), 191(28), 191 (28), 559 (3), 969 (124), 1960 (792)	3.1870			
SiSCC ^{1}**3** (^{1}A′)	56 (0), 184 (1), 207 (3), 508 (30), 794 (9), 1912 (637)	7.4311			
SiCSC ^{1}**4** ($^{1}\Sigma$)	49 (1), 49 (1), 146 (12), 146 (12), 518 (0), 1142 (108), 1355 (328)	2.4671			
S-cSiCC ^{1}**5** (^{1}A$_1$)	191 (30), 200 (20), 405 (25), 561 (2), 958 (268), 1775 (12)	0.5132	51.97895	2.77341	2.63293
S-cSiCC ^{1}**5**^{a} (^{1}A$_1$)	196 (31), 200 (20), 416 (26), 577 (6), 984 (280), 1747 (16)	0.6923	50.91877	2.79823	2.65246
Si-cCCS^{1} **6** (^{1}A′)	76 (1), 263 (1), 498(6), 595 (162), 758 (43), 1443 (190)	3.0025			
cCSCSi ^{1}**7** (^{1}A$_1$)	257 (13), 309 (48), 495 (63), 772(0), 996 (0), 1242 (7)	0.8104	43.40492	3.07305	2.86986
cCSCSi ^{1}**7**^{a} (^{1}A$_1$)	262 (13), 332 (48), 523 (58), 797 (0), 1040 (0), 1204 (9)	0.7400	41.81164	3.13611	2.91729
CCSCSi ^{1}**8** (^{1}A′)	369 (4), 416 (0), 451 (18), 690 (0), 712 (10), 798 (15)	1.8406			
SiCCS ^{3}**1** ($^{3}\Sigma$)	110 (0), 139 (2), 340 (0), 374 (0), 444 (50), 929 (14), 1786 (66)	0.0367			
SSiCC ^{3}**2** (^{3}A′)	107 (23), 154(0), 265(1), 563 (39), 656 (36), 1663 (672)	1.6784			
SiSCC ^{3}**3**	112 (3), 221 (55), 303 (7), 413 (56), 707 (7), 1777 (57)	4.3172			
trans-SiSCC **3′** (^{3}A′)	131 (3), 313 (67), 347 (1), 443 (25), 695 (11), 1656 (378)	3.9099			
SiSCC ^{3}**3″**(^{3}A′)	124 (11), 363 (25), 410 (64), 436 (58), 678 (4), 1640 (457)	3.3378			
Cis-SiSCC ^{3}**3‴** (^{3}A′)	132 (3), 312 (67), 346 (1), 443 (25), 695 (11), 1656 (375)	3.9129			
SiCSC ^{3}**4** (^{3}A′)	116 (2), 203 (13), 352 (28), 469 (7), 830 (48), 1216 (48)	2.8585			
SiCSC ^{3}**4′**	116 (2), 202 (11), 356 (29), 467 (7), 830 (47), 1216 (47)	2.8351			
S-cSiCC ^{3}**5** (^{3}B$_2$)	125 (4), 193 (11), 527 (2), 710 (0), 913 (131), 1443 (8)	1.3410			
S-cSiCC ^{3}**5′** (^{3}A′)	76 (2), 126 (38), 169 (11), 474 (18), 657 (14), 1760 (67)	2.4446			
Si-cCCS ^{3}**6** (^{3}A″)	133 (3), 197 (1), 402 (20), 536 (86), 625 (0), 1461 (164)	1.9163			
Si-cCCS ^{3}**6′**	181 (2), 197 (1), 403 (19), 536 (87), 625(0), 1462 (163)	1.9185			
cCSiCS ^{3}**7** (^{3}A″)	223 (18), 405 (13), 417 (38), 734 (39), 837 (2), 945 (2)	0.8582			
cCSiCS ^{3}**8** (^{3}A″)	355 (28), 357 (0), 471 (13), 552 (1), 586 (5), 708 (7)	1.8000			
SCSiC ^{3}**9** (^{3}A″)	92 (9), 284 (12), 301 (26), 524 (11), 789 (4), 1375 (174)	1.6622			
C-cSiSC ^{3}**10**	89 (10), 134 (12), 319 (4), 550 (14), 706 (31), 843 (19)	1.7244			
S-cCCSi ^{3}**11** (^{3}A′)	237 (7), 335 (6), 455 (1), 758 (28), 842 (9), 1359 (24)	1.6861			
cSiCCS ^{3}**12**	198 (7), 425 (1), 479 (34), 594 (32), 775 (39), 1360 (30)	1.8959			
cSiCCS ^{3}**13** (^{3}A′)	209 (6), 281 (2), 361 (2), 593 (18), 727 (3), 1453 (29)	2.1198			
SiCSC ^{3}**14** (^{3}A′)	177 (4), 311 (5), 402 (5), 452 (146), 738 (0), 877 (8)	0.1497			

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

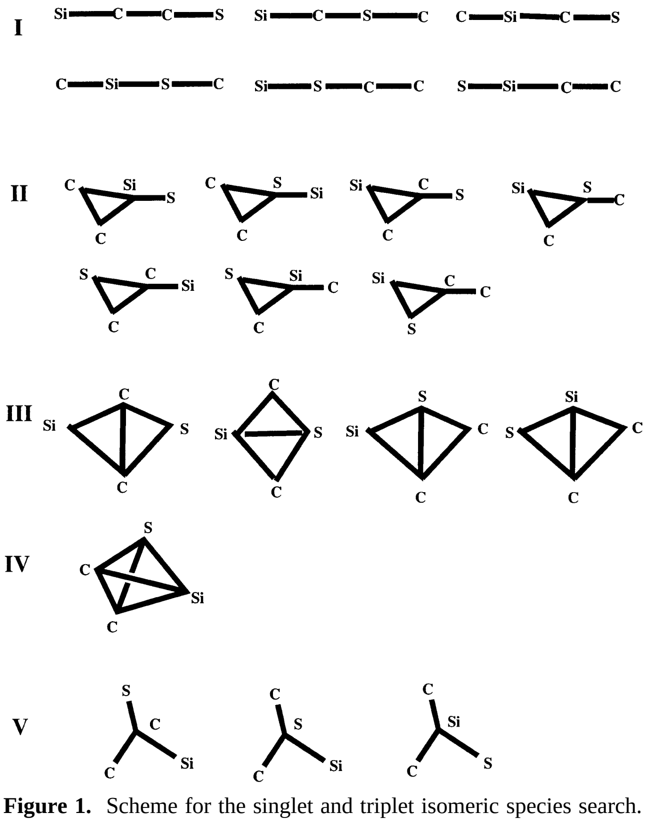


Figure 1. Scheme for the singlet and triplet isomeric species search.

6-311+G(2df)//QCISD/6-311G(d)+ZPVE, and CASPT2/6-311G(2df)//CASSCF(12,12)/6-311G(2df) are simplified by CCSD(T)//B3LYP, CCSD(T)//QCISD, and CASPT2//CASSCF.

3. Results and Discussion

For such a small system, it is desirable to include as many isomeric forms as possible. We initially considered five types of isomers, i.e., linear or chainlike species (I), three-membered ring species (II), four-membered ring species (III), closed species (IV), and branched-chain species (V), as depicted in Figure 1. After numerous searches, a total of 29 SiC$_2$S minimum isomers (9 for singlet and 20 for triplet) (^{s}**m**) and 37 interconversion transition states (11 for singlet and 26 for triplet) (^{s}TS**m**/**n**) are obtained at the B3LYP/6-311G(d) level. Note that the top left corner number *s* means the electronic state (1 for singlet and 3 for triplet) of the isomers or transition states.

