Cyclopropyne and Silacyclopropyne: A World of Difference

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Abstract: The lowest singlet and triplet states of cyclopropyne and silacyclopropyne have been investigated using *ab initio* electronic structure methods. Employing DZP and TZ(2df,2pd) basis sets, optimum geometries and harmonic vibrational frequencies have been obtained with the following methods: restricted Hartree−Fock or self-consistent-field (SCF), two-configuration self-consistent-field (TCSCF), single and double excitation configuration interaction (CISD) and coupled cluster (CCSD), and CCSD incorporating perturbative estimates of connected triple excitations [CCSD(T)]. Although silacyclopropyne has been observed via matrix isolation, cyclopropyne remains a high-lying saddle point on the C_3H_2 potential energy surface. Structural and electronic differences between these two molecules are explored. The triplet states of cyclopropyne and silacyclopropyne are minima on their potential energy surfaces and lie higher in energy than the corresponding singlet states, by 10 and 40 kcal mol^{-1}, respectively.

I. Introduction

Three C_3H_2 isomers have been generated in the laboratory to date: cyclopropenylidene (**1**), propargylene (**2**), and propadienylidene (**3**). Both **1** and **3** have also been identified in interstellar space,[1−3] where cyclopropenylidene is in fact the most abundant of all hydrocarbons. Propargylene has a triplet ground state and was first identified in 1965 by its ESR spectrum.[4] This isomer exhibits unusually fluxional bonding characteristics[5] that have heightened interest and until recently defied definitive description.[6,7] Although ESR zero-field splitting parameters implied that **2** has a linear geometry, Hehre and co-workers predicted in 1976 a W-shaped structure with C_2 symmetry at the STO-3G SCF level of theory.[8] Subsequent theoretical studies[5,9−11] suggested a planar structure, but the most recent experimental[6] and theoretical results—obtained using multireference configuration interaction methods[7]—indicate that the original C_2 structure is correct.

Theory predicted[8,12,13] that singlet **1** is the global C_3H_2 minimum, and this species was first detected in the laboratory in 1984 by Reisenauer, Maier, Riemann, and Hoffmann.[14] These workers isolated **1** in an argon matrix and confirmed its identity by comparison with the theoretical infrared spectrum determined by Lee, Bunge, and Schaefer at the DZP SCF and DZP TCSCF levels of theory.[13] They also showed that **1** could be converted photochemically to **2**, as shown in Scheme 1. Upon further irradiation, **2** is converted to **3**, as first demonstrated in 1987 by Maier and co-workers,[15] the structure of the propadienylidene isomer being confirmed with the aid of infrared spectral predictions from second-order Møller−Plesset perturbation theory (MP2) with a 6-31G** basis.

Notwithstanding the numerous spectroscopic and theoretical studies of C_3H_2 species, the only other isomer to receive more than a cursory examination is cyclopropyne (**4**),[10,16] long considered a high-lying saddle point on the potential energy surface.[17] In 1994 an unprecedented formal analog of cyclopropyne was trapped by Maier, Reisenauer, and Pacl, who detected silacyclopropyne (**6**) in a matrix isolation infrared study.[18] This surprising result contradicted previous theoretical predictions at the DZ SCF level of theory that silacyclopropyne is a transition state on the SiC_2H_2 potential energy surface.[19] Nevertheless, infrared absorption at 2229 and 2214 cm^{-1} strongly suggested the presence of a silylene moiety, prompting Maier and co-workers to employ the MP2/6-31G** method again to estimate the IR spectra of silacyclopropyne (**6**) and the vinylidene structure **7**. Silacyclopropyne becomes a minimum at this level of theory, and its theoretical spectrum matches the observed peaks more closely than does silapropadienylidene (**7**). The most serious discrepancy was the absence of a relatively intense band predicted at 819 cm^{-1}.

