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Silacyclopropenylidene and Its Most Important SiC₂H₂ Isomers[†]

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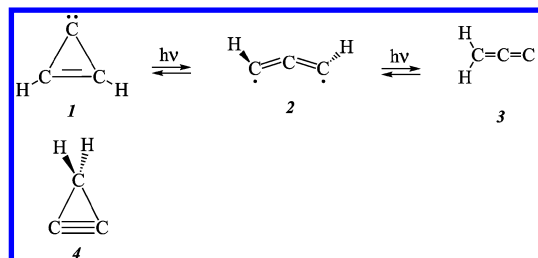
In pioneering matrix isolation experiments, Maier and Reisenauer reported and identified infrared spectra for 1-silacyclopropenylidene and three of its isomers. These experiments were followed by microwave spectroscopy identification of two of the structures. Seven low-lying isomers of SiC₂H₂ are systematically investigated here using ab initio restricted Hartree–Fock (RHF), coupled cluster with single and double excitations (CCSD), and CCSD with perturbative triple excitations [CCSD(T)] methods and the correlation-consistent polarized valence cc-pVXZ/cc-pV(X+d)Z (X = D, T, and Q) basis sets. Full valence complete active space self-consistent field (CASSCF) wave functions are used for interpretation. All levels of theory employed in this study confirm the global minimum of the SiC₂H₂ potential energy surface (PES) to be 1-silacyclopropenylidene (**1S**). Among the seven singlet stationary points, six isomers are found to be minima, whereas one structure (**6S**) is a second-order saddle point. For the lowest-lying six singlet minima, with our highest level of theory, cc-pVQZ(C,H)/cc-pV(Q+d)Z(Si) CCSD(T), the relative energies (in kcal mol^{−1}, with the zero-point vibrational-energy-corrected values in parentheses) are predicted to be 1-silacyclopropenylidene (**1S**) [0.0 (0.0)] < vinylidenesilanediyli (**3S**) [18.2 (17.6)] < ethynylsilanediyli (**2S**) [21.9 (18.6)] < ethynylsilylene (**7S**) [42.1 (38.7)] < silacyclopropyne (**4S**) [49.9 (46.1)] < silavinylidenecarbene (**5S**) [56.7 (52.1)]. Theoretically determined harmonic vibrational frequencies and associated infrared (IR) intensities for four isomers (**1S**–**4S**) are in good agreement with available experimental observations.

1. Introduction

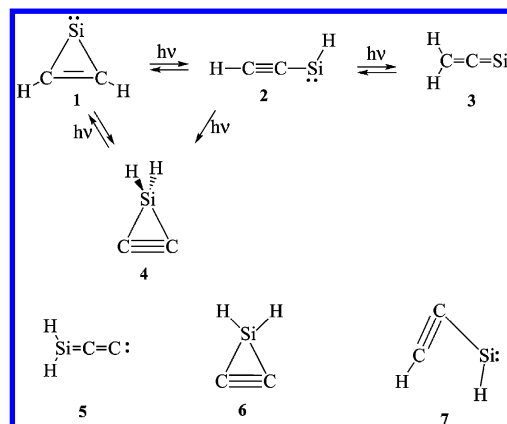
The singlet state of cyclopropenylidene (**1S**) is known to be the global minimum on the C₃H₂ potential energy surfaces (PESs). Isomer **1S** is abundant in molecular clouds of interstellar space and plays an important role in the chemistry of the interstellar medium. The first laboratory detection of **1S** was achieved by Reisenauer, Maier, Riemann, and Hoffmann in 1984.¹ This was enabled by the ab initio prediction of its vibrational frequencies and infrared (IR) intensities provided by Lee, Bunge, and Schaefer.² Shortly thereafter, Reisenauer and Maier were able to show that upon irradiation, **1S** is photoisomerized into propynylidene (propargylene, **2T**) and in a second photostep into propadienylidene (vinylidenecarbene, **3S**), as presented in Scheme 1.^{3,4} **1S** and **3S** have also been detected in interstellar space,^{5,6} where **1S** appears to be the most abundant of all hydrocarbons.

Maier and Reisenauer achieved another breakthrough in their research on the corresponding silicon-containing derivatives. In 1994 and 1995, they reported matrix spectroscopic identification of four SiC₂H₂ molecules.^{7–9} The global minimum of the SiC₂H₂ molecules was shown to be 1-silacyclopropenylidene (**1S**).¹⁰ **1S** has been generated by pulsed flash pyrolysis of 2-ethynyl-1,1,1-trimethyldisilane. By subsequent photolysis, **1S** can be isomerized into ethynylsilanediyli (**2S**), vinylidenesilanediyli (**3S**), and silacyclopropyne (**4S**), as shown in Scheme 2. The identification

SCHEME 1: For C₃H₂



SCHEME 2: For SiC₂H₂



of the SiC₂H₂ isomers and their ¹³C and D isotopologues was based on the comparison of their experimental and theoretical infrared (IR) spectra.^{7–12} Maier et al. also reported that isomer

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1S is the primary product after co-deposition of atomic silicon and acetylene in an argon matrix. They deduced that addition of the silicon atom to the π -system is preferred to the formation of insertion products.⁹ In 1994, Izuha, Yamamoto, and Saito reported the rotational spectra of isomer **1S** and its isotopologues in the frequency region of 220–400 GHz using a source-modulated microwave spectrometer.¹³ From the observed rotational constants, the r_s structure was determined: $r_s(\text{C}=\text{C}) = 1.3458 \text{ \AA}$, $r_s(\text{Si}-\text{C}) = 1.8200 \text{ \AA}$, $r_s(\text{C}-\text{H}) = 1.0795 \text{ \AA}$, and $\theta_s(\text{CCH}) = 135.16^\circ$. In another important experiment, the microwave rotational spectrum of singlet vinylidenesilanediyl (**3S**) was observed in a pulsed supersonic molecular beam by Fourier transform microwave spectroscopy by McCarthy and Thaddeus in 2001.¹⁴ An experimental r_0 structure was determined for **3S** by isotopic substitution: $r_0(\text{C}=\text{C}) = 1.321 \text{ \AA}$, $r_0(\text{Si}-\text{C}) = 1.703 \text{ \AA}$, $r_0(\text{C}-\text{H}) = 1.099 \text{ \AA}$, and $\theta_0(\text{HCH}) = 117.3^\circ$.

There have been several theoretical^{7–12,15–26} studies of the SiC_2H_2 molecular systems. In 1986, Frenking, Remington, and Schaefer investigated the molecular structures and relative energies of 15 different isomers of SiC_2H_2 molecules on the closed-shell singlet PES.¹⁰ They located eight equilibrium structures, the 1-silacyclopropenyldiene (**1S**) lying lowest in energy on the singlet PES. The three lowest-lying isomers were determined to be 1-silacyclopropenyldiene (**1S**, 0), vinylidenesilanediyl (**3S**, 17), and ethynylsilanediyl (**2S**, 22 kcal mol^{−1}) at the DZ+P CISD (configuration interaction with single and double excitations) level of theory. Five years later, Vacek and Colegrove reported an improved theoretical study on the **1S** isomer (global minimum) at the TZ+2P CISD and DZ+P CCSD (coupled cluster with singles and doubles) levels of theory.¹² After Maier et al.^{7–9} synthesized the four isomers (**1S**–**4S**) of SiC_2H_2 , Sherrill, Brandow, Allen, and Schaefer²¹ theoretically reinvestigated the singlet and triplet states of the three C_3H_2 isomers (**1**, **3**, and **4**) and three SiC_2H_2 isomers (**1**, **4**, and **5**) using coupled cluster theory with a triple ζ quality basis set. The relative energies [with zero-point vibrational energy (ZPVE) corrections] of SiC_2H_2 isomers at the TZ(2df, 2pd) CCSD(T) level of theory were predicted to be **1S** (0.0), **4S** (47.4), and **5S** (52.9) kcal mol^{−1}. Recently, Ikuta, Saitoh, and Wakamatsu²² studied the geometric structures and isomeric stabilities of various stationary points of SiC_2H_2 neutral and its cation and anion, also using coupled cluster theory. They located six neutral SiC_2H_2 isomers (**1S**–**5S**, and **7S**) at the cc-pVTZ CCSD(T) level of theory and refined the relative energies with aug-cc-pVTZ CCSD(T) single-point energies.

In this research, we focus on the singlet electronic states of the SiC_2H_2 structures. A total of seven singlet-state isomers (shown in Scheme 2) will be located and characterized employing high-level ab initio methodology. This is demonstrably the most systematic and reliable study on the low-lying isomers of the SiC_2H_2 molecules to date.

2. Electronic Structure Considerations

Among the various electronic states of SiC_2H_2 isomers, the global minimum has been known¹⁰ since 1986 to be the singlet state of 1-silacyclopropenyldiene (**1S**). The electronic ground state of **1S** has been theoretically and experimentally found to be the 1A_1 state with the electron configuration

$$[\text{core}]5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 4b_2^2 8a_1^2 \quad \tilde{X}^1A_1 \quad (1)$$

where [core] ($=1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2$ for the \tilde{X} state) denotes the seven lowest-lying core (Si: 1s, 2s, 2p-like and C:

1s-like) orbitals. The electron configurations of the other six isomers are described as follows

Ethynylsilanediyl (ethynylsilylene **2S**):

$$[\text{core}]7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 2a''^2 12a'^2 \quad ^1A' \quad (2)$$

Vinylidenesilanediyl (vinylidenesilylene **3S**):

$$[\text{core}]6a_1^2 7a_1^2 8a_1^2 2b_2^2 9a_1^2 2b_1^2 3b_2^2 \quad ^1A_1 \quad (3)$$

Silacyclopropyne (**4S**):

$$[\text{core}]5a_1^2 6a_1^2 3b_2^2 2b_1^2 7a_1^2 3b_1^2 8a_1^2 \quad ^1A_1 \quad (4)$$

Silavinylidenecarbene (**5S**):

$$[\text{core}]6a_1^2 7a_1^2 8a_1^2 2b_2^2 9a_1^2 2b_1^2 3b_2^2 \quad ^1A_1 \quad (5)$$

Planar silacyclopropyne (**6S**):

$$[\text{core}]5a_1^2 6a_1^2 3b_2^2 7a_1^2 4b_2^2 2b_1^2 8a_1^2 \quad ^1A_1 \quad (6)$$

Ethynylsilylene (**7S**):

$$[\text{core}]7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a'^2 \quad ^1A' \quad (7)$$

3. Theoretical Procedures

In this research, the correlation-consistent polarized valence cc-pVXZ (C, H, Si) and cc-pV(X+d)Z (Si) (where X = D, T, and Q) basis sets developed by Dunning and co-workers^{27–29} were utilized. The cc-pV(X+d)Z basis sets were formed by augmenting a high-exponent d function to the (2d) sets and by replacing the (3d) set by the (4d) set for the second-row atoms,²⁹ which has been shown to yield an improved description of main group elements.

Zeroth-order descriptions of all stationary points were obtained by using restricted Hartree–Fock (RHF) self-consistent field (SCF) theory. Dynamic correlation effects were included using coupled cluster with single and double excitations (CCSD)^{30,31} and CCSD with perturbative triple excitations [CCSD(T)] methods.^{32,33} The correlated wave functions were constructed by freezing the seven lowest-lying core (Si: 1s, 2s, 2p-like and C: 1s-like) orbitals. In order to ascertain the nature of the wave functions, full valence complete active space SCF (CASSCF) wave functions^{34–36} with 14 electrons in 14 molecular orbitals (14e/14MO) were constructed at the seven different cc-pV(Q+d)Z CCSD(T) optimized structures.