The optimized geometries of the singlet SiC$_2$S isomers and transition states are shown in Figure 2, and those of the triplet SiC$_2$S species shown in Figure 3. The spectroscopic properties (harmonic frequencies, infrared intensities, dipole moments and rotational constants) of the SiC$_2$S species are listed in Table 1. The relative energies of all species are collected in Table 2. The schematic singlet and triplet potential-energy surfaces (PESs) of SiC$_2$S are presented in Figure 5 and Figure 6, respectively.

3.1. Singlet SiC$_2$S PES. There are 9 isomers on the singlet PES. Among these, five isomers have linear or chainlike structures, i.e., linear SiCCS ^{1}**1**($^{1}\Sigma$) (0.0), bent SSiCC ^{1}**2** (^{1}A′) (33.9), linear SSiCC ^{1}**2′** ($^{1}\Sigma$) (34.0), bent SiSCC ^{1}**3** (^{1}A′) (81.2), and linear SiCSC ^{1}**4** ($^{1}\Sigma$) (107.9). The values in parentheses are relative energies with reference to isomer ^{1}**1** (0.0) at the CCSD(T)//B3LYP level. The species CSiCS and CSiSC of type

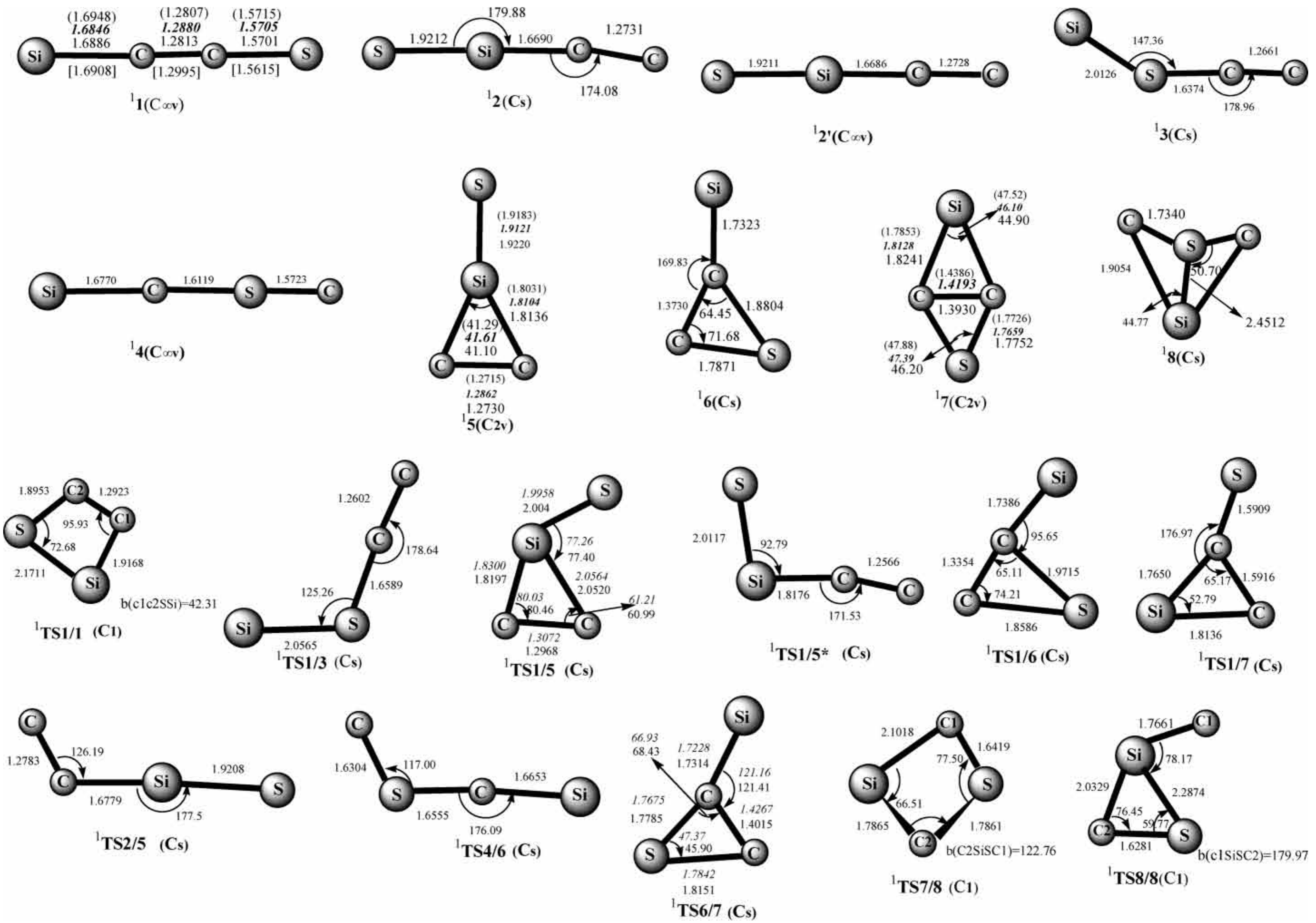
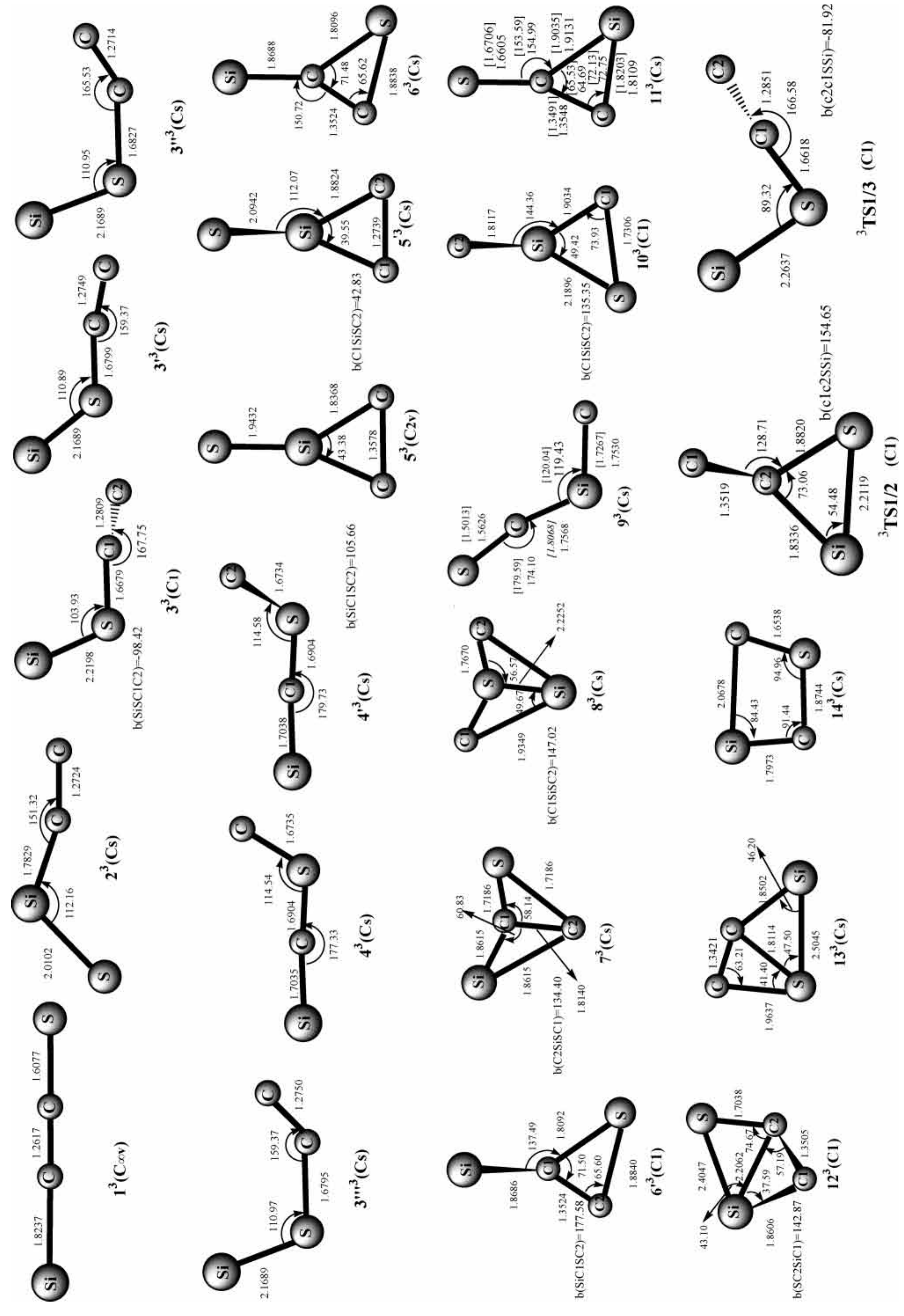
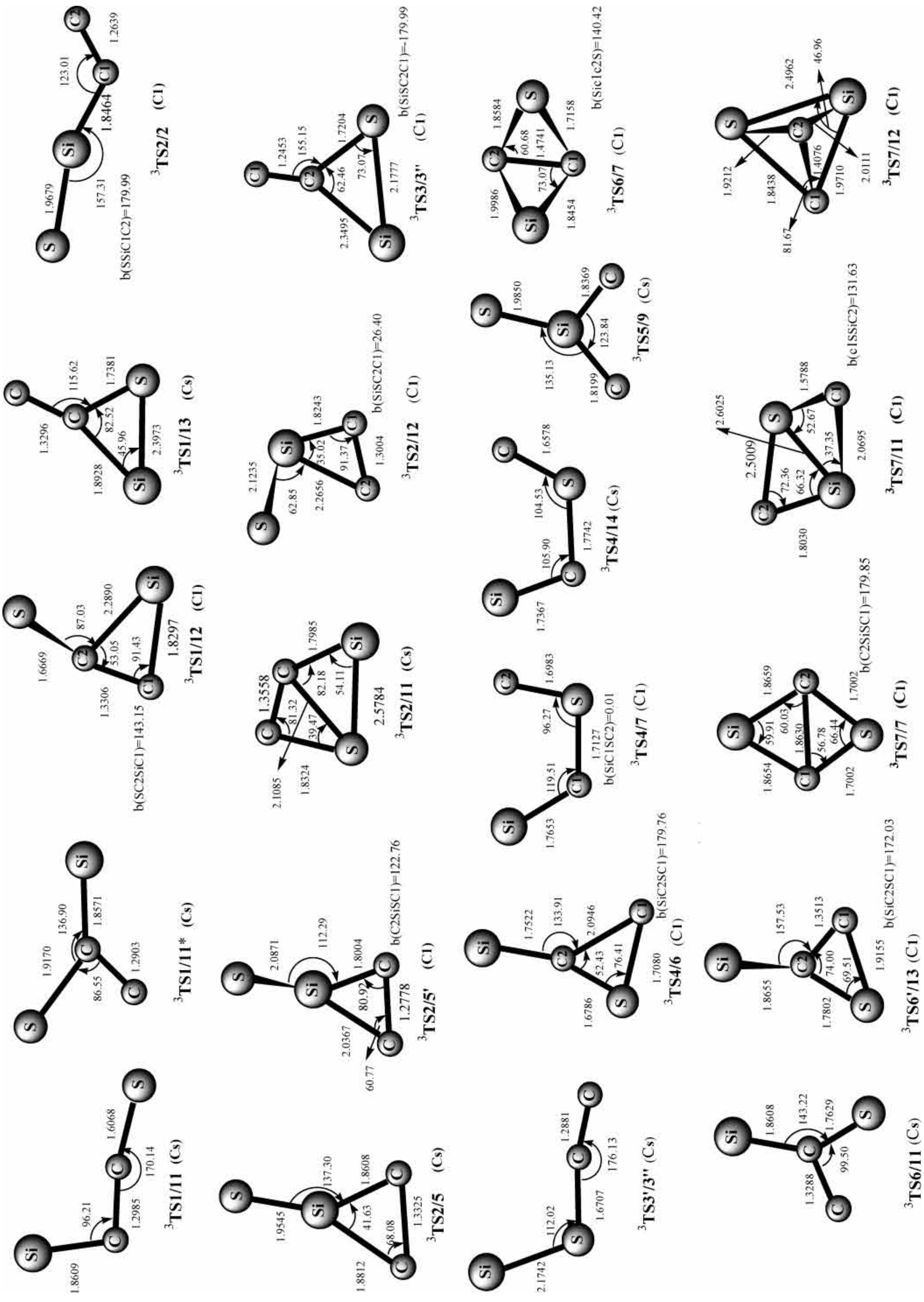