The identification of **6** would stand as one of the most important experimental discoveries in physical organic chemistry in recent years. Here harmonic vibrational frequencies and infrared intensities for **6** and **7** are presented at more reliable levels of theory, as well as corresponding energies relative to the SiC_2H_2 global minimum **5**. In addition, high-level estimates

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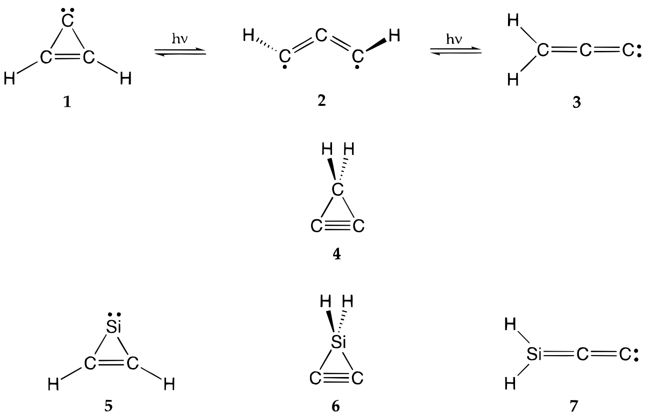
Scheme 1



of the singlet−triplet splitting in silacyclopropyne (**6**) are advanced. The reported detection of **6** also brings the prevailing theoretical view[16,17] of the parent cyclopropyne (**4**) into serious question, and accordingly a renewed and vigorous scrutiny of cyclopropyne is effected here by means of high-level *ab initio* methods.

II. Theoretical Approach

Two basis sets of contracted Gaussian functions were employed in the present study. The double-ζ plus polarization (DZP) set is the standard Huzinaga−Dunning[20−22] double-ζ basis augmented with a set of five d-type polarization functions on each carbon and silicon atom [$\alpha_d(C) = 0.75$, $\alpha_d(Si) = 0.50$] and a set of p-type functions on each hydrogen [$\alpha_p(H) = 0.75$]. The TZ(2df,2pd) basis is derived from Huzinaga's[20] (10s6p) set for carbon, (12s9p) set for silicon, and (5s) set for hydrogen, as contracted by Dunning[23] for carbon and hydrogen and by McLean and Chandler[24] for silicon. The triple-ζ set is supplemented by two manifolds of five d-type polarization functions and one set of seven f-type functions on each heavy atom [$\alpha_d(C) = 1.5, 0.375$, $\alpha_f(C) = 0.8$, $\alpha_d(Si) = 1.0, 0.25$, $\alpha_f(Si) = 0.32$] as well as two sets of p-type and one set of five d-type polarization functions on each hydrogen [$\alpha_p(H) = 1.5, 0.375$, $\alpha_d(H) = 1.0$]. Geometries were optimized using analytic first derivatives at the following levels of theory: SCF,[25,26] TCSCF,[26] CISD,[27−31] CCSD,[32−35] and CCSD(T),[36−39] which adds perturbatively the connected triples to the CCSD method. Harmonic vibrational frequencies were determined via analytic SCF and TCSCF second derivatives or by finite differences of analytic CISD, CCSD, and CCSD(T) first derivatives. For the configuration interaction and coupled cluster methods, the core orbitals [C(1s), Si(1s,2s,2p)] were constrained to be doubly occupied, and the highest-lying (1s*) virtual orbital on each heavy atom was also deleted from the correlation procedure. The finite difference procedure required the evaluation of gradients for geometries displaced into the C_s and C_2 point groups. For cyclopropyne, the largest single-reference configuration space required 145 281 single and double excitations in C_s symmetry with the TZ(2df,2pd) basis. In the CCSD and CCSD(T) calculations, the $\mathcal{T}_1$ diagnostic[40,41] was as high as 0.034, which indicates that the single-reference SCF method may conceivably be insufficient to provide a proper reference wave function for the coupled-cluster procedures. The molecular geometry was optimized under the confines of C_{2v} symmetry, and the Cartesian gradients were less than 10^{-5} for optimized structures in all cases.