The structures of the stationary points were optimized using analytic derivative methods.^{37–39} Dipole moments, harmonic vibrational frequencies, and corresponding IR intensities were determined analytically.^{40,41} Electronic structure computations were carried out using the ACESII (Mainz–Austin–Budapest version),^{42,43} MOLPRO,⁴⁴ PSI2,⁴⁵ and PSI3⁴⁶ suites of quantum chemistry packages.

4. Results and Discussion

The optimized geometries for the seven SiC_2H_2 isomers are depicted in Figures 1–7, while the predicted total energies and physical properties are presented in Tables 1–7. The relative energies of the seven SiC_2H_2 isomers are compared in Table 8.

4.1. CASSCF Wave Functions. The cc-pV(Q+d)Z CASSCF wave functions at the cc-pV(Q+d)Z CCSD(T) optimized geometries are described in terms of CASSCF natural orbitals

TABLE 1: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm⁻¹), Infrared Intensities (in parentheses in km mol⁻¹), and Zero-Point Vibrational Energy (ZPVE in kcal mol⁻¹) for the \tilde{X}^1A_1 State of the 1-Silacyclopropenylidene (1S) Molecule

level of theory	energy	μ_e	$\omega_1(a_1)$ CH s-str	$\omega_2(a_1)$ C—C str	$\omega_3(a_1)$ CCH s-bend	$\omega_4(a_1)$ Si—C s-str	$\omega_5(a_2)$ CCH oop	$\omega_6(b_1)$ CCH oop	$\omega_7(b_2)$ CH a-str	$\omega_8(b_2)$ CCH a-bend	$\omega_9(b_2)$ Si—C a-str	ZPVE
cc-pVDZ RHF	-365.750 122	1.149	3362(4.4)	1582(0.0)	967(5.9)	825(59.7)	1091(0.0)	757(69.0)	3337(7.0)	1223(61.3)	708(44.0)	19.80
cc-pV(D+d)Z RHF	-365.756 197	1.164	3364(4.2)	1581(0.1)	968(9.0)	835(59.5)	1096(0.0)	762(67.5)	3339(7.1)	1227(59.2)	719(42.3)	19.86
cc-pVTZ RHF	-365.784 582	1.171	3349(5.1)	1565(0.1)	981(6.8)	840(61.4)	1110(0.0)	767(73.4)	3324(8.0)	1241(56.6)	730(47.2)	19.88
cc-pV(T+d)Z RHF	-365.787 098	1.179	3349(5.0)	1564(0.0)	982(7.8)	841(62.2)	1112(0.0)	769(72.6)	3325(8.0)	1242(56.0)	733(46.4)	19.90
cc-pVQZ RHF	-365.793 206	1.195	3349(4.9)	1563(0.1)	982(7.2)	841(64.5)	1113(0.0)	769(73.2)	3326(7.2)	1243(54.7)	734(47.6)	19.90
cc-pV(Q+d)Z RHF	-365.794 497	1.198	3349(4.9)	1562(0.0)	981(7.8)	842(64.9)	1113(0.0)	770(72.8)	3326(7.2)	1244(54.3)	735(47.2)	19.91
cc-pVDZ CCSD	-366.110 911	0.958	3227(5.5)	1499(0.9)	901(2.5)	764(39.6)	989(0.0)	681(57.7)	3202(7.6)	1139(49.8)	657(41.6)	18.64
cc-pV(D+d)Z CCSD	-366.117 030	0.957	3228(5.4)	1497(0.4)	901(4.1)	774(39.3)	994(0.0)	685(56.8)	3204(7.7)	1124(47.5)	668(40.7)	18.69
cc-pVTZ CCSD	-366.209 542	0.991	3234(4.0)	1496(1.2)	911(3.3)	787(41.3)	1012(0.0)	698(62.5)	3210(6.2)	1137(45.9)	691(46.5)	18.84
cc-pV(T+d)Z CCSD	-366.211 952	0.993	3234(4.0)	1495(0.9)	912(3.9)	790(41.8)	1015(0.0)	700(62.0)	3210(6.2)	1139(45.1)	695(46.0)	18.86
cc-pVQZ CCSD	-366.238 601	1.010	3235(3.6)	1499(1.1)	910(4.3)	795(43.9)	1017(0.0)	701(61.6)	3212(5.3)	1140(43.5)	698(48.1)	18.88
cc-pV(Q+d)Z CCSD	-366.239 926	1.011	3235(3.6)	1499(1.0)	909(4.7)	796(44.1)	1018(0.0)	702(61.3)	3213(5.3)	1141(43.1)	699(47.8)	18.89
cc-pVDZ CCSD(T)	-366.127 433	0.997	3200(7.1)	1469(0.7)	891(2.0)	746(34.0)	969(0.0)	666(55.8)	3176(9.4)	1098(49.6)	642(40.5)	18.38
cc-pV(D+d)Z CCSD(T)	-366.133 471	0.996	3202(6.9)	1467(0.3)	891(3.3)	756(33.7)	974(0.0)	671(55.0)	3178(9.4)	1104(47.2)	652(39.7)	18.43
cc-pVTZ CCSD(T)	-366.232 910	1.030	3206(4.9)	1465(1.2)	898(2.6)	768(35.0)	990(0.0)	683(60.3)	3182(7.0)	1113(45.5)	676(45.2)	18.56
cc-pV(T+d)Z CCSD(T)	-366.235 259	1.030	3207(4.8)	1464(0.9)	898(3.1)	771(35.5)	992(0.0)	685(59.8)	3183(7.1)	1115(44.7)	680(44.8)	18.58
cc-pVQZ CCSD(T)	-366.263 764	1.043	3206(4.3)	1468(1.1)	895(3.4)	775(37.5)	994(0.0)	686(59.4)	3184(6.0)	1114(42.9)	682(47.1)	18.59
cc-pV(Q+d)Z CCSD(T)	-366.265 062	1.043	3206(4.3)	1467(1.0)	895(3.8)	777(37.6)	994(0.0)	687(59.1)	3184(6.0)	1116(42.5)	684(46.8)	18.60
expt. (refs 7 and 8)			3048.7(10)		875.3(26)	761.9(56)		677.2(100)	3026.5(9)	1085.8(87)	672.1(90)	

TABLE 2: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm⁻¹), Infrared Intensities (in parentheses in km mol⁻¹), and Zero-Point Vibrational Energy (ZPVE in kcal mol⁻¹) for the $^1A'$ State of the EthynylsilanediyI (2S) Molecule

level of theory	energy	μ_e	$\omega_1(a')$ C—H str	$\omega_2(a')$ C—C str	$\omega_3(a')$ Si—H str	$\omega_4(a')$ HSiC bend	$\omega_5(a')$ CCH bend	$\omega_6(a')$ Si—C str	$\omega_7(a')$ CCSi bend	$\omega_8(a'')$ CCH oop	$\omega_9(a'')$ CCSi oop	ZPVE
cc-pVDZ RHF	-365.718 428	0.930	3619(44.5)	2249(91.3)	2147(299.8)	896(121.5)	755(51.8)	616(98.8)	272(7.9)	891(23.6)	209(7.8)	16.66
cc-pV(D+d)Z RHF	-365.723 006	0.971	3619(44.6)	2249(92.7)	2156(292.2)	900(126.1)	755(52.0)	622(95.6)	275(7.8)	892(23.5)	211(7.7)	16.69
cc-pVTZ RHF	-365.753 295	0.978	3603(41.4)	2241(85.8)	2152(294.6)	899(123.0)	776(60.2)	623(99.7)	279(8.5)	904(28.8)	217(7.8)	16.72
cc-pV(T+d)Z RHF	-365.755 242	0.994	3603(41.4)	2241(86.4)	2149(291.2)	900(124.1)	776(60.5)	623(98.9)	279(8.4)	905(28.8)	217(7.7)	16.72
cc-pVQZ RHF	-365.761 750	1.004	3596(42.1)	2240(81.9)	2156(288.8)	899(126.5)	777(62.0)	623(100.9)	278(8.3)	905(29.6)	216(7.6)	16.71
cc-pV(Q+d)Z RHF	-365.762 763	1.011	3596(42.1)	2240(82.4)	2158(287.1)	900(127.4)	777(61.9)	623(100.5)	279(8.3)	905(29.5)	216(7.6)	16.72
cc-pVDZ CCSD	-366.078 454	0.715	3456(37.0)	2065(96.6)	2062(204.0)	835(100.1)	742(21.4)	595(78.2)	234(5.9)	742(21.4)	193(5.9)	15.44
cc-pV(D+d)Z CCSD	-366.083 589	0.750	3456(37.2)	2064(84.5)	2075(210.1)	841(104.3)	616(40.8)	601(74.2)	237(5.8)	744(21.4)	195(5.8)	15.48
cc-pVTZ CCSD	-366.175 954	0.762	3467(38.5)	2082(57.0)	2072(240.1)	839(104.7)	641(44.3)	608(79.1)	246(6.5)	762(25.8)	195(6.1)	15.60
cc-pV(T+d)Z CCSD	-366.177 958	0.813	3467(38.6)	2082(57.4)	2070(237.0)	841(106.0)	642(44.4)	609(78.5)	247(6.4)	763(25.9)	196(6.1)	15.61
cc-pVQZ CCSD	-366.204 435	0.823	3461(39.5)	2089(56.5)	2083(231.9)	840(107.3)	653(44.9)	612(79.9)	248(6.6)	772(26.0)	195(6.1)	15.66
cc-pV(Q+d)Z CCSD	-366.205 555	0.831	3461(39.5)	2089(56.8)	2085(219.0)	841(108.0)	653(44.9)	613(79.5)	248(6.6)	772(26.0)	195(6.0)	15.66
cc-pVDZ CCSD(T)	-366.094 801	0.772	3433(35.5)	2008(74.8)	2048(225.1)	824(95.1)	573(37.9)	594(74.4)	224(5.2)	710(21.0)	185(5.7)	15.15
cc-pV(D+d)Z CCSD(T)	-366.099 989	0.810	3433(35.8)	2008(74.0)	2059(219.3)	830(99.2)	573(37.7)	600(72.1)	227(5.2)	712(20.9)	188(5.6)	15.20
cc-pVTZ CCSD(T)	-366.198 822	0.845	3440(37.4)	2024(72.2)	2056(218.8)	826(99.2)	600(52.9)	609(63.8)	237(6.0)	731(25.0)	189(5.9)	15.31
cc-pV(T+d)Z CCSD(T)	-366.200 832	0.861	3440(37.5)	2023(73.4)	2055(214.8)	827(100.5)	601(51.7)	609(64.5)	238(6.0)	731(25.1)	189(5.8)	15.32
cc-pVQZ CCSD(T)	-366.229 115	0.866	3433(38.4)	2029(66.8)	2067(214.4)	826(101.7)	618(48.7)	608(69.0)	239(6.3)	741(25.1)	188(5.9)	15.37
cc-pV(Q+d)Z CCSD(T)	-366.230 242	0.874	3433(38.4)	2029(66.8)	2069(213.1)	826(102.4)	618(49.6)	608(67.7)	240(6.3)	741(25.1)	188(5.9)	15.37
expt. (refs 7 and 8)			3304.2(31)	1969.9(100)	1995.7(27)	814.8(49)	613.9(32)	605.0(41)		722.8(14)		