Figure 2. Optimized geometries of singlet SiC_2S isomers and transition states at the B3LYP/6-311G(d) level. The geometrical parameters in italics are at the QCISD/6-311G(d) level, those in parentheses are at the CASSCF(12,12)/6-311g(2df) level, and those in brackets are at the MP2/6-311G(d) level, respectively. Bond lengths are in ångstroms, and angles, in degrees.


1³(C∞v)
2³(Cs)
3³(C1)
b(SiSC1C2)=-98.42
3'³(Cs)
3''³(Cs)
3'''³(Cs)
4³(Cs)
4'³(Cs)
b(SiC1SC2)=105.66
5³(C2v)
5'³(Cs)
b(C1SiSC2)=42.83
6³(Cs)
6'³(C1)
b(SiC1SC2)=177.58
7³(Cs)
b(C2SiSC1)=134.40
8³(Cs)
b(C1SiSC2)=147.02
9³(Cs)
10³(C1)
b(C1SiSC2)=135.35
11³(Cs)
12³(C1)
b(SC2SiC1)=142.87
13³(Cs)
14³(Cs)
³TS1/2 (C1)
b(c1c2SSi)=154.65
³TS1/3 (C1)
b(c2c1SSi)=-81.92


S
Si
C1
C2
1.9679
157.31
1.8464
123.01
1.2639
b(SSiC1C2)=179.99
³TS2/2 (C1)
C
S
Si
1.3296
115.62
1.7381
82.52
45.96
2.3973
1.8928
³TS1/13 (Cs)
S
C2
C1
Si
1.6669
87.03
2.2890
53.05
91.43
1.3306
1.8297
b(SC2SiC1)=143.15
³TS1/12 (C1)
S
C
Si
1.9170
136.90
1.8571
86.55
1.2903
³TS1/11* (Cs)
Si
C
S
1.8609
96.21
1.2985
170.14
1.6068
³TS1/11 (Cs)
C1
C2
S
Si
1.2453
155.15
1.7204
62.46
73.07
2.1777
2.3495
b(SiSC2C1)=-179.99
³TS3/3'' (C1)
S
Si
C1
C2
2.1235
62.85
1.8243
35.02
91.37
2.2656
1.3004
b(SiSC2C1)=26.40
³TS2/12 (C1)
C
Si
S
1.3558
1.7985
81.32
82.18
39.47
54.11
2.1085
1.8324
2.5784
³TS2/11 (Cs)
S
Si
C
2.0871
112.29
1.8004
80.92
2.0367
60.77
1.2778
b(C2SiSC1)=122.76
³TS2/5' (C1)
S
Si
C
1.9545
137.30
1.8608
41.63
68.08
1.3325
1.8812
³TS2/5 (Cs)
C2
C1
S
Si
1.8584
60.68
1.4741
1.7158
73.07
1.9986
1.8454
b(Sic1c2S)=140.42
³TS6/7 (C1)
S
Si
C
1.9850
1.8369
135.13
123.84
1.8199
³TS5/9 (Cs)
C
S
Si
1.6578
104.53
105.90
1.7742
1.7367
³TS4/14 (Cs)
C2
S
C1
Si
1.6983
96.27
119.51
1.7127
1.7653
b(SiC1SC2)=0.01
³TS4/7 (C1)
Si
C2
C1
S
1.7522
133.91
2.0946
52.43
76.41
1.6786
1.7080
b(SiC2SC1)=179.76
³TS4/6 (C1)
Si
S
C
2.1742
112.02
1.6707
1.2881
176.13
³TS3'/3'' (Cs)
S
C2
Si
C1
2.4962
46.96
1.9212
1.8438
1.4076
1.9710
2.0111
81.67
³TS7/12 (C1)
S
C1
Si
C2
2.6025
1.5788
52.67
37.35
2.5009
72.36
66.32
2.0695
1.8030
b(c1SSiC2)=131.63
³TS7/11 (C1)
Si
C2
C1
S
1.8659
60.03
59.91
1.8630
56.78
66.44
1.8654
1.7002
1.7002
b(C2SiSC1)=179.85
³TS7/7 (C1)
Si
C2
C1
S
157.53
1.3513
74.00
69.51
1.8655
1.7802
1.9155
b(SiC2SC1)=172.03
³TS6'/13 (C1)
Si
C
S
1.8608
143.22
1.7629
99.50
1.3288
³TS6/11 (Cs)

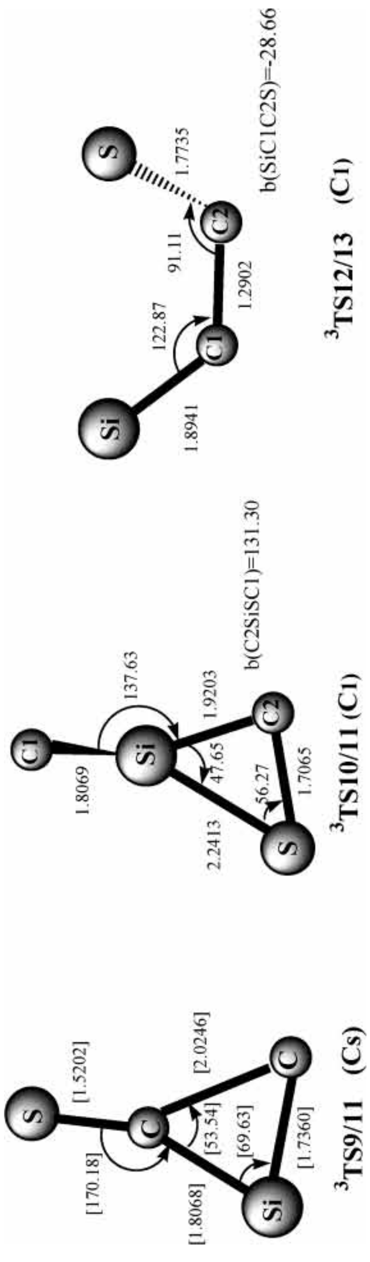


Figure 3. Optimized geometries of triplet SiC$_2$S isomers and transition states at the B3LYP/6-311G(d) level. The geometrical parameters in brackets are at the MP2/6-311G(d) level. Bond lengths are in ångstroms, and angles, in degrees.

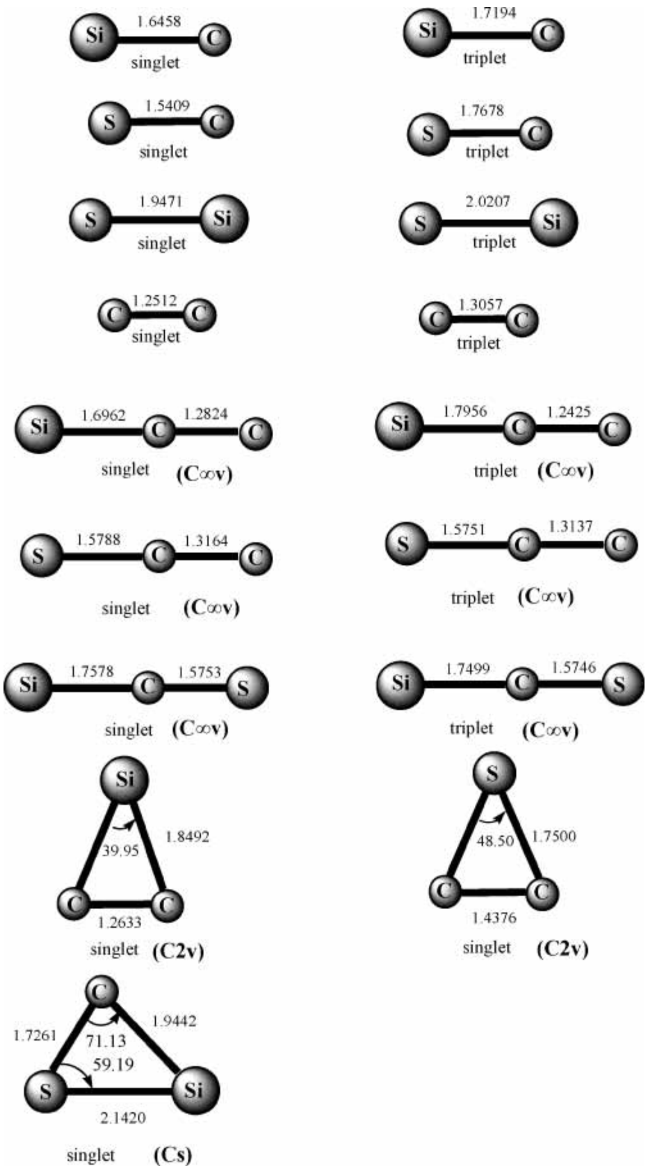


Figure 4. Optimized fragments of the dissociations of SiC$_2$S at the B3LYP/6-311G(d) level. Bond lengths are in ångstroms, and angles, in degrees.

I in Figure 1 are not minima. As will be shown later, the lower energy species ^{1}**2** and ^{1}**2′** are not energy minima at the QCISD/6-311G(d) level. Therefore, the linear or chainlike species with internal −S− or −Si− bonding are of little importance compared to ^{1}**1** with the Si and S atoms at two terminal sites. ^{1}**1** is the global minimum on the SiC$_2$S PES.