The primary electronic configuration of cyclopropyne is

$$(1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(4a_1)^2\,(1b_1)^2(2b_2)^2(5a_1)^2(6a_1)^2(2b_1)^2$$

However, ring strain engenders a second important configuration, promoting both electrons of the second highest occupied molecular orbital ($6a_1$), which corresponds to the in-plane π bond, into an in-plane orbital ($3b_2$) which is antibonding with respect to the multiple bond. The CI coefficients of the two-configuration (TC) SCF wave function with a TZ(2df,2pd) basis set are $C_1 = 0.948$ and $C_2 = -0.318$ for cyclopropyne, indicating a substantial degree of diradical character. Silacyclopropyne has an analogous electronic structure, but the contribution by the second [$(8a_1)^2 \rightarrow (4b_2)^2$] configuration is smaller; at the same level of theory the two CI coefficients are $C_1 = 0.975$ and $C_2 = -0.221$. This comparison provides clear evidence that silacyclopropyne is better described as a closed-shell species than the parent cyclopropyne.[42] Plots of the $6a_1$ and $3b_2$ orbitals of cyclopropyne and the analogous $8a_1$ and $4b_2$ orbitals of silacyclopropyne are found in Figure 1.

Zero-point vibrational energies (ZPVEs) were evaluated at the DZP SCF level of theory for all structures except cyclopropyne and silacyclopropyne, for which the DZP TCSCF level was used. To account for theoretical errors and vibrational anharmonicity, the ZPVEs have been scaled by 0.91, as recommended by Grev *et al.*[43] Compared to the DZP CCSD(T) level of theory, this procedure yields ZPVEs which are slightly lower because it includes estimates of vibrational anharmonicity; for **4**, **6**, and **7**, the scaled SCF ZPVEs are lower by 0.0, 0.8, and 0.3 kcal mol^{-1}, respectively. Relative energies of triplet species were predicted by single-point energy evaluations using the TZ(2df,2pd) CCSD(T) level of theory at the DZP CISD optimized geometries, designated TZ(2df,2pd) CCSD(T)//DZP CISD. Relative energies computed in this manner for the singlet states differed by 0.1 kcal mol^{-1} or less from the energies obtained using the TZ(2df,2pd) CCSD(T) geometries. The PSI package of *ab initio* quantum chemistry programs[44] was used for the present study.

III. Singlet States.

Total energies and optimized geometries at several levels of theory are presented in Tables 1−4. The full tables, which include results at all levels of theory considered and total

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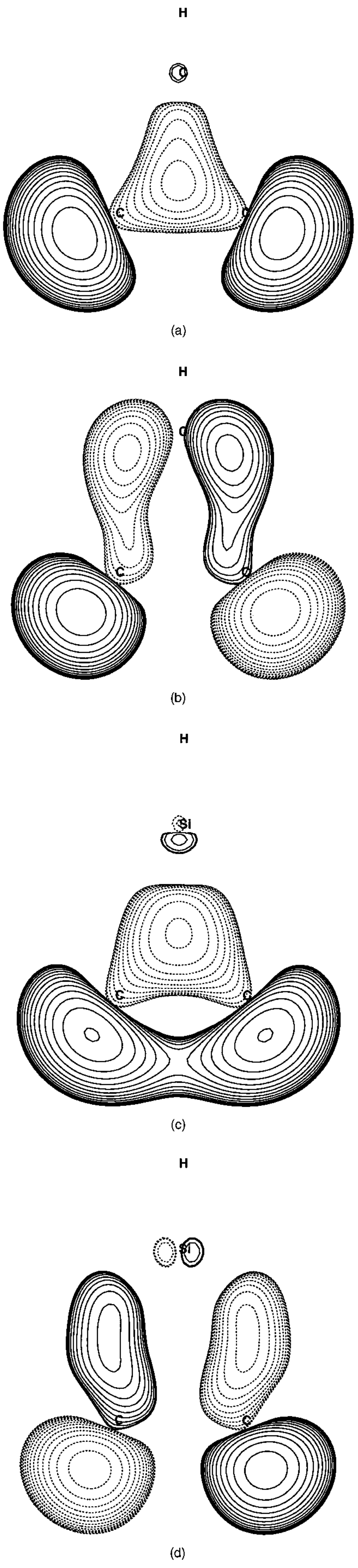

Figure 1. DZP TCSCF molecular orbitals for cyclopropyne (a and b) and silacyclopropyne (c and d) which are fractionally occupied in the TCSCF wave function: (a) $6a_1$, (b) $3b_2$, (c) $8a_1$, (d) $4b_2$.