TABLE 3: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm⁻¹), Infrared Intensities (in parentheses in km mol⁻¹), and Zero-Point Vibrational Energy (ZPVE in kcal mol⁻¹) for the 1A_1 State of the VinylidenesilanediyI (3S) Molecule

level of theory	energy	μ_e	$\omega_1(a_1)$ CH ₂ s-str	$\omega_2(a_1)$ CC str	$\omega_3(a_1)$ CH ₂ scissor	$\omega_4(a_1)$ SiC str	$\omega_5(b_1)$ CH ₂ wag	$\omega_6(b_1)$ SiCC oop	$\omega_7(b_2)$ CH ₂ a-str	$\omega_8(b_2)$ CH ₂ rock	$\omega_9(b_2)$ SiCC bend	ZPVE
cc-pVDZ RHF	-365.717 847	1.162	3251(37.8)	1873(55.8)	1521(1.0)	798(23.0)	1111(22.1)	223(7.3)	3329(5.4)	1095(9.1)	299(27.9)	19.30
cc-pV(D+d)Z RHF	-365.722 423	1.135	3251(38.4)	1875(60.6)	1523(1.3)	805(22.6)	1113(21.7)	224(7.5)	3329(5.6)	1098(9.3)	303(28.3)	19.33
cc-pVTZ RHF	-365.749 919	1.058	3230(39.0)	1859(57.5)	1543(2.0)	803(25.3)	1131(25.1)	226(8.1)	3295(5.1)	1110(11.9)	303(31.1)	19.30
cc-pV(T+d)Z RHF	-365.751 962	1.048	3230(39.4)	1859(60.4)	1544(2.3)	804(25.5)	1132(24.9)	227(8.1)	3295(5.3)	1112(12.0)	304(31.2)	19.31
cc-pVQZ RHF	-365.758 373	1.030	3231(38.7)	1855(57.5)	1545(2.3)	804(26.6)	1134(25.3)	224(8.6)	3298(3.8)	1112(13.0)	303(33.1)	19.31
cc-pV(Q+d)Z RHF	-365.759 374	1.022	3231(38.8)	1855(59.1)	1545(2.5)	805(26.8)	1134(25.3)	224(8.6)	3298(3.8)	1113(13.0)	303(33.1)	19.31
cc-pVDZ CCSD	-366.086 126	0.928	3115(26.4)	1737(35.5)	1437(0.9)	729(21.4)	976(20.7)	194(4.4)	3195(6.5)	1018(6.1)	258(19.6)	18.09
cc-pV(D+d)Z CCSD	-366.090 982	0.901	3115(26.9)	1740(35.7)	1438(0.8)	736(20.0)	978(20.4)	196(4.5)	3195(6.7)	1020(6.2)	261(19.8)	18.13
cc-pVTZ CCSD	-366.180 161	0.888	3113(24.3)	1745(32.6)	1458(1.7)	747(21.6)	1006(23.7)	197(5.2)	3183(4.1)	1032(8.0)	265(22.5)	18.22
cc-pV(T+d)Z CCSD	-366.182 115	0.878	3113(24.6)	1746(33.1)	1458(1.7)	748(21.3)	1007(23.6)	198(5.2)	3183(4.2)	1033(8.0)	267(22.6)	18.23
cc-pVQZ CCSD	-366.208 077	0.854	3114(24.0)	1750(32.5)	1456(2.0)	753(22.7)	1008(23.5)	195(5.8)	3188(2.8)	1035(8.8)	266(24.1)	18.25
cc-pV(Q+d)Z CCSD	-366.209 108	0.847	3114(24.1)	1750(32.8)	1456(2.0)	754(22.6)	1008(23.5)	195(5.6)	3188(2.9)	1035(8.8)	267(24.1)	18.25
cc-pVDZ CCSD(T)	-366.104 402	1.013	3090(28.0)	1688(43.9)	1425(1.3)	711(20.4)	951(19.7)	183(4.0)	3171(7.5)	1007(5.7)	245(18.8)	17.83
cc-pV(D+d)Z CCSD(T)	-366.109 263	0.993	3091(28.4)	1692(43.5)	1426(1.1)	718(18.8)	953(19.4)	186(4.1)	3171(7.7)	1009(5.7)	249(19.0)	17.86
cc-pVTZ CCSD(T)	-366.205 279	0.980	3086(24.7)	1696(38.5)	1442(2.3)	728(20.1)	979(22.6)	186(4.6)	3157(4.6)	1018(7.3)	252(21.2)	17.93
cc-pV(T+d)Z CCSD(T)	-366.207 200	0.973	3086(25.0)	1697(38.6)	1442(2.2)	729(19.6)	980(22.5)	187(4.6)	3157(4.6)	1019(7.3)	254(21.3)	17.94
cc-pVQZ CCSD(T)	-366.235 059	0.946	3086(24.3)	1700(37.8)	1439(2.5)	734(21.0)	980(22.3)	185(5.0)	3161(3.1)	1020(8.1)	254(22.7)	17.95
cc-pV(Q+d)Z CCSD(T)	-366.236 080	0.941	3087(24.3)	1700(37.9)	1440(2.5)	735(20.8)	981(22.3)	185(5.0)	3161(3.1)	1020(8.1)	254(22.7)	17.96
expt. (refs 7 and 8)					1667.9(100)		957.7(100)					

(NOs). The reference configuration (Φ_1) and several excited configurations with large CI coefficients ($|C_i| \geq 0.070$) are presented in Table 9, while the electron occupation numbers in the active MOs of CASSCF wave functions are provided in

Table 10. The dominant excited configurations for the structures **1S** and **2S** may be interpreted in the following manner.

1-Silacyclopropenylidene (1S). For the ground state of **1S**, three important doubly excited configurations, $\Phi_2[(3b_1)^2 \leftarrow$

TABLE 4: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in parentheses in km mol^{-1}), and Zero-Point Vibrational Energy (ZPVE in kcal mol^{-1}) for the 1A_1 State of the Silacyclopripyne (4S) Molecule

level of theory	energy	μ_e	$\omega_1(a_1)$ SiH ₂ s-str	$\omega_2(a_1)$ C–C str	$\omega_3(a_1)$ SiH ₂ scissor	$\omega_4(a_1)$ Si–C s-str	$\omega_5(a_2)$ SiH ₂ twist	$\omega_6(b_1)$ SiH ₂ a-str	$\omega_7(b_1)$ SiH ₂ rock	$\omega_8(b_2)$ SiH ₂ wag	$\omega_9(b_2)$ Si–C a-str	ZPVE
cc-pVDZ RHF	–365.658 657	3.894	2360(107.2)	2022(12.2)	1103(207.0)	809(151.4)	143(0.0)	2354(127.6)	701(68.0)	825(81.9)	224i	14.75
cc-pV(D+d)Z RHF	–365.668 455	3.750	2367(107.9)	2029(11.1)	1115(210.4)	821(154.7)	184(0.0)	2363(126.4)	709(68.9)	831(85.8)	181i	14.89
cc-pVTZ RHF	–365.698 418	3.880	2368(107.9)	2015(13.3)	1112(199.3)	823(158.3)	214(0.0)	2365(120.5)	709(62.2)	829(71.4)	110i	14.92
cc-pV(T+d)Z RHF	–365.702 621	3.819	2366(109.5)	2017(13.0)	1117(199.0)	826(160.6)	227(0.0)	2361(119.3)	713(61.8)	831(73.1)	84i	14.95
cc-pVQZ RHF	–365.709 498	3.884	2372(107.9)	2019(12.9)	1117(199.2)	826(162.3)	229(0.0)	2368(113.0)	717(62.3)	832(69.3)	56i	14.98
cc-pV(Q+d)Z RHF	–365.711 666	3.853	2374(108.9)	2020(12.8)	1118(198.7)	827(163.5)	235(0.0)	2369(112.9)	718(62.1)	832(70.0)	13i	15.00
cc-pVDZ CCSD	–366.020 586	3.254	2270(91.5)	1824(3.5)	1039(179.7)	803(108.0)	267(0.0)	2278(103.1)	659(57.2)	775(71.3)	261(94.2)	14.55
cc-pV(D+d)Z CCSD	–366.030 571	3.120	2280(92.2)	1827(3.4)	1052(185.1)	814(109.7)	287(0.0)	2287(102.1)	667(58.4)	782(74.9)	302(92.9)	14.72
cc-pVTZ CCSD	–366.124 163	3.306	2285(93.7)	1845(5.1)	1050(176.5)	823(119.3)	296(0.0)	2292(100.0)	667(52.7)	782(61.0)	333(103.0)	14.83
cc-pV(T+d)Z CCSD	–366.128 391	3.246	2284(94.9)	1846(5.1)	1056(177.2)	826(121.0)	304(0.0)	2289(98.9)	670(52.7)	784(62.6)	345(101.9)	14.87
cc-pVQZ CCSD	–366.156 424	3.319	2294(92.8)	1859(5.2)	1052(175.3)	830(124.2)	309(0.0)	2300(92.5)	676(52.3)	783(58.3)	352(106.3)	14.95
cc-pV(Q+d)Z CCSD	–366.158 720	3.288	2297(93.5)	1859(5.2)	1054(175.4)	831(125.0)	312(0.0)	2302(92.3)	677(52.2)	783(58.9)	359(105.6)	14.97
cc-pVDZ CCSD(T)	–366.039 498	3.100	2254(92.4)	1768(3.7)	1031(172.9)	795(97.2)	275(0.0)	2263(103.1)	651(54.2)	764(68.8)	300(97.4)	14.44
cc-pV(D+d)Z CCSD(T)	–366.049 471	2.972	2264(93.1)	1770(3.6)	1044(178.5)	806(98.6)	294(0.0)	2273(102.1)	659(55.4)	771(72.3)	337(94.9)	14.61
cc-pVTZ CCSD(T)	–366.149 278	3.161	2267(93.9)	1785(5.1)	1040(170.4)	814(107.8)	301(0.0)	2276(98.9)	657(49.7)	770(58.7)	363(105.6)	14.69
cc-pV(T+d)Z CCSD(T)	–366.153 486	3.104	2267(95.0)	1785(5.1)	1046(171.3)	817(109.3)	308(0.0)	2274(97.7)	660(49.7)	774(60.3)	374(103.9)	14.73
cc-pVQZ CCSD(T)	–366.183 309	3.179	2277(93.0)	1798(5.3)	1041(169.5)	820(112.4)	312(0.0)	2285(91.4)	666(49.1)	771(56.0)	381(108.7)	14.80
cc-pV(Q+d)Z CCSD(T)	–366.185 604	3.149	2279(93.6)	1798(5.4)	1043(169.7)	822(113.2)	316(0.0)	2287(91.2)	667(49.0)	772(56.7)	387(107.8)	14.82
expt. (refs 7 and 8)			2214.4(49)	1769.8(7)	1023.1(100)	836.5(50)		2228.9(49)	676.4(25)	757.4(42)		