Among the postulated three-membered ring species of type II in Figure 1, only S-cSiCC ^{1}**5**($^{1}A_{1}$) and Si-cCCS ^{1}**6**($^{1}A'$) are located as minima. The planar isomer ^{1}**5** (23.0, 23.2, 24.6) contains a SiCC three-membered ring with exocyclic SSi bonding. The second and third values in parentheses are for CCSD(T)//QCISD and CASPT2//CASSCF. The planar isomer ^{1}**6** (63.5) has a CCS three-membered ring with exocyclic SiC bonding. The remaining two species are the SiCSC four-membered ring species cSiCSC ^{1}**7** ($^{1}A_{1}$) (44.1, 44.3, 48.0) with CC cross bonding and cSiCSC ^{1}**8** ($^{1}A'$) (90.0) with SSi cross bonding. The SiCCS four-membered species with SiC cross bonding (as in type III) is only an energy minimum at the HF/6-311G(d) level. The SiCCS four-membered ring species with SC cross bonding (in type III), the closed species (in type IV)

TABLE 2: Total (au) and Relative (kcal/mol) Energies of the Singlet and Triplet SiC_2S Structures and Transition States at B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311g(2df) Levels[a]

species	B3LYP[d]	ΔZPVE B3LYP[d]	CCSD(T)[e] //B3LYP[d]	total 1	QCISD[d]	ΔZPVE QCISD[d]	CCSD(T)[f] //QCISD[d]	total 2	CASPT2//CAS SCF(12,12)[e]
SiCCS ^{1}**1** ($^{1}\Sigma$)[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SSiCC ^{1}**2** ($^{1}A'$)	42.2	−1.3	35.2	33.9					
SSiCC ^{1}**2′** ($^{1}\Sigma$)	42.2	−1.2	35.2	34.0					
SiSCC ^{1}**3** ($^{1}A'$)	89.9	−1.7	82.9	81.2					
SiCSC ^{1}**4** ($^{1}\Sigma$)	120.9	−2.1	110.0	107.9					
S-cSiCC ^{1}**5** ($^{1}A_1$)	35.8	−1.1	24.1	23.0	28.2	−0.8	24.0	23.2	24.6
Si-cCCS ^{1}**6** ($^{1}A'$)	70.7	−1.7	65.2	63.5					
cCSCSi ^{1}**7** ($^{1}A_1$)	54.1	−1.1	45.2	44.1	44.6	−0.8	45.1	44.3	48.0
cCSCSi ^{1}**8** ($^{1}A'$)	112.6	−2.0	92.0	90.0					
^{1}TS1/1	63.0	−1.9	51.5	49.6					
^{1}TS1/3($^{1}A'$)	90.3	−2.0	84.0	82.0					
^{1}TS1/5 ($^{1}A'$)	74.3	−1.7	60.8	59.1	67.6	−1.5	60.3	58.8	
^{1}TS1/5* ($^{1}A'$)	92.2	−2.3	64.8	62.5					
^{1}TS1/6($^{1}A'$)	71.1	−2.0	64.3	62.3					
^{1}TS1/7 ($^{1}A'$)	86.3	−2.2	78.6	76.4					
^{1}TS2/5 ($^{1}A'$)	42.9	−1.3	34.4	33.1					
^{1}TS4/6 ($^{1}A'$)	127.8	−2.5	118.5	116.0					
^{1}TS6/7($^{1}A'$)	72.6	−1.9	66.5	64.6	65.1	−1.6	65.8	64.2	
^{1}TS7/8	117.2	−2.4	99.5	97.1					
^{1}TS8/8	148.8	−2.9	132.4	129.5					
SiCCS ^{3}**1** ($^{3}\Sigma$)	50.6	−1.0	51.2	50.2					
SSiCC ^{3}**2** ($^{3}A'$)	74.5	−2.0	74.0	72.0					
SiSCC ^{3}**3**	95.6	−1.9	92.9	91.0					
trans-SiSCC**3′** ($^{3}A'$)	99.9	−1.8	97.4	95.6					
SiSCC ^{3}**3″** ($^{3}A'$)	99.7	−1.7	97.0	95.3					
Cis-SiSCC **3‴** ($^{3}A'$)	99.9	−1.8	97.4	95.6					
SiCSC ^{3}**4** ($^{3}A'$)	128.6	−2.4	126.1	123.7					
SiCSC ^{3}**4′**	128.6	−2.4	126.1	123.7					
S-cSiCC ^{3}**5** ($^{3}B_2$)	89.6	−1.3	81.1	79.8					
S-cSiCC ^{3}**5′** ($^{3}A'$)	84.5	−2.3	78.8	76.5					
Si-cCCS ^{3}**6** ($^{3}A''$)	89.1	−2.1	85.3	83.2					
Si-cCCS ^{3}**6′**	89.1	−2.1	85.3	83.2					
cCSiCS ^{3}**7** ($^{3}A''$)	98.1	−1.8	87.9	86.1					
cCSiCS ^{3}**8** ($^{3}A''$)	140.4	−2.6	125.3	122.7					
SCSiC ^{3}**9** ($^{3}A''$)	134.0	−2.1	127.4	125.3					
SCSiC ^{3}**9** ($^{3}A''$)[c]	159.8	−0.9	134.3	133.4					
C-cSiSC ^{3}**10**	152.4	−3.1	142.2	139.1					
S-cCCSi ^{3}**11** ($^{3}A'$)	60.3	−1.2	59.6	58.4					
S-cCCSi ^{3}**11** ($^{3}A'$)[c]	66.8	−1.0	59.6	58.6					
cSiCCS ^{3}**12**	75.3	−1.4	69.1	67.7					
cSiCCS ^{3}**13** ($^{3}A'$)	84.1	−1.7	76.3	74.6					
SiCSC ^{3}**14** ($^{3}A'$)	143.1	−2.7	133.4	130.7					
^{3}TS1/2	90.0	−2.7	87.1	84.4					
^{3}TS1/3	97.7	−2.2	94.4	92.2					
^{3}TS1/11 ($^{3}A'$)	68.9	−1.6	69.2	67.6					
^{3}TS1/11* ($^{3}A'$)	115.8	−2.7	114.5	111.8					
^{3}TS1/12	76.2	−1.8	72.0	70.2					
^{3}TS1/13 ($^{3}A'$)	89.7	−2.3	86.5	84.2					
^{3}TS2/2	92.4	−2.1	85.8	83.7					
^{3}TS2/5($^{3}A'$)	90.6	−1.9	83.1	81.2					
^{3}TS2/5′	84.6	−2.4	79.3	76.9					
^{3}TS2/11 ($^{3}A''$)	97.4	−1.5	90.8	89.3					
^{3}TS2/12	87.8	−2.3	81.9	79.6					
^{3}TS3/3″	111.8	−1.0	104.5	103.5					
^{3}TS3′/3″ ($^{3}A'$)	100.6	−2.1	98.4	96.3					
^{3}TS4/6	137.4	−3.0	131.6	128.6					
^{3}TS4/7	138.6	−2.7	132.9	130.2					
^{3}TS4/14 ($^{3}A'$)	145.1	−2.4	137.8	135.4					
^{3}TS5/9 ($^{3}A'$)	190.5	−3.4	185.8	182.4					
^{3}TS6/7	104.7	−2.7	98.2	95.5					
^{3}TS6/11 ($^{3}A''$)	97.4	−2.5	96.7	94.2					
^{3}TS6′/13	90.0	−2.1	86.1	84.0					
^{3}TS7/7	100.1	−2.0	88.9	86.9					
^{3}TS7/11	152.0	−3.4	143.1	139.7					
^{3}TS7/12	114.5	−2.8	105.3	102.5					
^{3}TS9/11[c] ($^{3}A''$)	160.8	−2.4	137.2	134.8					
^{3}TS10/11	152.5	−3.4	142.0	138.6					
^{3}TS12/13	99.2	−2.2	93.4	91.2					

[a] For the relevant species, the values at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) and CASPT2/6-311G(2df)//CASSCF/6-311G(2df) are listed also. The symbols in parentheses of the column denote the point group symmetry. Only the electronic states of the species that are not of C_1 symmetry are given. [b] The total energies of reference isomer ^{1}**1** at the B3LYP/6-311G(d) level is −763.8828863 au, at the MP2/6-311G(d) level is −762.6000231 au, at CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) level is −762.7542372 au, at CCSD(T)/6-311G(2df)//MP2/6-311G(d) level is −762.754096 au, at the QCISD/6-311G(d) level is −762.6161967 au, at the CCSD(T)/6-311+G(2df)/QCISD/6-311G(d) level is −762.758084 au, at the CASPT2(12,12)/6-311G(2df)//CASSCF(12,12)/6-311G(2df) is −763.01503329 au, respectively. The ZPVE at the B3LYP, MP2, and QCISD level are 0.011030, 0.010804, and 0.010686 au, respectively. [c] The values are obtained at MP2/6-311G(d) level. [d] The basis set is 6-311G(d) for B3LYP and QCISD. [e] The basis set is 6-311G(2df) for both the CCSD(T) and CASSCF and CASPT2. [f] The 6-311+G(2df) basis set is used for CCSD(T).