Table 1. Stationary Point Structures of $\tilde{X}\ {}^1A_1$ and $\tilde{a}\ {}^3B_2$ Cyclopropyne (**4**) at Several Levels of Theory[a]

method	r(C≡C)	r(C−C)	r(C−H)	$\theta_{C(CH_2)C}$	θ_{HCH}
		$^1A_1$ Cyclopropyne			
DZP SCF	1.234	1.552	1.085	46.8	113.6
DZP TCSCF	1.241	1.522	1.084	48.1	113.3
DZP CISD	1.252	1.538	1.093	48.0	113.3
DZP TC-CISD	1.259	1.531	1.092	48.6	113.4
TZ(2df,2pd) CCSD(T)	1.253	1.534	1.088	48.2	113.9
		$^3B_2$ Cyclopropyne			
DZP SCF	1.276	1.530	1.083	49.3	114.5
DZP CISD	1.300	1.556	1.089	49.4	115.4

[a] Bond lengths are in Å, and bond angles are in deg.

Table 2. Stationary Point Structures of $\tilde{X}\ {}^1A_1$ and $\tilde{a}\ {}^3B_2$ Silacyclopropyne (**6**) at Several Levels of Theory[a]

method	r(C≡C)	r(C−Si)	r(Si−H)	θ_{CSiC}	θ_{HSiH}
		$^1A_1$ Silacyclopropyne			
DZP SCF	1.246	1.824	1.464	40.0	108.9
DZP TCSCF	1.257	1.808	1.465	40.7	108.8
DZP CISD	1.267	1.817	1.463	40.8	108.8
TZ(2df,2pd) CCSD(T)	1.270	1.825	1.475	40.7	108.8
		$^3B_2$ Silacyclopropyne			
DZP SCF	1.313	1.844	1.465	41.7	111.8
DZP CISD	1.320	1.880	1.461	41.1	113.9

[a] Bond lengths are in Å, and bond angles are in deg.

Table 3. Stationary Point Structures of the $^1A_1$ Ground States of Cyclopropenylidene (**1**) and Silacyclopropenylidene (**5**) at Several Levels of Theory[a,b]

method	r(C=C)	r(X−C)	r(C−H)	θ_{CXC}	$\theta_{HC=C}$
		Cyclopropenylidene			
DZP SCF	1.316	1.412	1.074	55.6	148.0
DZP CISD	1.331	1.431	1.081	55.4	148.0
TZ(2df,2pd) CCSD(T)	1.328	1.427	1.076	55.5	148.0
expt (r_m)[c]	1.320	1.417	1.075	55.5	149.8
		Silacyclopropenylidene			
DZP SCF	1.342	1.806	1.078	43.6	134.2
DZP CISD	1.353	1.819	1.085	43.7	134.7
TZ(2df,2pd) CCSD(T)[e]	1.350	1.833	1.081	43.2	135.1
expt (r_s)[d]	1.346	1.820	1.080	43.4	135.2

[a] X denotes the apex atom, C or Si. [b] Bond lengths in are Å, and bond angles are in deg. [c] Microwave structure from ref 59. All parameters are r_m values except for C−H distances and angles, which are r_s values. [d] Microwave r_s structure from ref 53.