TABLE 5: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in parentheses in km mol^{-1}), and Zero-Point Vibrational Energy (ZPVE in kcal mol^{-1}) for the 1A_1 State of the Silavinylidenecarbene (5S) Molecule

level of theory	energy	μ_e	$\omega_1(a_1)$ SiH ₂ s-str	$\omega_2(a_1)$ C–C str	$\omega_3(a_1)$ SiH ₂ scissor	$\omega_4(a_1)$ Si–C str	$\omega_5(b_1)$ SiH ₂ wag	$\omega_6(b_1)$ SiCC oop	$\omega_7(b_2)$ SiH ₂ a-str	$\omega_8(b_2)$ SiH ₂ rock	$\omega_9(b_2)$ SiCC bend	ZPVE
cc-pVDZ RHF	–365.663 059	6.066	2382(71.9)	2098(920.0)	1057(131.1)	853(34.4)	743(93.1)	95(0.5)	2387(82.3)	721(98.6)	121(1.5)	14.95
cc-pV(D+d)Z RHF	–365.671 290	6.009	2390(73.8)	2100(920.6)	1067(139.3)	859(34.1)	747(98.4)	95(0.6)	2396(82.0)	726(98.8)	120(1.5)	15.00
cc-pVTZ RHF	–365.699 005	6.286	2387(75.6)	2090(980.0)	1064(135.2)	857(40.6)	751(82.9)	91(0.3)	2394(76.6)	725(88.7)	129(1.1)	14.99
cc-pV(T+d)Z RHF	–365.702 732	6.253	2386(76.4)	2090(980.0)	1069(138.2)	859(41.2)	752(85.3)	93(0.3)	2392(76.6)	728(87.9)	129(1.0)	15.00
cc-pVQZ RHF	–365.709 362	6.367	2393(74.3)	2088(990.3)	1070(137.5)	859(42.9)	752(78.5)	82(0.3)	2399(70.1)	731(84.6)	126(1.0)	15.01
cc-pV(Q+d)Z RHF	–365.711 193	6.350	2394(75.0)	2088(991.6)	1071(138.7)	859(43.2)	752(79.4)	81(0.3)	2400(70.1)	732(84.0)	125(1.0)	15.01
cc-pVDZ CCSD	–366.016 846	5.621	2290(49.2)	1945(544.9)	984(82.8)	789(7.5)	648(57.9)	66(0.2)	2307(61.0)	671(75.8)	113(0.3)	14.03
cc-pV(D+d)Z CCSD	–366.024 705	5.592	2299(51.2)	1950(545.0)	997(89.6)	796(7.8)	655(62.3)	67(0.1)	2317(60.6)	677(76.7)	113(0.3)	14.11
cc-pVTZ CCSD	–366.114 897	6.007	2301(56.0)	1969(620.6)	995(90.5)	806(13.4)	671(56.5)	60(0.2)	2319(58.2)	675(70.6)	119(0.2)	14.17
cc-pV(T+d)Z CCSD	–366.118 340	5.988	2300(56.8)	1970(620.4)	1001(93.5)	807(14.0)	674(58.6)	63(0.2)	2317(57.9)	679(70.3)	118(0.2)	14.20
cc-pVQZ CCSD	–366.145 577	6.165	2312(54.8)	1976(644.5)	1000(92.9)	811(15.5)	675(54.9)	44(0.3)	2329(51.8)	682(67.0)	114(0.1)	14.21
cc-pV(Q+d)Z CCSD	–366.147 375	6.154	2313(55.5)	1977(645.4)	1003(94.1)	812(15.8)	677(55.8)	42(0.3)	2330(51.7)	682(66.6)	113(0.1)	14.22
cc-pVDZ CCSD(T)	–366.036 439	5.454	2271(48.1)	1894(430.0)	976(81.1)	764(3.7)	621(50.7)	59(0.5)	2290(61.5)	658(69.7)	106(0.3)	13.78
cc-pV(D+d)Z CCSD(T)	–366.044 236	5.429	2281(49.9)	1898(432.5)	989(87.2)	771(3.9)	630(54.7)	62(0.5)	2300(60.8)	664(70.5)	106(0.2)	13.87
cc-pVTZ CCSD(T)	–366.140 504	5.845	2282(53.7)	1917(497.3)	984(85.6)	782(7.5)	646(50.0)	58(0.7)	2301(57.4)	661(65.0)	114(0.1)	13.93
cc-pV(T+d)Z CCSD(T)	–366.143 879	5.830	2281(54.6)	1917(498.6)	991(88.4)	784(8.0)	650(52.0)	61(0.6)	2299(57.0)	665(64.8)	114(0.1)	13.96
cc-pVQZ CCSD(T)	–366.172 904	6.014	2293(52.8)	1924(520.4)	989(87.5)	788(9.0)	650(49.0)	43(0.8)	2311(50.8)	668(61.9)	109(0.1)	13.97
cc-pV(Q+d)Z CCSD(T)	–366.174 678	6.005	2294(53.4)	1925(521.9)	991(88.5)	789(9.3)	651(49.8)	41(0.7)	2313(50.7)	669(61.5)	109(0.1)	13.98

TABLE 6: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), and Harmonic Vibrational Frequencies (in cm^{-1}) for the 1A_1 Stationary Point of the Planar Silacyclopripyne (6S) Molecule

level of theory	energy	μ_e	$\omega_1(a_1)$ SiH ₂ s-str	$\omega_2(a_1)$ C–C str	$\omega_3(a_1)$ SiH ₂ scissor	$\omega_4(a_1)$ Si–C s-str	$\omega_5(a_2)$ SiH ₂ twist	$\omega_6(b_1)$ SiH ₂ wag	$\omega_7(b_2)$ SiH ₂ a-str	$\omega_8(b_2)$ SiH ₂ rock	$\omega_9(b_2)$ Si–C a-str
cc-pVDZ RHF	–365.655 189	3.794	2364	1900	1106	783	167i	756	2358	761	288i
cc-pV(D+d)Z RHF	–365.663 227	3.689	2369	1910	1120	791	197i	760	2363	771	301i
cc-pVTZ RHF	–365.691 770	3.841	2366	1899	1119	791	215i	761	2362	771	282i
cc-pV(T+d)Z RHF	–365.695 270	3.796	2365	1902	1124	793	225i	762	2359	775	289i
cc-pVQZ RHF	–365.701 918	3.866	2370	1904	1123	792	228i	762	2365	779	280i
cc-pV(Q+d)Z RHF	–365.703 741	3.843	2372	1906	1126	793	233i	762	2366	780	283i
cc-pVDZ CCSD	–366.012 608	3.293	2264	1717	1044	765	191i	697	2267	729	197i
cc-pV(D+d)Z CCSD	–366.020 970	3.184	2271	1725	1059	773	218i	703	2274	739	199i
cc-pVTZ CCSD	–366.113 191	3.395	2274	1743	1057	784	246i	709	2277	740	169i
cc-pV(T+d)Z CCSD	–366.116 773	3.345	2273	1746	1063	786	255i	711	2274	744	172i
cc-pVQZ CCSD	–366.144 156	3.438	2282	1759	1058	789	265i	708	2284	746	155i
cc-pV(Q+d)Z CCSD	–366.146 132	3.413	2284	1760	1061	791	270i	708	2286	748	154i
cc-pVDZ CCSD(T)	–366.031 551	3.163	2246	1661	1032	750	175i	682	2252	718	195i
cc-pV(D+d)Z CCSD(T)	–366.039 892	3.056	2253	1669	1047	759	205i	689	2258	728	193i
cc-pVTZ CCSD(T)	–366.138 410	3.269	2254	1683	1043	769	235i	694	2260	728	155i
cc-pV(T+d)Z CCSD(T)	–366.141 968	3.219	2254	1686	1050	772	245i	696	2267	732	156i
cc-pVQZ CCSD(T)	–366.171 149	3.316	2263	1698	1043	775	255i	693	2267	734	136i
cc-pV(Q+d)Z CCSD(T)	–366.173 118	3.291	2265	1700	1046	776	260i	693	2269	736	134i

$(8a_1)^2$, $\Phi_3[(1a_2)^2 \leftarrow (2b_1)^2]$, and $\Phi_4[(5b_2)^2 \leftarrow (4b_2)^2]$, contribute to the CASSCF wave function.

Ethynylsilanediyl (2S). For the $^1A'$ state of **2S**, three prominent doubly excited configurations, $\Phi_2[(3a'')^2 \leftarrow (12a'')^2]$, $\Phi_3[(13a'')^2 \leftarrow (11a'')^2]$, and $\Phi_4[(4a'')^2 \leftarrow (2a'')^2]$, contribute to the CASSCF wave function.

The excited configurations for the five remaining structures shown in Table 9 may be described in a manner similar to the

wave functions of **1S** and **2S**. For all structures, the leading CI coefficients are sufficiently large for single-reference theoretical treatments to be used.

4.2. Geometries. 1-Silacyclopripynylidene (1S) (in Figure 1). The three bond lengths [$r_e(\text{Si}-\text{C})$, $r_e(\text{C}-\text{C})$, and $r_e(\text{C}-\text{H})$] decrease with increasing basis set size, while they increase with an advanced treatment of correlation effects. This latter feature is mainly attributed to the doubly excited configurations,

TABLE 7: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm⁻¹), Infrared Intensities (in parentheses in km mol⁻¹), and Zero-Point Vibrational Energy (ZPVE in kcal mol⁻¹) for the ¹A₁ State of the Ethynylsilylene (7S) Molecule

level of theory	energy	μ_e	$\omega_1(a')$ C–H str	$\omega_2(a')$ Si–H str	$\omega_3(a')$ C–C str	$\omega_4(a')$ CCH bend	$\omega_5(a')$ CSiH bend	$\omega_6(a')$ C–Si str	$\omega_7(a')$ CCSi bend	$\omega_8(a')$ CCH oop	$\omega_9(a')$ CSiH oop	ZPVE
cc-pVDZ RHF	-365.678 478	2.735	3568(65.1)	2066(335.8)	1962(5.1)	903(23.5)	874(116.5)	535(86.7)	257(5.8)	791(70.1)	298(0.2)	16.09
cc-pV(D+d)Z RHF	-365.682 653	2.708	3568(65.3)	2072(328.1)	1965(3.8)	906(24.5)	886(121.2)	542(89.5)	259(6.8)	796(68.8)	300(0.2)	16.15
cc-pVTZ RHF	-365.712 490	2.755	3557(60.3)	2056(342.9)	1963(4.2)	917(18.2)	893(126.2)	555(101.3)	268(8.2)	811(64.4)	292(0.5)	16.17
cc-pV(T+d)Z RHF	-365.714 354	2.746	3557(60.3)	2053(339.3)	1965(3.8)	918(18.2)	897(128.3)	559(103.1)	268(8.7)	813(64.1)	292(0.5)	16.18
cc-pVQZ RHF	-365.720 747	2.777	3554(60.9)	2058(342.8)	1965(4.1)	918(17.7)	897(128.9)	558(106.4)	265(8.8)	813(62.0)	290(0.8)	16.18
cc-pV(Q+d)Z RHF	-365.721 771	2.771	3554(60.9)	2060(340.8)	1966(3.9)	919(17.6)	899(130.1)	560(107.4)	265(9.1)	814(61.7)	290(0.9)	16.19
cc-pVDZ CCSD	-366.043 296	2.370	3385(43.2)	1963(263.4)	1765(1.1)	788(15.8)	830(98.3)	561(62.9)	292(3.6)	717(53.0)	326(0.2)	15.19
cc-pV(D+d)Z CCSD	-366.048 296	2.345	3386(43.6)	1973(254.4)	1765(1.0)	790(15.7)	840(103.2)	566(61.0)	298(3.7)	721(52.5)	334(0.2)	15.26
cc-pVTZ CCSD	-366.140 730	2.428	3401(46.5)	1958(272.7)	1786(1.1)	797(14.6)	848(106.1)	587(72.1)	310(5.4)	735(50.9)	323(0.0)	15.36
cc-pV(T+d)Z CCSD	-366.142 759	2.419	3401(46.6)	1957(268.6)	1787(1.1)	798(15.0)	852(107.8)	590(72.0)	313(5.5)	736(50.6)	325(0.0)	15.38
cc-pVQZ CCSD	-366.169 173	2.462	3400(48.1)	1967(271.8)	1795(1.3)	798(15.4)	855(106.4)	595(74.2)	314(5.7)	738(48.6)	327(0.0)	15.42
cc-pV(Q+d)Z CCSD	-366.170 360	2.457	3400(48.2)	1970(269.5)	1795(1.3)	798(15.7)	857(107.4)	596(74.1)	316(5.8)	738(48.4)	329(0.0)	15.44
cc-pVDZ CCSD(T)	-366.062 203	2.309	3353(38.2)	1935(253.7)	1699(1.6)	759(15.4)	813(88.9)	560(52.9)	307(3.1)	702(50.6)	348(0.4)	14.98
cc-pV(D+d)Z CCSD(T)	-366.067 283	2.287	3354(38.6)	1945(244.1)	1699(1.5)	761(15.7)	822(92.9)	565(50.6)	314(3.0)	706(50.1)	356(0.4)	15.04
cc-pVTZ CCSD(T)	-366.166 349	2.371	3364(41.9)	1930(257.2)	1715(1.9)	764(15.5)	829(94.2)	585(58.4)	331(4.3)	719(48.6)	349(0.1)	15.13
cc-pV(T+d)Z CCSD(T)	-366.168 392	2.362	3365(42.1)	1929(252.9)	1716(1.9)	764(16.0)	832(95.6)	588(58.0)	333(4.3)	721(48.4)	351(0.1)	15.15
cc-pVQZ CCSD(T)	-366.197 919	2.403	3363(43.4)	1938(255.6)	1722(2.4)	763(16.8)	835(93.8)	593(59.1)	336(4.4)	722(46.5)	355(0.0)	15.19
cc-pV(Q+d)Z CCSD(T)	-366.197 919	2.398	3363(43.5)	1941(253.2)	1722(2.5)	763(17.2)	837(94.6)	594(58.8)	338(4.4)	723(46.3)	356(0.0)	15.21