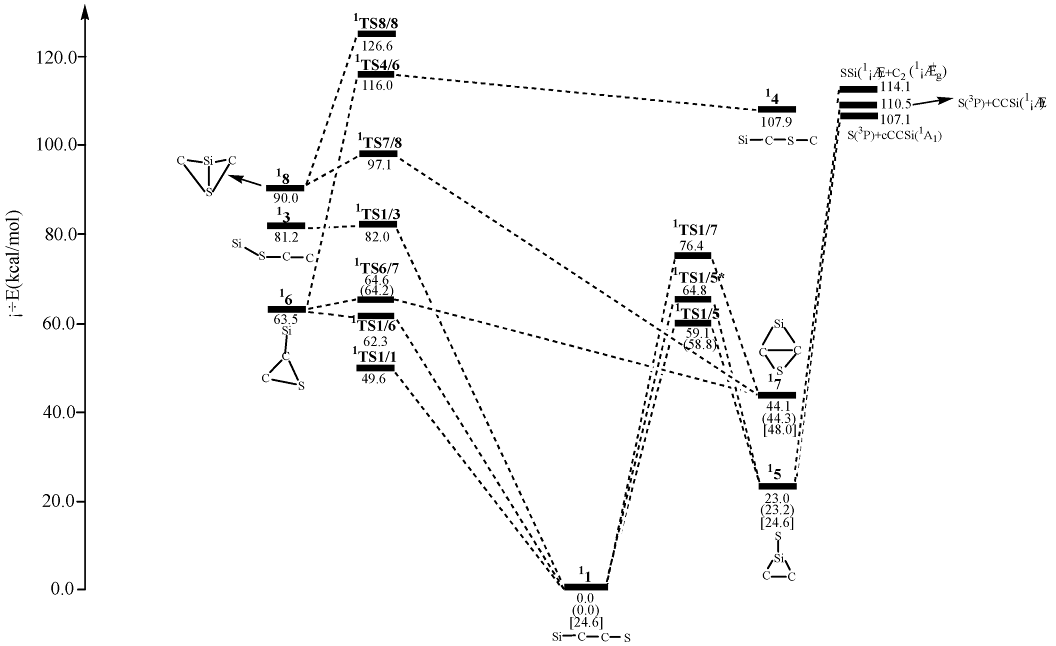


Figure 5. Schematic singlet potential-energy surface of SiC_2S at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE level. The relative energies in parentheses are at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level and the values in brackets are at the CASPT2(12,12)/6-311G(2df)//CASSCF/6-311G(2df) level.

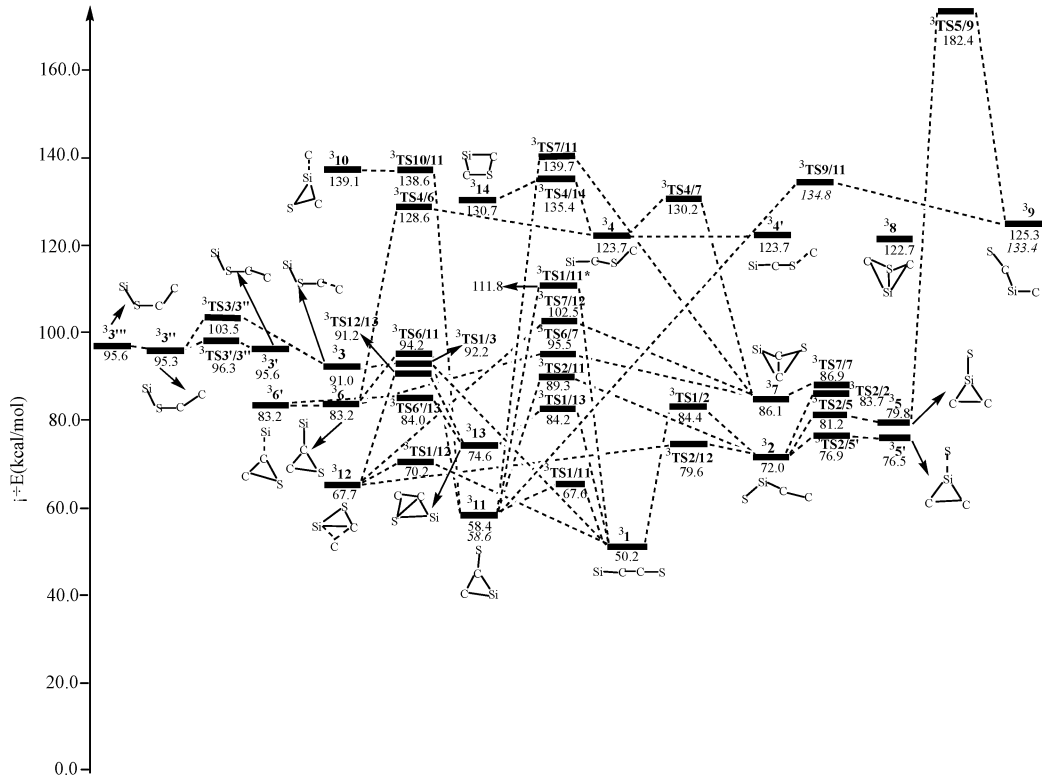


Figure 6. Schematic triplet potential-energy surface of SiC_2S at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE level. The relative energies in italics are at the CCSD(T)/6-311G(2df)//MP2/6-311G(d) level.

and the branched-chain species (in type V) are not minima at any levels.

To discuss the kinetic stability, one needs to consider various isomerization and dissociation pathways. The lowest dissociation or isomerization barrier usually governs the kinetic stability of an isomer. As shown in Table 3, the relative energies of the dissociation products $SiS(^1\Sigma) + C_2(^1\Sigma^+g)$, $SiC(^1\Sigma) + CS(^1\Sigma)$, $C(^3P) + SiCS(^1\Sigma)$, $S(^3P) + SiCC(^1A_1)$, and $Si(^3P) + CCS(^1A_1)$ in both singlet and triplets are rather high (more than 107 kcal/mol at the CCSD(T)//B3LYP level). So the isomerization process determines the kinetic stability of SiC_2S isomers. Because ^{1}**2** and ^{1}**2′** do not exist at the QCISD level and their kinetic stability is almost zero (0.7 and −0.8 kcal/mol at the B3LYP and CCSD(T)//B3LYP levels), the ^{1}**5** → ^{1}**1** conversion governs the kinetic stability of ^{1}**5**. We can see that only the three isomers ^{1}**1**, ^{1}**5**, and ^{1}**7** may be of interest. The linear ^{1}**1**, cyclic ^{1}**5**, and cyclic ^{1}**7** have considerably high kinetic stabilities as 59.1 (^{1}**1** → ^{1}**5**), 36.1 (^{1}**5** → ^{1}**1**), and 20.5 (^{1}**7** → ^{1}**6**) kcal/mol, respectively, at the CCSD(T)//B3LYP level. The respective CCSD(T)//QCISD values are 58.8, 35.6, and 19.9 kcal/mol. Such kinetic stabilities are high enough to allow the existence of the three species ^{1}**1**, ^{1}**5**, and ^{1}**7** under both laboratory and