Table 4. Stationary Point Structures of the $^1A_1$ Ground States of Propadienylidene (**3**) and Silapropadienylidene (**7**) at Several Levels of Theory[a,b]

method	r(C=C:)	r(X=C)	r(X−H)	θ_{HXH}
		Propadienylidene		
DZP SCF	1.283	1.318	1.080	117.8
DZP CISD	1.299	1.333	1.087	117.7
TZ(2df,2pd) CCSD(T)	1.293	1.333	1.085	117.3
expt (r_e)[c]	1.291	1.328	1.083	117.6
		Silapropadienylidene		
DZP SCF	1.264	1.677	1.462	112.3
DZP CISD	1.281	1.686	1.461	112.5
TZ(2df,2pd) CCSD(T)	1.280	1.694	1.472	112.9

[a] X = C, Si. [b] Bond lengths are in Å, and bond angles are in deg. [c] Recommended structure of ref 60 combining experimental and theoretical data.

energies in hartrees, are available as supporting information. Bond lengths generally exhibit the expected trends: the larger basis set leads to shorter bonds, while more complete treatments of electron correlation lead to longer bonds due to the admixture of antibonding configurations. For small molecules at their equilibrium geometries, the DZP CISD and TZ(2df,2pd) CCSD-

Table 5. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km mol^{-1}, in Parentheses) for $\tilde{X}$ $^1A_1$ Cyclopropyne (**4**)

	DZP					
vibrational mode	SCF	TCSCF	CISD	TZ(2df,2pd) CISD	DZP CCSD(T)	TZ(2df,2pd) CCSD(T)
a_1 sym C−H str	3256 (71)	3246 (81)	3175 (67)	3174 (51)	3098 (58)	3087 (46)
a_1 C≡C str	2092 (<1)	2049 (<1)	1983 (2)	2019 (1)	1842 (<1)	1874 (<1)
a_1 CH_2 scissor	1655 (20)	1664 (17)	1605 (18)	1596 (12)	1555 (12)	1539 (8)
a_1 sym C−C str	1084 (207)	1180 (171)	1138 (154)	1125 (168)	1105 (105)	1089 (119)
a_2 CH_2 twist	1035*i* (0)	417 (0)	256 (0)	300*i* (0)	309*i* (0)	93*i* (0)
b_1 asym C−H str	3343 (12)	3324 (13)	3259 (18)	3251 (7)	3182 (20)	3164 (9)
b_1 CH_2 rock	1130 (<1)	1158 (2)	1110 (<1)	1112 (<1)	1079 (<1)	1075 (<1)
b_2 asym C−C str	1115*i* (580)	630*i* (597)	955*i* (774)	937*i* (707)	582*i* (527)	618*i* (520)
b_2 CH_2 wag	1258 (1)	1236 (<1)	1198 (<1)	1204 (<1)	1136 (1)	1137 (<1)

(T) methods typically provide the most balanced predictions of equilibrium geometries.[45−47]

Geometrical parameters for cyclopropyne (**4**) are given in Table 1. For this isomer, the importance of a second configuration in the zeroth-order wave function suggests that the DZP CISD geometry [and conceivably even the TZ(2df,2pd) CCSD(T) geometry] may be less reliable than usual, but nevertheless the DZP CISD and TZ(2df,2pd) CCSD(T) geometries are in good agreement. The H−C−H bond angle is fairly constant at 113−114°, while the methylene ring angle shows somewhat more variation with theoretical method and is predicted to have the remarkably small value of 47−49°. Using a two-configuration reference wave function lengthens the C−C multiple bond (since the second configuration replaces a bonding orbital with an antibonding orbital) and concomitantly increases the methylene ring angle and shortens the C−C single bonds. Despite ring strain and an unusually small methylene ring angle, the C−C single bonds at the TZ(2df,2pd) CCSD(T) level of theory have nearly the same length as in ethane [r_z(C−C) = 1.535 Å].[48]

The multiple bond in cyclopropyne is characterized as a weak triple bond, as evidenced by a bond length of 1.253 Å, which is certainly shorter than the double bond in cyclopropene (1.296 Å),[49] yet longer than the triple bond in acetylene (1.202 Å).[50] The harmonic vibrational frequencies of cyclopropyne, presented in Table 5, also support this conclusion: at the TZ(2df,2pd) CCSD(T) level, the stretching frequency of the multiple bond is predicted to be 1874 cm^{-1}, which falls in between the expected values for carbon−carbon double and triple bonds.