TABLE 8: Relative Energies (in kcal mol⁻¹) of the SiC₂H₂ Isomers with Respect to the \tilde{X} ¹A₁ State of the 1-Silacyclopentenylidene (1S) Molecule at the 18 Levels of Theory

isomer state	1S ¹ A ₁	2S ¹ A'	3S ¹ A ₁	4S ¹ A ₁	5S ¹ A ₁	6S ¹ A ₁	7S ¹ A'
symmetry	C _{2v}	C _s	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _s
N (imaginary frequencies)	0	0	0	0	0	2	0
cc-pVDZ RHF	0.00	19.89	20.25	57.40	54.63	59.57	44.96
cc-pV(D+d)Z RHF	0.00	20.83	21.19	55.06	53.28	58.34	46.15
cc-pVTZ RHF	0.00	19.63	21.75	54.07	53.70	58.24	45.24
cc-pV(T+d)Z RHF	0.00	19.99	22.05	53.01	52.94	57.62	45.65
cc-pVQZ RHF	0.00	19.74	21.86	52.53	52.61	57.28	45.47
cc-pV(Q+d)Z RHF	0.00	19.91	22.04	51.98	52.27	56.95	45.64
cc-pVDZ CCSD	0.00	20.37	15.55	56.68	59.03	61.69	42.43
cc-pV(D+d)Z CCSD	0.00	20.98	16.35	54.25	57.93	60.28	43.13
cc-pVTZ CCSD	0.00	21.08	18.44	53.58	59.39	60.46	43.18
cc-pV(T+d)Z CCSD	0.00	21.33	18.72	52.44	58.74	59.73	43.42
cc-pVQZ CCSD	0.00	21.44	19.15	51.57	58.37	59.27	43.57
cc-pV(Q+d)Z CCSD	0.00	21.57	19.34	50.96	58.08	58.86	43.65
cc-pVDZ CCSD(T)	0.00	20.48	14.45	55.18	57.10	60.17	40.93
cc-pV(D+d)Z CCSD(T)	0.00	21.01	15.19	52.71	56.00	58.72	41.53
cc-pVTZ CCSD(T)	0.00	21.39	17.34	52.48	57.99	59.30	41.77
cc-pV(T+d)Z CCSD(T)	0.00	21.60	17.61	51.31	57.34	58.54	41.96
cc-pVQZ CCSD(T)	0.00	21.74	18.01	50.49	57.01	58.12	42.07
cc-pV(Q+d)Z CCSD(T)	0.00	21.85	18.19	49.86	56.72	57.70	42.13

$\Phi_3[(1a_2)^2 \leftarrow (2b_1)^2]$ and $\Phi_4[(5b_2)^2 \leftarrow (4b_2)^2]$, noted in Table 9. The 2b₁ and 4b₂ molecular orbitals (MOs) describe an out-of-plane SiCC π -bonding and an in-plane Si–C σ -bonding, whereas the 1a₂ and 5b₂ MOs represent out-of-plane C–C π -antibonding and in-plane Si–C σ -antibonding, respectively. The double excitations from the π - and σ -bonding MOs to the π - and σ -antibonding MOs necessarily elongate the Si–C and C–C bond distances. The C–C bond distance [1.348 Å at the cc-pV(Q+d)Z CCSD(T) level of theory] is considerably longer than that [1.326 Å at the cc-pVQZ CCSD(T) level] of the corresponding C₃H₂ derivative, cyclopropenylidene (1S). The difference between the predicted equilibrium (r_e) structure at our highest level of theory and the experimental r_s structure by Izuha et al.¹³ are $r_e(\text{C}=\text{C})$ (+0.0025 Å), $r_e(\text{Si}=\text{C})$ (+0.0055 Å), $r_e(\text{C}=\text{H})$ (+0.0024 Å), and $\theta_e(\text{CCH})$ (−0.09°), although the r_e structure may be slightly different from the r_s structure. Using the natural bond order (NBO) method with the MP2/6-311G(d,p) level of theory, Maier et al. suggested that the best Lewis structure for the isomer 1S may be described as a delocalized three-center π -bond structure.⁸

Ethynylsilylanediyl (2S) (in Figure 2). Since both the CCH and CCSi bond angles are larger than 170°, the C–C bond has an sp-hybridized electronic structure and near-triple-bond

character. The C–C bond distance [1.222 Å at the cc-pV(Q+d)Z CCSD(T) level] is not much greater than that of the isolated acetylene molecule [1.207 Å at the cc-pVQZ CCSD(T) level].

Vinylidenesilanediyl (3S) (in Figure 3). The C–C and Si–C bond distances are shorter than those for 1S, while the C–H bond distance is longer than that of 1S. The 2b₁ MO in eq 3 has out-of-plane C–C π -bonding character, while the 3b₂ MO has in-plane Si–C π -bonding nature. Consequently, both the C–C and Si–C bonds may be assigned to be double bonds, as expected from the propadienylidene Lewis structure. At our highest level of theory, the equilibrium structure (r_e) of the 3S isomer has been predicted to be $r_e(\text{C}=\text{C}) = 1.3304$ Å, $r_e(\text{Si}=\text{C}) = 1.7039$ Å, $r_e(\text{C}=\text{H}) = 1.0877$ Å, and $\theta_e(\text{HCH}) = 116.26^\circ$. The equilibrium geometry is consistent with the experimental r_0 structure, obtained by isotopic substitution:¹⁴ $r_0(\text{C}=\text{C}) = 1.321$ Å, $r_0(\text{Si}=\text{C}) = 1.703$ Å, $r_0(\text{C}=\text{H}) = 1.099$ Å, and $\theta_0(\text{HCH}) = 117.3^\circ$.

Silacyclopropyne (4S) (in Figure 4). The isomer 4S represents the first example of a “formal” cyclopropyne. 4S was first thought to be a transition state, based on a 1986 DZ SCF theoretical study.¹⁰ However, when electron correlation effects were taken into account (at the MP2/6-311G* level of theory), sturcture 4S was found to be a minimum.^{7–9} The doubly excited

TABLE 9: Dominant Natural Orbital Configurations and Associated CI Coefficients for the cc-pV(Q+d)Z CASSCF Wave Functions of the Seven SiC₂H₂ Isomers at the cc-pV(Q+d)Z CCSD(T) Optimized Geometries ($|C_i| \geq 0.070$)

isomers	configuration	CI
1-Silacyclopentenylidene (1S)		
$C_{2v} \ ^1A_1$	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_2^2 4b_2^2$	0.944
	[core] $5a_1^2 6a_1^2 7a_1^2 2b_1^2 3b_1^2 3b_2^2 4b_2^2$	-0.129
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 3b_2^2 4b_2^2 1a_2^2$	-0.116
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_2^2 5b_2^2$	-0.071
Ethynylsilanediyl (2S)		
$C_s \ ^1A'$	[core] $7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 2a''^2$	0.925
	[core] $7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 2a''^2 3a''^2$	-0.183
	[core] $7a'^2 8a'^2 9a'^2 10a'^2 12a'^2 13a'^2 2a''^2$	-0.109
	[core] $7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 4a''^2$	-0.097
Vinylidenesilanediyl (3S)		
$C_{2v} \ ^1A_1$	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 2b_1^2 2b_2^2 3b_2^2$	-0.921
	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 2b_1^2 2b_2^2 4b_2^2$	-0.163
	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 3b_1^2 2b_2^2 3b_2^2$	-0.135
	[core] $6a_1^2 7a_1^2 8a_1^2 2b_1^2 4b_1^2 2b_2^2 3b_2^2$	-0.095
	[core] $6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_1^2 4b_1^2 2b_2^2 3b_2^2$	0.073
	[core] $6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_1^2 4b_1^2 2b_2^2 3b_2^2$	-0.073
Silacyclopentyne (4S)		
$C_{2v} \ ^1A_1$	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_1^2 3b_2^2$	0.938
	[core] $5a_1^2 6a_1^2 7a_1^2 2b_1^2 3b_1^2 3b_2^2 4b_2^2$	-0.146
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_2^2 1a_2^2$	-0.105
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_1^2 3b_2^2 4b_2^2$	0.074
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_1^2 3b_2^2 4b_2^2 1a_2^2$	0.074
Silavinylidenecarbene (5S)		
$C_{2v} \ ^1A_1$	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 2b_1^2 2b_2^2 3b_2^2$	0.934
	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 3b_1^2 2b_2^2 3b_2^2$	-0.122
	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 2b_1^2 2b_2^2 4b_2^2$	-0.118
	[core] $6a_1^2 7a_1^2 8a_1^2 9a_1^2 4b_1^2 2b_2^2 3b_2^2$	-0.071
Planar Silacyclopentyne (6S)		
$C_{2v} \ ^1A_1$	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 2b_1^2 3b_2^2 4b_2^2$	0.943
	[core] $5a_1^2 6a_1^2 7a_1^2 2b_1^2 3b_2^2 4b_2^2 5b_2^2$	-0.111
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 3b_2^2 4b_2^2 1a_2^2$	-0.083
	[core] $5a_1^2 6a_1^2 7a_1^2 8a_1^2 3b_1^2 3b_2^2 4b_2^2$	-0.071
Ethynylsilylene (7S)		
$C_s \ ^1A'$	[core] $7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 2a''^2$	0.926
	[core] $7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 2a''^2 3a''^2$	-0.178
	[core] $7a'^2 8a'^2 9a'^2 10a'^2 12a'^2 13a'^2 2a''^2$	-0.105
	[core] $7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 4a''^2$	-0.097

configurations from the C–C π -bonding ($3b_1$ and $8a_1$) MOs to the C–C π -antibonding ($4b_2$ and $1a_2$) MOs (Φ_2 – Φ_5 in Table 9) preferentially elongate the C–C bond distance. The longer C–C bond distance and larger CSiC bond angle appear to release the ring strain and stabilize the three-membered ring structure as an equilibrium rather than a transition state. The

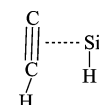
C–C bond distance of **4S** is considerably shorter than that for isomer **1S**, indicating higher multiple bond character. The $3b_1$ and $8a_1$ MOs in eq 4 give rise to out-of-plane and in-plane C–C π -bonding, respectively. The C–C bond of **4S**, therefore, has some triple bond character. According to the NBO analysis, the best Lewis structure for **4S** may be described as a localized π -bond orbital and an almost nonbonding C–C σ' orbital.⁸

Silavinylidenecarbene (5S) (in Figure 5). These three doubly excited configurations from the π -bonding ($2b_1$ and $3b_2$) MOs to the nonbonding ($3b_1$) and π -antibonding ($4b_1$ and $4b_2$) MOs (Φ_2 – Φ_4 in Table 9) lengthen the C–C and Si–C bond distances. The C–C and Si–C bond lengths of **5S** are shorter than those of the **3S** isomer. It is observed that the sum of electron occupation numbers (0.184) in the three virtual MOs for **5S** is smaller than that (0.234) for **3S**.