TABLE 3: Relative (kcal/mol) Energies of Dissociation Fragments of the SiC$_2$S Structures at B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311g(2df) Levels

species	B3LYP^b	ΔZPVE B3LYP^b	CCSD(T)^c //B3LYP^b	total
SiS($^1\Sigma$) + CC($^1\Sigma^+$g)	150.1	−3.2	117.3	114.1
SiC($^1\Sigma$) + SC($^1\Sigma$)	172.3	−3.5	151.8	148.3
S(^{3}P) + CCSi($^1\Sigma$)	115.7	−2.9	113.4	110.5
S(^{3}P) + CCSi(^{1}A$_1$)	117.1	−3.0	110.1	107.1
S(^{3}P) + CCSi($^{3\prime}$)	161.7	−2.7	151.9	149.2
Si(^{3}P) + CCS(^{1}A$_1$)	169.1	−3.1	158.6	155.5
Si(^{3}P) + CCS($^1\Sigma$)	155.9	−2.4	150.3	147.9
C(^{3}P) + SiCS(^{1}A′)	197.6	−4.2	183.6	179.4
C(^{3}P) + SiCS($^1\Sigma$)	185.6	−3.5	178.4	174.9
Si(^{3}P) + CCS($^3\Sigma$)	135.8	−2.5	136.6	134.1
C(^{3}P) + SiCS($^3\Sigma$)	170.1	−3.5	167.7	164.2

[a] The symbols in parentheses of the column denote the point group symmetry. [b] The total energies of reference isomer ^{1}**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. [c] The basis set is 6-311G(d) for B3LYP. [c] The basis set is 6-311G(2df) for CCSD(T).

interstellar conditions. At the CCSD(T)//B3LYP level, the kinetic stabilities of the remaining species are ^{1}**3** (0.8, ^{1}**3** → ^{1}**1**), ^{1}**4** (8.1, ^{1}**4** → ^{1}**6**), ^{1}**6** (−1.2, ^{1}**6** → ^{1}**1**), and ^{1}**8** (7.1, ^{1}**8** → ^{1}**7**) kcal/mol, respectively. Along with their high energy, they may be of little interest as observable species either in laboratory or in space.

3.2. Triplet PES of SiC$_2$S. As shown in Figure 6, the triplet PES SiC$_2$S with 20 isomers and 26 transition states is much more complex than the singlet. Fortunately, the energies of the triplet isomers are energetically very high lying. For example, ^{3}**1** (50.2), ^{3}**5** (79.8), ^{3}**5′** (76.5), and ^{3}**7** (86.1) are higher than ^{1}**1** (0.0), ^{1}**5** (23.0), and ^{1}**7** (44.1) by at least 40 kcal/mol. Moreover, the triplet isomers are kinetically very unstable except for the linear SiCCS ^{3}**1** ($^3\Sigma$) with a barrier 17.4 kcal/mol for ^{3}**1** → ^{3}**11** conversion. Yet, even this value is significantly lower than that 59.1 (^{1}**1** → ^{1}**5**) of the singlet ^{1}**1**. The kinetic stabilities of the triplet ^{3}**5** (1.4, ^{3}**5** → ^{3}**2**), ^{3}**5′** (0.4, ^{3}**5′** → ^{3}**2**), and ^{3}**7** (9.4, ^{3}**7** → ^{3}**6**) are much lower than those of the singlet ^{1}**5** (36.1, ^{1}**5** → ^{1}**1**) and ^{1}**7** (20.5, ^{1}**7** → ^{1}**6**). This indicates that when the singlet SiC$_2$S isomers are electronically excited to the triplet states, their kinetic stabilities are greatly decreased and even become unstable. The corresponding singlet−triplet energy gaps of the linear SiCCS **1**, three-membered ring **5**, and four-membered ring **7** are as large as 50.2, 56.8 (53.5 for ^{1}**5** → ^{3}**5′**) and 42.0 kcal/mol at the CCSD(T)//B3LYP level, respectively. All the triplet SiC$_2$S isomers can be easily converted to ^{3}**1** via direct or indirect pathways. The triplet PES is of minor importance for SiC$_2$S. For simplicity, the structural and isomerization details of the other triplet species are not discussed here.

It should be pointed that at the CCSD(T)//B3LYP level, two transition states, i.e., ^{1}TS**1/6** (62.3) and ^{3}TS**10/11** (138.6), are energetically a little lower than the corresponding isomers ^{1}**6** (63.5) and ^{3}**10** (139.1), as shown in Table 2 and Figures 5 and 6. In principle, a transition state should be the highest energy point between a reactant and a product. This anomaly is caused by the CCSD(T)//B3LYP single-point energy calculations without optimizing the structures at the CCSD(T) level. In fact, at the B3LYP/6-311G(d) level, ^{1}TS**1/6** (71.1) and ^{3}TS**10/11** (152.5) are reasonably higher in energy than ^{1}**6** (70.7) and ^{3}**10** (152.4), which are indicative of the rather high instability of the isomers ^{1}**6** and ^{3}**10**. Such instability is not expected to be changed at higher levels. So we decided not to perform the rather expensive optimization calculations for ^{1}TS**1/6**, ^{3}TS**10/11**, ^{1}**6**, and ^{3}**10** at the CCSD(T) level. The connection of the two transition states is confirmed by IRC calculations.

3.3. Properties and Implications of SiCCS ^{1}1, S-cSiCC ^{1}5, and cSiCSC ^{1}7. Unless specified, the following discussions of the three species are based on the B3LYP level. The dominant electronic configuration of SiCCS ^{1}**1** ($^1\Sigma$) is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^4$. The 1$\pi$ orbital is mainly delocalized over CCS with little on Si, whereas 2π is a delocalized orbital mainly of SiC with little on internal CC. Its SiC bond length (1.6886 Å) is closer to the typical Si═C bond value (1.7071 Å in SiH$_2$CH$_2$) than to the Si≡C bond value (1.6474 Å in SiHCH).[14] The CS bond value (1.5701 Å) lies well between the normal C≡S (1.5409 Å in CS) and C═S (1.6149 Å in SiH$_2$S) ones. The internal CC bond value (1.2813 Å) is between C═C (1.3270 Å in C$_2$H$_4$) and C≡C (1.1981 Å in C$_2$H$_2$). As a result, though structurally SiCCS ^{1}**1**($^1\Sigma$) may be viewed as a cumulene Si═C═C═S, the form Si≡C−C≡S has significant contribution along with certain from Si−C≡C−S. The natural bond orbital (NBO) analysis fails in the structural description of ^{1}**1**. The direct combination between SiC and CS or between Si-atom and C$_2$S may lead to ^{1}**1**.