At no level of theory employed in the present study did cyclopropyne become a minimum on the C_3H_2 potential energy surface. For all single-reference techniques, cyclopropyne was found to have imaginary vibrational frequencies for the b_2 antisymmetric C−C stretch and the a_2 methylene twist, making it a saddle point of Hessian index two on the potential energy surface. However, when the important $(6a_1)^2 \rightarrow (3b_2)^2$ configuration is included in the reference wave function via the TCSCF method, the vibrational frequency for the a_2 methylene twist becomes real.

Note also that the CCSD(T) method with a TZ(2df,2pd) basis, which provides the most extensive treatment of electron correlation of any of the single-reference methods employed, yields the imaginary frequency for the methylene twist with the smallest magnitude. In order to further examine whether the a_2 twisting mode attains a real frequency at highly correlated levels, we determined this frequency using the TCSCF wave function in a two-reference CISD procedure (TC-CISD). A value of 381 cm^{-1} was obtained with the DZP basis set, suggesting that when both non-dynamical correlation are accounted for, cyclopropyne may become a true transition state with only one imaginary frequency corresponding to the b_2 antisymmetric C−C stretch. This mode leads to ring opening and presumably to propadienylidene (**3**). Indeed, cyclopropyne has previously been implicated as the transition state in the automerization of propadienylidene **3**.[51] This reaction is important in explaining the isotopic scrambling experiments of C_3H_2 carbenes used to prove the C_2 structure of propargylene (**2**).[6]

After the successful detection of cyclopropenylidene in the laboratory[13,14] and in interstellar sources,[1,2] Vacek, Colegrove, and Schaefer suggested that silacyclopropenylidene (**5**) might also be detected.[52] These authors provided theoretical equilibrium geometries and harmonic vibrational frequencies at levels up to TZ2P CISD. Our predicted geometries for **5**, given in Table 3, are in agreement with those from the previous investigation at similar levels of theory. Isomer **5** has recently been identified in the laboratory by microwave spectroscopy,[53] and our best r_e structure is in reasonable agreement with the experimental r_s structure. The substantial lengthening of the C−C double bond (1.350 Å) relative to cyclopropene (1.296 Å) can be attributed to a delocalization of the π electrons into the empty p orbital on silicon. Silacyclopropenylidene was also among the SiC_2H_2 species detected by Maier and co-workers.[18,54]

Table 2 presents the equilibrium geometry of silacyclopropyne (**6**). The multiple bond in **6** is 1.270 Å, which is significantly longer than that in cyclopropyne (1.253 Å) and approaches the bond length in cyclopropene (1.296 Å).[49] The unusually short C−Si bonds in **7** have nearly the same length as in **5**. For the parent cyclopropyne, the smaller DZP basis is sufficient to obtain real harmonic frequencies which are in excellent agreement with those obtained using the larger TZ(2df,2pd) basis (cf. Table 5). Accordingly, the vibrational frequencies for **6** have been determined using only the DZP basis set in conjunction with the SCF, TCSCF, CISD, CCSD, and CCSD(T) methods. These frequencies are presented in the supporting information. Although **6** is predicted to be a transition state at the DZP SCF level of theory (having a frequency of 133*i* cm^{-1} for the b_2 antisymmetric Si−C stretch), it becomes a minimum if the $[(6a_1)^2 \rightarrow (3b_2)^2]$ diradical configuration is added to the zeroth-order wave function (via the TCSCF method) or if