Planar Silacyclopentyne (6S) (in Figure 6). Structure **6S** is a second-order saddle point on the PES with imaginary vibrational frequencies corresponding to the SiH₂ twisting and Si–C antisymmetric stretching motions (vide infra). The C–C bond distance of **6S** is considerably longer than that of **4S**, suggesting weaker multibond character. The Si–C bond distance for **6S** is also longer than that for the related **4S**, implying a weaker single bond.

Ethynylsilylene (7S) (in Figure 7). The C–C bond length increases with more advanced treatments of correlation effects, while the Si–C bond distance and all three bond angles decrease. The C–C bond distance of **7S** is longer than that of **2S** but is close to that of **4S**. The Si–C bond length is the longest among the seven isomers, and the Si–H bond distance is also the longest among the five isomers possessing a Si–H bond (**2S**, **4S**, **5S**, **6S**, and **7S**). The isomer **7S** may be regarded as a silylene or T-type complex, as shown in Scheme 3, which is similar to the electronic structure of the silacyclopentynylidene molecule.^{47,48}

SCHEME 3



4.3. Dipole Moments. 1-Silacyclopentenylidene (1S). With our most reliable cc-pV(Q+d)Z CCSD(T) method, the dipole moment of isomer **1S** is predicted to be 1.043 debye, which is significantly smaller than that of the analogous C₃H₂ isomer [cyclopentenylidene **1S**, 3.408 debye with the cc-pVQZ CCSD(T) level]. The standard electronegativities (by Pauling) of the three constituent atoms are Si (1.8), C (2.5), and H (2.1).⁴⁹

TABLE 10: Natural Orbital Electron Occupation Numbers of the Valence MOs of the cc-pV(Q+d)Z CASSCF Wave Functions for the Seven SiC₂H₂ Structures at the cc-pV(Q+d)Z CCSD(T) Optimized Geometries

1S	2S	3S	4S	5S	6S	7S
5a ₁ (1.995)	7a'(1.985)	6a ₁ (1.984)	5a ₁ (1.992)	6a ₁ (1.988)	5a ₁ (1.993)	7a'(1.987)
6a ₁ (1.981)	8a'(1.982)	7a ₁ (1.979)	6a ₁ (1.989)	7a ₁ (1.983)	6a ₁ (1.989)	8a'(1.980)
7a ₁ (1.967)	9a'(1.978)	8a ₁ (1.975)	7a ₁ (1.970)	8a ₁ (1.969)	7a ₁ (1.970)	9a'(1.977)
8a ₁ (1.937)	10a'(1.974)	9a ₁ (1.933)	8a ₁ (1.911)	9a ₁ (1.968)	8a ₁ (1.930)	10a'(1.970)
	11a'(1.937)					11a'(1.938)
	12a'(1.899)					12a'(1.905)
	13a'(0.068)					13a'(0.071)
2b ₁ (1.938)		2b ₁ (1.915)	2b ₁ (1.983)	2b ₁ (1.909)	2b ₁ (1.934)	
3b ₁ (0.059)		3b ₁ (0.087)	3b ₁ (1.936)	3b ₁ (0.077)	3b ₁ (0.032)	
		4b ₁ (0.059)		4b ₁ (0.037)		
3b ₂ (1.994)	2a''(1.934)	2b ₂ (1.975)	3b ₂ (1.966)	2b ₂ (1.981)	3b ₂ (1.988)	2a''(1.939)
4b ₂ (1.959)	3a''(0.099)	3b ₂ (1.915)	4b ₂ (0.096)	3b ₂ (1.927)	4b ₂ (1.960)	3a''(0.088)
5b ₂ (0.044)	4a''(0.062)	4b ₂ (0.088)	5b ₂ (0.021)	4b ₂ (0.070)	5b ₂ (0.073)	4a''(0.060)
1a ₂ (0.055)			1a ₂ (0.062)		1a ₂ (0.053)	

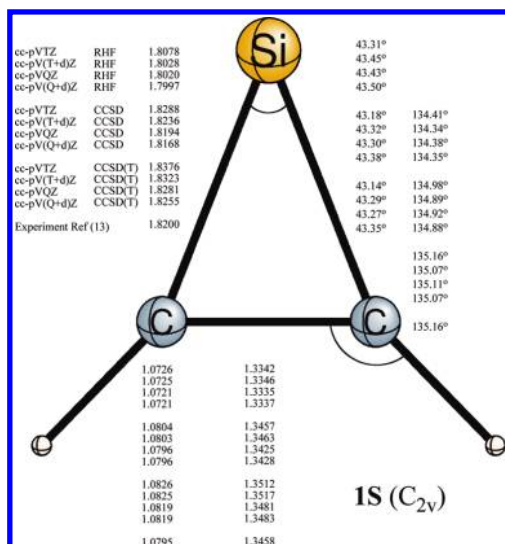


Figure 1. Predicted geometries for the closed-shell singlet ground state of 1-silacyclopentenylidene (**1S**). Bond lengths are in Å.

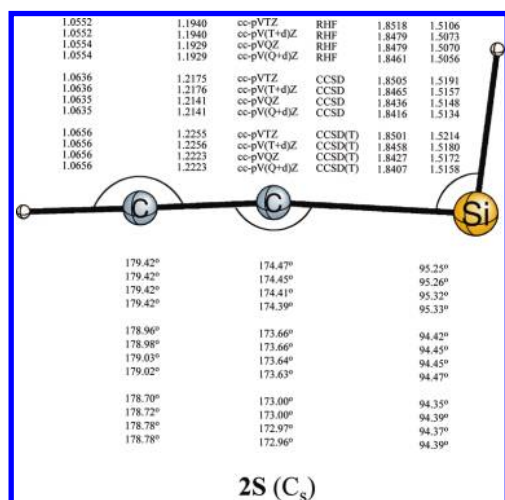


Figure 2. Predicted geometries for ethynylsilanediyl (**2S**). Bond lengths are in Å.

Since the Si atom has a smaller electronegativity (i.e., more electropositive) than the C atom, **1S** possesses a smaller dipole moment than its carbon analogue. However, the sign of the dipole moment remains the same ($^-\text{SiC}_2\text{H}_2^+$) along the C_2 axis as that in the case for the cyclopropenylidene (**1S**), $^-\text{C}_3\text{H}_2^+$. The dipole moment of **1S** increases with the size of basis set, while it decreases with inclusion of correlation effects due to the $\Phi_2[(3b_1)^2 \leftarrow (8a_1)^2]$ excitation. The $8a_1$ MO is related to the lone pair orbital localized on the Si atom (parallel to the C_2 axis), while the $3b_1$ MO (nonbonding) resembles the 3p (perpendicular to the C_2 axis) orbital of the Si atom. The double excitation, therefore, lowers the degree of charge separation along the C_2 axis, which decreases the magnitude of the dipole moment. This interpretation is supported by the fact that the natural orbital electron occupation numbers for the $8a_1$ and $3b_1$ MOs in Table 10 are 1.937 and 0.059, respectively.

Ethynylsilanediyl (2S). The dipole moment of isomer **2S** is predicted to be 0.874 debye at the cc-pV(Q+d)Z CCSD(T) level of theory, this value being the smallest in magnitude among the seven isomers. The small magnitude may be attributed to the fact that the electropositive Si and H atoms reside at the two ends of the molecule. The theoretical dipole moment decreases with inclusion of correlation effects due to the double excitation from the in-plane $12a'$ MO (lone pair orbital on the

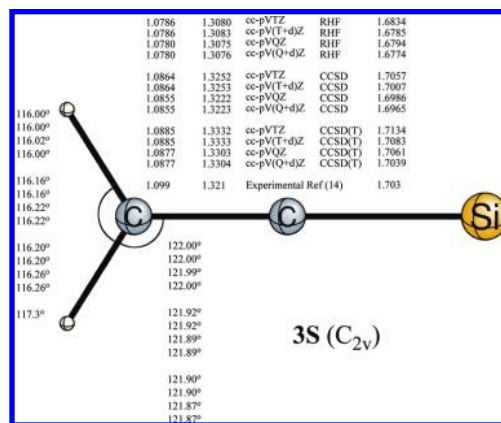


Figure 3. Predicted geometries for vinylidenesilanediyl (**3S**). Bond lengths are in Å.

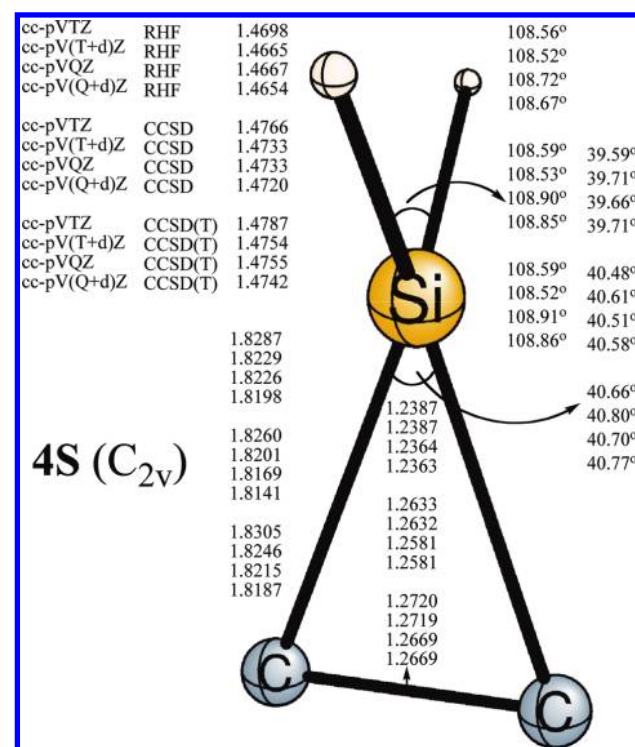


Figure 4. Predicted geometries for silacyclopentyne (**4S**). Bond lengths are in Å.

Si atom, occupation number 1.899) to the out-of-plane $3a''$ MO ($3p$ orbital on the Si atom, occupation number 0.099), $\Phi_2[(3a'')^2 \leftarrow (12a')^2]$ in Table 9.

Vinylidenesilanediyl (3S). The isomer **3S** has a relatively small dipole moment of 0.941 debye at the cc-pV(Q+d)Z CCSD(T) level of theory, the direction being necessarily along the C_2 axis with sign $^+\text{H}_2\text{SiCC}^-$. As with **2S**, the small magnitude is a consequence of the two electropositive atoms (Si and H) residing at opposite ends of the molecule.

Silacyclopentyne (4S). The dipole moment of **4S** [3.149 debye with the cc-pV(Q+d)Z CCSD(T) method] is third largest among the seven isomers, the direction being necessarily along the C_2 axis with sign $^+\text{H}_2\text{SiC}^-$. The large magnitude of this dipole moment may be attributed to the fact that the electropositive Si and H atoms inhabit the same side of the molecule as a SiH_2 group.