For the three-membered ring species S-cSiCC ^{1}**5** (^{1}A$_1$), the dominant configuration is $1a_1^2 2a_1^2 3a_1^2 1b_2^2 4a_1^2 1b_1^2 2b_2^2 2b_1^2 5a_1^2$ with three sets of π orbitals 1b$_1$, 2b$_2$, and 2b$_1$. The low-lying 1b$_1$ spreads over the whole molecule with most on the SiC$_2$ ring. The 2b$_2$ orbital is localized within the exocyclic SiS bond with slightly more on S. 2b$_1$ almost completely resides within the CC bond. Thus, ^{1}**5** can be considered as having Si≡S and C≡C triple bonding. NBO supports this description. Actually, the SSi (1.9220 Å) and CC (1.2730 Å) bonds are shorter than the typical S═Si (1.9557 Å in SiH$_2$S) and C═C (1.3270 Å in C$_2$H$_4$) double bonds, respectively. Interestingly, the SSi and CC bond values of ^{1}**5** are closer to those of the doublet SiS$^+$ (1.9265 Å) and C$_2^-$ (1.2597 Å) than to those of the singlet SiS (1.9471 Å) and C$_2$ (1.2512 Å). The natural charge distributions in ^{1}**5** are −0.4901 (Si), +1.2652 (S), −0.3875 (C), and −0.3875 (C). Isomer ^{1}**5** can be thought of as a charge-transfer species comprising SiS$^+$ and C$_2^-$. Compared to the normal Si−C single (1.8852 Å in SiH$_3$CH$_3$) and Si═C double (1.7071 Å in SiH$_2$CH$_2$) bonds, the shortened peripheral SiC bond (1.8136 Å) of ^{1}**5** is a result of the delocalized 1b$_1$ π-bonding orbital. In interstellar space, isomer ^{1}**5** may be formed via the perpendicular addition between the singlet SiS and C$_2$. Notice that the similar structure S-cC$_3$ in C$_3$S is not a minimum. Instead, it is a transition state associated with the interexchange of the two terminal C-atoms in the linear CCCS.

One point worthy of note is that multiply bonding between the second-row elements is usually not preferred both thermodynamically and kinetically. In interstellar space, even the species containing single Si−S bonding is very rare. Up to now, only the simplest diatomic SiS has been detected, which also contains Si≡S triple bonding. The isomer S-cSiCC ^{1}**5** (^{1}A$_1$) may provide a new more "complex" example with SiS multiple bonding.

The four-membered ring isomer ^{1}**7** has an electronic configuration $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2 5a_1^2 2b_1^2$. π-orbital 1b$_1$ is delocalized over the whole molecule with the major part on the C$_2$S ring. π-orbital 2b$_1$ simply spreads over the SiC$_2$ ring. Consequently, the peripheral SiC (1.8241 Å) and CS (1.7752 Å) bonds are between the single (1.8852 Å for Si−C in SiH$_3$CH$_3$ and 1.8354 Å for C−S in CH$_3$SH) and double (1.7071 Å for Si═C in SiH$_2$CH$_2$ and 1.6149 Å for C═S in CH$_2$S) bonds. Moreover, the bridged CC bond (1.3930 Å) contains significant double-bonding character as in C$_6$H$_6$ (C−C bond value is 1.3940 Å) compared to the normal C═C (1.3270 Å in C$_2$H$_4$) and C−C (1.5303 Å in C$_2$H$_6$) bonds. The two sets of π-bonding orbitals (4 π-electrons) result in the much shorter CC cross bond (1.3930

Å) in ^{1}**7** than those in the similar rhombic structures for SiC_3 (1.483 Å)[5] and Si_2C_2 (1.432 Å)[9b] with one π orbital (2 π electrons) and SiC_2N (1.479 Å)[15] and SiC_2P (1.426 Å)[10] with one π orbital and one π electron (3 π electrons). The similar structure cCCSC in the isoelectronic C_3S is kinetically unstable toward conversion to linear CCCS.[7] Interestingly, the CC crossed bond in ^{1}**7** is also considerably shorter than that in cCCSC (1.470 Å). This can be ascribed to the much stronger electron-accepting ability of carbon than silicon. In C_3S, one π-bonding is greatly delocalized along the two peripheral CC bonds (1.417 Å).

At the QCISD/6-311G(d) level, the dipole moments of ^{1}**5** and ^{1}**7** are very small as 0.6923 and 0.7400 D. Only ^{1}**1** has a reasonable value as 1.4411 D. It seems that their microwave detection is difficult. Yet, they can be identified by their infrared spectrum. ^{1}**1** and ^{1}**5** have very acute bands at 1920 (associated with the breathing vibration of the internal CC bond) and 984 cm^{-1} (associated with the breathing vibration of the exocyclic SSi bond) with the corresponding infrared intensities 1880 and 280 km/mol. Isomer ^{1}**7** has two neighboring low-frequency bands at 332 and 523 cm^{-1} with comparable intensities 48 and 58 km/mol, respectively. Both bands are associated with the in-plane vibration. The former corresponds to the left-right movement of the CC bond (with reference to the structure of ^{1}**7** in Figure 1). The latter corresponds to the breathing vibration of the SiS bond (because there is no bonding between Si and S within ^{1}**7**, the term "bond" is used here just for clarity).

It is worth mentioning that the geometrical parameters and spectroscopic properties of the species ^{1}**1**, ^{1}**5**, ^{1}**7**, ^{1}TS**1/5**, and ^{1}TS**6/7** at the B3LYP/6-311G(d) level are in good agreement with those at the QCISD/6-311G(d) level (in Figure 2, and Table 1). The respective relative energies at the CCSD(T)//B3LYP level are rather close to those at the CCSD(T)//QCISD levels (in Table 2). Moreover, the CASPT2//CASSCF relative energies and structures of ^{1}**1**, ^{1}**5**, and ^{1}**7** are very close to the CCSD(T)//B3LYP and CCSD(T)//QCISD values, and at the CASSCF level, the leading electronic configurations occupied by ^{1}**1**, ^{1}**5**, and ^{1}**7** are 85.74%, 87.79%, and 90.05%, respectively, are the same as corresponding to that spanned the Slater Determinant of B3LYP. This indicates that the SiC_2S system has negligible multiconfigurational effect, and the CCSD(T)//B3LYP method is adequate for calculation of the structures, spectrocopies and energies.

4. Conclusions

The detailed singlet and triplet potential energy surface study on the new SiC_2S molecule leads to the following conclusions:

1. Among the total 29 minimum isomers, only the three low-lying singlet species SiCCS ^{1}**1** ($^1\Sigma$), S-cSiCC ^{1}**5**($^1A_1$), and cSiCSC ^{1}**7** ($^1A_1$) are of interest. High-level CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE calculations predict ^{1}**1** as the ground state followed by ^{1}**5** and ^{1}**7** lying 23.2 and 43.3 kcal/mol higher, respectively. The lowest conversion or dissociation barriers of ^{1}**1**, ^{1}**5**, and ^{1}**7** are 59.1, 36.1, and 20.5 kcal/mol, respectively, which are considerably high to guarantee their laboratory and interstellar existence.

2. The valence structure of isomer ^{1}**1** resonates between the cumulenic double bonding $Si{=}C{=}C{=}S$ and the conjugative triplet bonding $Si{\equiv}C{-}C{\equiv}S$. The form $Si{-}C{\equiv}C{-}S$ has a slight contribution. For the three-membered ring ^{1}**5**, there exists considerable triple $Si{\equiv}S$ and $C{\equiv}C$ triple-bonding character. ^{1}**5** can formally be viewed as a charge-transfer molecule comprising SiS^+ and C_2^- groups. The four-membered ring ^{1}**7** has two sets of π-bonding orbital which result in a much shorter CC crossed bond than in other molecules.

3. Though for C_3S, no other singlet species are kinetically stable, replacement of one C-atom by the second-row Si-atom truly introduces two very stable cyclic forms ^{1}**5** and ^{1}**7** in addition to the linear ^{1}**1**. This again reinforces the importance of heteroatomic doping in cluster chemistry.

The present study is expected to provide a useful basis for future laboratory and interstellar identification of the three SiC_2S isomers.

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(14) The comparative bond lengths of C_2H_2, C_2H_4, C_2H_6, C_6H_6, SiHCH, SiH_2CH_2, SiH_3CH_3, $CH_2{=}S$, CH_3SH, SiH_2S, SiC_3, C_3S, Si_2C_2, SiS^+, and C_2^- are calculated at the B3LYP/6-311G(d) and B3LYP/6-311G(d,p) (for H-containing species) levels.

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