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Table 6. Harmonic Vibrational Frequencies (cm^{-1}) and Relative Infrared Intensities (in Parentheses) for Silacyclopropyne (**6**) and Silapropadienylidene (**7**) at the DZP CCSD(T) Level of Theory, and Experimentally Observed Fundamental Frequencies for the SiC_2H_2 Isomer Detected by Maier *et al.*[18,54]

silapropadienylidene		silacyclopropyne		expt[a]
2354 (14)	b_2 asym Si−H str	2330 (52)	b_1 asym Si−H str	2229 (49)
2335 (12)	a_1 sym Si−H str	2321 (48)	a_1 sym Si−H str	2214 (49)
1903 (100)	a_1 C=C str	1779 (1)	a_1 C≡C str	1770 (7)
1028 (24)	a_1 SiH_2 sym def	1092 (100)	a_2 SiH_2 scissor	1023 (100)
783 (1)	a_1 Si−C str	834 (51)	a_1 sym Si−C str	837 (50)
677 (18)	b_2 SiH_2 rock	796 (43)	b_2 SiH_2 wag	[757 (42)]
636 (16)	b_1 SiH_2 wag	686 (29)	b_1 SiH_2 rock	601 (7) [676 (25)]
148 (<1)	b_2 SiCC bend	382 (57)	b_2 asym Si−C str	
136 (<1)	b_1 SiCC oop bend	332 (0)	a_2 SiH_2 twist	

[a] Values in square brackets are from the more recent experimental data in ref 54.

Table 7. Relative Energies (kcal mol^{-1}) for the Singlet States of Three C_3H_2 and Three SiC_2H_2 Isomers at Several Levels of Theory[a,b]

method	1	3	4	5	6	7
DZP SCF	0.0	16.2	81.9	0.0	54.0	48.7
TZP TCSCF	0.0	16.2	58.7	0.0	36.8	48.7
DZP CISD	0.0	15.1	70.1	0.0	51.4	52.8
DZP TC-CISD	0.0	15.1	58.5			
DZP CCSD(T)	0.0	10.2	57.6	0.0	48.4	50.9
TZ(2df,2pd) CISD	0.0	17.4	70.9	0.0	49.4	54.0
TZ(2df,2pd) TC-CISD	0.0	17.4	59.8			
TZ(2df,2pd) CCSD(T)	0.0	12.4	58.6	0.0	47.4	52.9
TZ(2df,2pd) CCSD(T)//DZP CISD	0.0	12.4	58.6	0.0	47.3	52.9

[a] Unless otherwise noted, reported energies are evaluated at geometries optimized at the same level of theory. [b] Energies have been corrected for zero-point vibrational energy (ZPVE) using DZP SCF harmonic frequencies scaled by 0.91. TCSCF frequencies were used for cyclopropyne and silacyclopropyne. The ZPVE corrections were 19.7, 19.0, 18.6, 18.1, 14.3, and 14.0 kcal mol^{-1}, respectively.

electron correlation is included via the single-reference CISD, CCSD, or CCSD(T) methods. The stretching frequency of the multiple bond is 1779 cm^{-1} at the best level of theory, which is extremely low for a triple bond and again indicates that the multiple bond in silacyclopropyne is closer to a double bond.

The theoretical harmonic frequencies for **6** and **7** at the DZP CCSD(T) level of theory are presented in Table 6 along with the experimental fundamentals by Maier *et al.*[18,54] The predicted vibrational spectrum for silacyclopropyne (**6**) matches the original experimental spectrum[18] very well, with the exception of a theoretically predicted peak at approximately 796 cm^{-1} which was initially absent from the experimental spectrum. However, a more recent study by Maier and co-workers,[54] which was published while the present article was in preparation, reports two new experimental spectral features at 757.4 and 676.4 cm^{-1}. The former corresponds to the previously missing peak predicted by theory, and the latter provides a better match to the theoretically predicted value of 686 cm^{-1} for the b_1 SiH_2 rock. Maier's recent article also reports spectra of isotopomers which unambiguously prove the experimental detection of **6**.