Silavinylidenecarbene (5S). The dipole moment of **5S** [6.005 debye with the cc-pV(Q+d)Z CCSD(T) method] is the largest among the seven isomers, the direction being along the C_2 axis

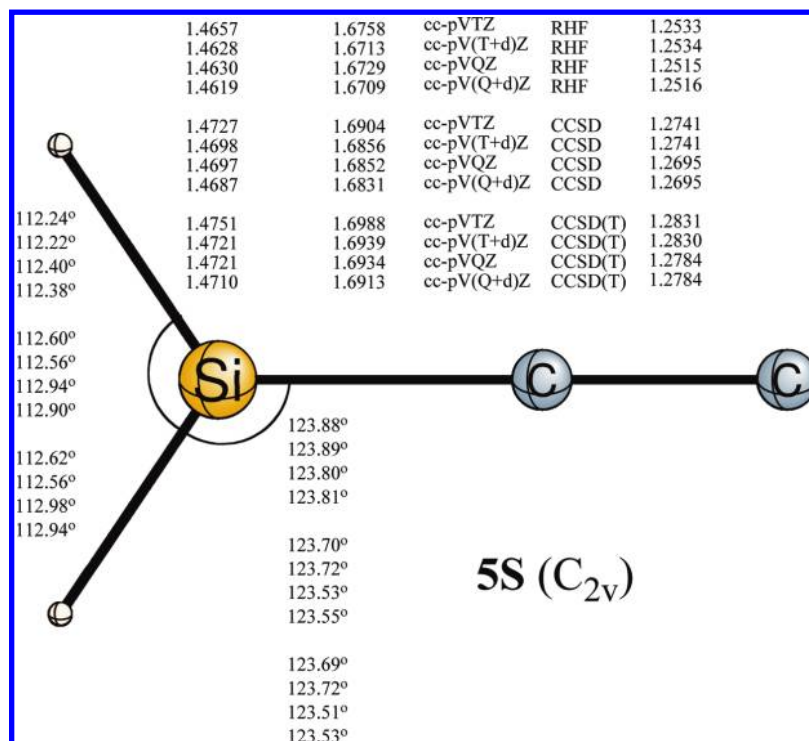


Figure 5. Predicted geometries for silavinylidenecarbene (5S). Bond lengths are in Å.

with sign $^+H_2SiC_2^-$. The large magnitude of this dipole moment may be attributed to considerations similar to those just discussed for 4S. Electron occupation numbers of the three a_1 ($7a_1$, $8a_1$, and $9a_1$) MOs, which are parallel to the C_2 axis, are all noticeably smaller than 2.0 (in Table 10), indicating a diminished polarization of the molecule with correlation effects, decreasing the magnitude of the dipole moment.

Planar Silacyclopropyne (6S). The dipole moment of isomer 6S [3.291 debye with the cc-pV(Q+d)Z CCSD(T) method] is second largest among the seven isomers, the direction being along the C_2 axis with sign $^+H_2SiC_2^-$. The responses of the dipole moment for 6S to basis set and correlation effects are similar to those for 4S.

Ethynylsilylene (7S). The dipole moment of 7S [2.398 debye with the cc-pV(Q+d)Z CCSD(T) method] is the median among the seven isomers. The dipole moment decreases with the advanced treatment of correlation effects, which may be associated with the double excitation from the in-plane $12a'$ MO (lone pair orbital on the Si atom, occupation number is 1.905) to the out-of-plane $3a''$ MO (3p orbital on the Si atom, occupation number is 0.088), $\Phi_2[(3a'')^2 \leftarrow (12a')^2]$, shown in Table 9.

4.4. Harmonic Vibrational Frequencies and Infrared (IR) Intensities. Among the seven low-lying singlet stationary points of SiC_2H_2 located in this study, six structures have been found to be minima, and one structure (6S) is a second-order saddle point.

1-Silacycloprenylidene (1S). For 1S, seven vibrational modes have been observed experimentally by Maier and Reisenauer.^{7,8} Theoretically predicted harmonic vibrational frequencies for ω_3 , ω_4 , ω_6 , ω_8 , and ω_9 modes [895, 777, 687, 1116, and 684 cm^{-1} at the cc-pV(Q+d)Z CCSD(T) level, respectively] are reasonably consistent with the experimental fundamental frequencies (875, 762, 677, 1086, and 672 cm^{-1} , respectively). Furthermore, it is encouraging that these seven observed vibrational modes have relatively strong theoretical IR intensities, as seen in Table 1. All of the predicted harmonic

vibrational frequencies decrease with improved treatment of correlation effects, reflecting the elongated bond distances and larger CCH bond angle. The ω_2 (a_1) frequency for the C—C stretching mode [1467 cm^{-1} at the cc-pV(Q+d)Z CCSD(T) level] is 155 cm^{-1} lower than the corresponding frequency [1622 cm^{-1} at the cc-pVQZ CCSD(T) level] of cyclopropenylidene (1S), reflecting a considerably longer C—C bond distance.

Ethynylsilanediyl (2S). For structure 2S, seven vibrational modes have been observed experimentally.^{7,8} Theoretically predicted harmonic vibrational frequencies for ω_2 , ω_4 , ω_5 , ω_6 , and ω_8 modes [2029, 826, 618, 608, and 741 cm^{-1} at the cc-pV(Q+d)Z CCSD(T) level, respectively] are reasonably consistent with the experimental fundamental frequencies (1970, 815, 614, 605, and 723 cm^{-1} , respectively). The C—C stretching frequency [$\omega_2(a') = 2029$ cm^{-1} at the cc-pV(Q+d)Z CCSD(T) level] for isomer 2S is the highest among the seven structures and very close to that (2006 cm^{-1}) for the isolated acetylene molecule.

Vinylidenesilanediyl (3S). For 3S, only two vibrational modes at $\nu_2(a_1) = 1667.9$ and $\nu_5(b_1) = 957.7$ cm^{-1} have been reported.^{7,8} Theoretically predicted harmonic vibrational frequencies for these corresponding modes are 1700 and 981 cm^{-1} at the cc-pV(Q+d)Z CCSD(T) level. Since the $\omega_1(a_1)$ and $\omega_4(a_1)$ modes have comparable IR intensities to the ω_2 and ω_5 modes, it may be reasonable to expect the future experimental detection of at least two more vibrational frequencies.

Silacycloprenylidene (4S). At the RHF level of theory, the Si—C asymmetric mode $\omega_9(b_2)$ for the 4S isomer possesses an imaginary vibrational frequency, indicating a C_s symmetry equilibrium structure at this level of theory. This is consistent with the DZ SCF prediction by Frenking et al.¹⁰ However, this ω_9 frequency becomes real with the coupled cluster wave functions, as shown in Table 4, in accord with the MP2/6-31G** study by Maier et al.^{7,8} Seven vibrational modes have been detected for 4S in Ar matrixes at 10 K.^{7,8} Theoretically predicted harmonic vibrational frequencies for the ω_2 , ω_3 , ω_4 , ω_7 , and ω_8 modes [1798, 1043, 822, 667, and 772 cm^{-1} at the cc-

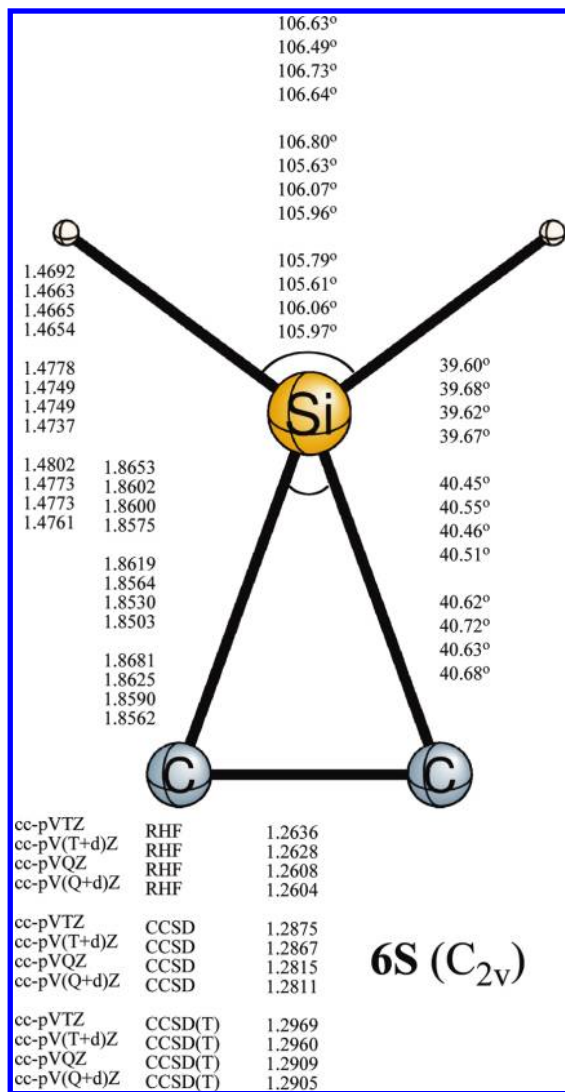


Figure 6. Predicted geometries for planar silacyclopropyne (**6S**). Bond lengths are in Å.

pV(Q+d)Z CCSD(T) level, respectively] are reasonably consistent with the experimental fundamental frequencies (1770, 1023, 837, 676, and 757 cm⁻¹, respectively); the differences can be reasonably attributed to anharmonicity. The vibrational frequency for the C–C stretching mode $\omega_2(a_1)$ of **4S** [1798 cm⁻¹ at the cc-pV(Q+d)Z CCSD(T) level] is higher than that for **1S** (1467 cm⁻¹ with the same method), reflecting the shorter C–C bond length (higher multiple-bond character).

Silavinylidenecarbene (5S). For this isomer, no vibrational modes have been observed experimentally. The two vibrational frequencies for the C–C [$\omega_2(a_1)$] and Si–C [$\omega_4(a_1)$] stretching modes of **5S** are considerably higher than the corresponding values of **3S**, reflecting the shorter bond distances. Although isomer **5S** is energetically the highest lying among the six equilibrium structures, all vibrational modes except the SiCC bending motions [$\omega_6(b_1)$ and $\omega_9(b_2)$] are determined to have strong IR intensities.

Planar Silacyclopropyne (6S). Structure **6S** has two imaginary vibrational frequencies, for the SiH₂ twisting [$\omega_5(a_2)$] and Si–C antisymmetric stretching [$\omega_9(b_2)$] modes, at all levels of theory. The eigenvectors of the two imaginary frequencies lead the molecule from **6S** to **4S** and from **6S** to **5S**, respectively, as expected. The harmonic vibrational frequency for the C–C stretching mode [$\omega_2(a_1)$ = 1700 cm⁻¹ at the cc-pV(Q+d)Z CCSD(T) level] is 98 cm⁻¹ lower than the corresponding

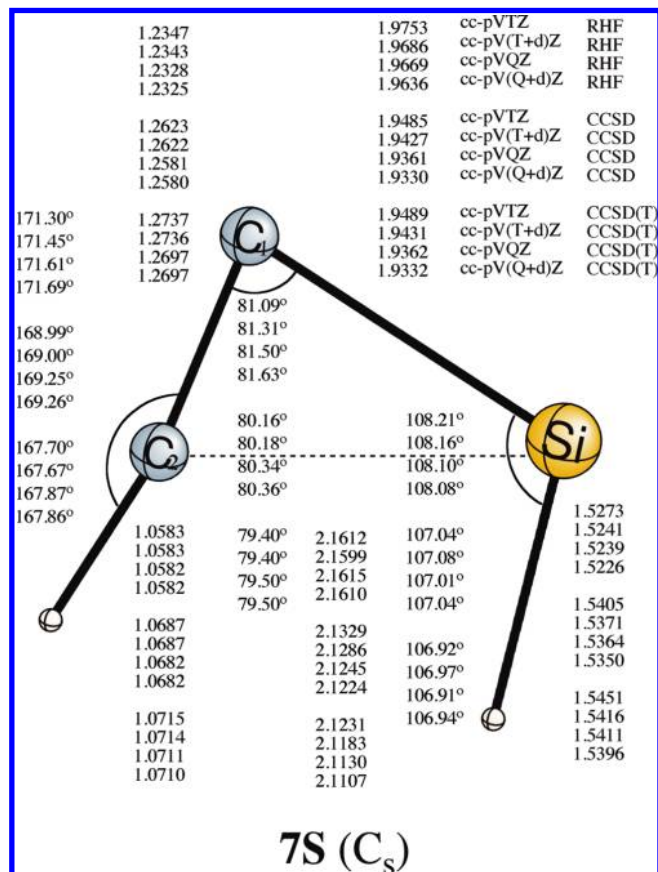


Figure 7. Predicted geometries for ethynylsilylene (**7S**). Bond lengths are in Å.

frequency (1798 cm⁻¹ at the same level) for structure **4S** due to the latter's shorter C–C bond distance.

Ethynylsilylene (7S). The harmonic vibrational frequency for the C–C stretching mode of **7S** [$\omega_3(a')$ = 1722 cm⁻¹ and $r_e(C-C)$ = 1.270 Å at the cc-pV(Q+d)Z CCSD(T) level] is 307 cm⁻¹ lower than the corresponding frequency for structure **2S** [$\omega_2(a')$ = 2029 cm⁻¹ and $r_e(C-C)$ = 1.222 Å] and 76 cm⁻¹ lower than that for isomer **4S** [$\omega_2(a_1)$ = 1798 cm⁻¹ and $r_e(C-C)$ = 1.267 Å]; however, it is 22 cm⁻¹ higher than that of **6S** [$\omega_2(a_1)$ = 1700 cm⁻¹ and $r_e(C-C)$ = 1.291 Å]. Since **7S** is energetically lower lying than **4S** and most of the vibrational modes show IR intensities comparable with the four experimentally detected isomers (**1S**–**4S**), it may be possible to identify this isomer (**7S**) with appropriate laboratory conditions.

4.5. Energetics. The relative energies of the seven SiC₂H₂ isomers are presented in Table 8. There, 1-silacyclopropenylidene (**1S**) is confirmed to be the global minimum on the singlet SiC₂H₂ PES. The second lowest-lying isomer is predicted to be vinylidenesilanediyl (**3S**). The relative energies (with ZPVE-corrected values in parentheses) of isomer **3S** (with respect to **1S**) are determined to be 22.04 (21.44) (RHF), 19.34 (18.70) (CCSD), and 18.19 (17.55) kcal mol⁻¹ [CCSD(T)] with the cc-pVQZ(C,H)/cc-pV(Q+d)Z(Si) basis sets. The energy difference between **1S** and **3S** diminishes with the level of sophistication. This implies that **3S** is preferentially stabilized with correlation effects compared to **1S**. The third lowest-lying isomer is predicted to be ethynylsilanediyl (**2S**). The relative energy of isomer **2S** with respect to **1S** is determined to be 21.85 (18.62) kcal mol⁻¹ at the cc-pV(Q+d)Z [CCSD(T)] level of theory. The energy ordering of the first three lowest-lying SiC₂H₂ isomers is consistent with the predictions at the DZ+P CISD level of theory by Frenking et al.¹⁰

The fourth lowest-lying isomer is predicted to be ethynylsilylene (**7S**), lying 42.13 (38.74) kcal mol⁻¹ above **1S** at the CCSD(T) level with our largest basis set, while the fifth lowest-lying isomer is determined to be silacyclopropyne (**4S**), lying 49.86 (46.08) kcal mol⁻¹ above the global minimum **1S** with the same method. It is seen that **4S** is favorably stabilized by correlation effects, probably due to the C–C bond's higher multiple bond character.

Isomer **5S** is the highest-lying equilibrium structure located in this research. The relative energies with respect to **1S** are determined to be 52.27 (47.37) (RHF), 58.08 (53.41) (CCSD), and 56.72 (52.08) kcal mol⁻¹ [CCSD(T)] with our largest basis set. The decrease in the total electron occupation number for the seven occupied orbitals is 0.33 [14.0 (RHF) – 13.67 (CASSCF)] for **3S**, while it is 0.28 [14.0 (RHF) – 13.72 (CASSCF)] for **5S**. It is clearly seen that **3S** is effectively stabilized by correlation effects relative to **5S**. It is well-known that the Si atom generally does not form multiple bonds in molecular species.^{8,47,50} The planar silacyclopropyne (**6S**) structure has two imaginary vibrational frequencies; the corresponding eigenvectors lead to isomers **4S** and **5S**. The relative energy of **6S** with respect to **1S** is, therefore, higher than those for **4S** and **5S**. The qualitative energy ordering of the six equilibrium structures is consistent with the predictions at the DZ+P SCF level of theory by Frenking et al.¹⁰ and at the aug-cc-pVTZ CCSD(T) level of theory by Ikuta et al.²²

5. Concluding Remarks

Ab initio electronic structure theory has been employed in order to systematically investigate the closed-shell singlet electronic state potential energy surfaces of SiC₂H₂. Among the seven SiC₂H₂ structures located in this research, six are found to be equilibrium structures, and one (**6S**) is a second-order saddle point. With our highest level of theory, cc-pVQZ(C,H)/cc-pV(Q+d)Z(Si) CCSD(T), the energy ordering and energy differences (in kcal mol⁻¹, with the ZPVE-corrected values in parentheses) for the six equilibrium structures are predicted to be 1-silacyclopropenylidene (**1S**) [0.0 (0.0)] < vinylidenesilanediyli (**3S**) [18.2 (17.6)] < ethynylsilanediyli (**2S**) [21.9 (18.6)] < ethynylsilylene (**7S**) [42.1 (38.7)] < silacyclopropyne (**4S**) [49.9 (46.1)] < silavinylidenecarbene (**5S**) [56.7 (52.1)]. Theoretically computed vibrational frequencies and related IR intensities for the four isomers (**1S**, **2S**, **3S**, and **4S**) are in good agreement with existing experimentally observed values. High-quality theoretical spectroscopic fingerprints are provided to aid the identification of the isomers that have not yet been synthesized.

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Note Added in Proof. After submission of our manuscript we became aware of a similar study, performed independently, that covers many of the compounds discussed herein [Thorwirth, S.; Harding, M. E. *J. Chem. Phys.* 2009, 130, 214303].

References and Notes

(1) Reisenauer, H. P.; Maier, G.; Riemann, A.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 641.

- (2) Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, 107, 137.
- (3) Maier, G.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, 109, 5183.
- (4) Maier, G.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Spirko, V.; Hess, B. A.; Schaad, L. J. *J. Chem. Phys.* **1989**, 91, 4763.
- (5) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *Astrophys. J.* **1985**, 299, L63.
- (6) Cernicharo, J.; Gottlieb, C. A.; Guélin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1991**, 368, L39.
- (7) Maier, G.; Reisenauer, H. P.; Pacl, H. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1248.
- (8) Maier, G.; Pacl, H.; Reisenauer, H. P.; Meudt, A.; Janoschek, R. *J. Am. Chem. Soc.* **1995**, 117, 12712.
- (9) Maier, G.; Reisenauer, H. P.; Egenolf, H. *Eur. J. Org. Chem.* **1998**, 1313.
- (10) Frenking, G.; Remington, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, 108, 2169.
- (11) Cooper, D. L. *Astrophys. J.* **1990**, 354, 229.
- (12) Vacek, G.; Colegrove, B. T.; Schaefer, H. F. *J. Am. Chem. Soc.* **1991**, 113, 3192.
- (13) Izuha, M.; Yamamoto, S.; Saito, S. *Can. J. Phys.* **1994**, 72, 1206.
- (14) McCarthy, M. C.; Thaddeus, P. *J. Mol. Spectrosc.* **2002**, 211, 228.
- (15) Francisco, J. S.; Kurz, C.; McDouall, J. J. W. *Chem. Phys. Lett.* **1989**, 162, 79.
- (16) McDouall, J. J. W.; Schlegel, H. B.; Francisco, J. S. *J. Am. Chem. Soc.* **1989**, 111, 4622.
- (17) Su, M.-D.; Amos, R. D.; Handy, N. C. *J. Am. Chem. Soc.* **1990**, 112, 1499.
- (18) Apeloig, Y.; Karni, M.; West, R.; Welsh, K. *J. Am. Chem. Soc.* **1994**, 116, 9719.
- (19) Largo, A.; Barrientos, C. *J. Phys. Chem.* **1994**, 98, 3978.
- (20) Ketvirtis, A. E.; Bohme, D. K.; Hopkinson, A. C. *J. Phys. Chem.* **1995**, 99, 16121.
- (21) Sherrill, C. D.; Brandow, C. G.; Allen, W. D.; Schaefer, H. F. *J. Am. Chem. Soc.* **1996**, 118, 7158.
- (22) Ikuta, S.; Saitoh, T.; Wakamatsu, S. *J. Chem. Phys.* **2004**, 121, 3478.
- (23) Takahashi, M.; Sakamoto, K. *J. Phys. Chem. A* **2004**, 108, 7301.
- (24) Talbi, D. *Chem. Phys.* **2005**, 313, 17.
- (25) Kassaei, M. Z.; Musavi, S. M.; Buazar, F.; Ghambarian, M. *J. Mol. Struct.* **2005**, 722, 151.
- (26) Kassaei, M. Z.; Musavi, S. M.; Ghambarian, M. *Heteroat. Chem.* **2007**, 18, 283.
- (27) Dunning, T. H. *J. Chem. Phys.* **1989**, 90, 1007.
- (28) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, 98, 1358.
- (29) Dunning, T. H.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, 114, 9244.
- (30) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, 76, 1910.
- (31) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, 92, 3033.
- (32) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, 157, 479.
- (33) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, 176, 27.
- (34) Siegbahn, P. E. M.; Heiberg, A.; Roos, B. O.; Levy, B. *Phys. Scr.* **1980**, 21, 323.
- (35) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, 48, 157.
- (36) Roos, B. O. *Int. J. Quantum Chem.* **1980**, S14, 175.
- (37) Pulay, P. *Mol. Phys.* **1969**, 17, 197.
- (38) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer H. F., Ed.; Plenum: New York, 1977; Vol. 4, pp 153–185.
- (39) Yamaguchi, Y.; Osamura, Y.; Goddard, J. D.; Schaefer, H. F. *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford University Press: New York, 1994.
- (40) Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, 276, 70.
- (41) Szalay, P.; Gauss, J.; Stanton, J. F. *Theor. Chim. Acc.* **1998**, 100, 5.
- (42) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem., Symp.* **1992**, 26, 879.
- (43) *ACES II*; Stanton, J. F.; Gauss, J.; Watts, J. D.; Szalay, P. G.; Bartlett, R. J.; with contributions from Auer, A. A.; Bernholdt, D. E.; Christiansen, O.; Harding, M. E.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Lauderdale, W. J.; Metzroth, T.; Michauk, C.; O'Neill, D. P.; Price, D. R.; Ruud, K.; Schiffmann, F.; Tajti, A.; Varner, M. E.; Vázquez, J.; and the integral packages: *MOLECULE* (Almlöf, J.; Taylor, P. R.), *PROPS* (Taylor, P. R.), and *ABACUS* (Helgaker T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.). Current version see <http://www.aces2.de>.
- (44) Werner, H. J.; Knowles, P. J.; MOLPRO, version 2002.1, a package of ab initio programs; <http://www.molpro.net> (2002).
- (45) *PSI 2.0.8*; Janssen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamilton, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fennann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald,

G. B.; Fox, D. J.; Gaw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F. PSITECH, Inc., Watkinsville, GA, 1994.

(46) Crawford, T. D.; Sherrill, C. D.; Valeev, E. F.; Fermann, J. T.; King, R. A.; Leininger, M. L.; Brown, S. T.; Janssen, C. L.; Seidl, E. T.; Kenny, J. P.; Allen, W. D. *J. Comput. Chem.* **2007**, 28, 1610.

(47) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1984**, 80, 3552.

(48) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, 109, 6577.

(49) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

(50) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 272.

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