Relative energies among the singlet states of the C_3H_2 and SiC_2H_2 isomers are presented in Table 7. The data clearly demonstrate that using a single-configuration wave function for cyclopropyne (**4**) leads to unreliable relative energies unless very high-order treatments of electron correlation, such as CCSD(T), are employed: for example, the DZP TCSCF energy of **4** relative to **1** is more than 23 kcal mol^{-1} lower than the DZP SCF energy. These differences are smaller for silacyclopropyne (**6**), which has less diradical character. At the most reliable level of theory, TZ(2df,2pd) CCSD(T), the relative energies (in kcal mol^{-1}) are predicted to be **1** (0.0) < **3** (12.4) < **4** (58.6) for C_3H_2 isomers and **5** (0.0) < **6** (47.4) < **7** (52.9) for SiC_2H_2 isomers. Thus both cyclopropyne (**4**) and silacyclopropyne (**6**) are substantially higher in energy than the global minima (**1** and **5**), but the relative energy of silapropadienylidene (**7**) is much higher than that of its parent **3**, in fact becoming 5.5 kcal mol^{-1} higher in energy than the highly strained silacyclopropyne (**6**). This conclusion is in qualitative agreement with Maier's prediction that **7** lies 8.8 kcal mol^{-1} above **6** at the less reliable MP2/6-31G** level of theory.[18]

The fact that silacyclopropyne is a minimum on the potential energy surface and exhibits somewhat different bonding begs further comparison of these two structures. As revealed by the TCSCF CI coefficients, **6** has much less diradical character than **4** (5% vs 10%), a characteristic generally associated with greater stability. Note, however, that **4** is 58.6 kcal mol^{-1} above C_3H_2 global minimum **1**, while **6** is 47.4 kcal mol^{-1} above SiC_2H_2 global minimum **5**, i.e. relative to their respective global minima, **4** is only 11.2 kcal mol^{-1} higher-lying than **6**. Much more striking is the difference between the vinylidene structures **3** and **7**: structure **3** is 12.4 kcal mol^{-1} above **1**, whereas **7** is 52.9 kcal mol^{-1} above **5** and 5.5 kcal mol^{-1} above **6**. Although **4** is a transition state for the automerization of **3**, this cannot be the case for **6** because energetically **7** lies above **6**. The high energy of **7** is consistent with the general observation that sp^2-hybridized organosilicon molecules are rarely observed.[55] In brief, the simplest explanation as to why **6** is a minimum whereas **4** is a transition state may be that in the silicon derivative, the closest rearrangement possibility, the propadienylidene isomer, is not viable energetically due to the persistent weakness of carbon−silicon π bonds.

IV. Triplet States.

In his recent semipopular review of the silacyclopropyne problem, Sander[56] asks,"how large is the singlet−triplet gap?" The lowest-lying triplet state of the parent cyclopropyne is the $^3B_2$ state arising from a $(6a_1) \rightarrow (3b_2)$ single excitation. The lowest-lying triplet state of silacyclopropyne is also the $^3B_2$ state, arising from the analogous $(8a_1) \rightarrow (4b_2)$ excitation. The $^3B_2$ state of cyclopropyne is a potential energy surface minimum[57] and lies 9.2 kcal mol^{-1} above the singlet at the TZ(2df,2pd) CCSD(T)//DZP CISD level of theory. The scaled ZPVEs are 18.6 kcal mol^{-1} for the singlet and 19.8 kcal mol^{-1} for the triplet, giving a ZPVE-corrected energy difference of 10.4 kcal mol^{-1}. This result is in excellent agreement with the value of 10.1 kcal mol^{-1} predicted by Jonas, Böhme, and Frenking at the PMP4/6-311G(2df)//MP2/6-31G(d) level of theory,[10] but it may not be fully converged.

For silacyclopropyne (**6**), the $^3B_2$ state is once again a potential energy minimum,[58] but the singlet−triplet gap is much larger than in the parent **4**: the TZ(2df,2pd) CCSD(T)//DZP CISD energy difference is 40.4 kcal mol^{-1}. Employing scaled ZPVEs of 14.3 and 14.4 kcal mol^{-1} for the singlet and triplet, respectively, this energy difference becomes 40.5 kcal mol^{-1}. This enhanced singlet−triplet splitting demonstrates once more that **6** is better described as a closed-shell singlet than **4**.

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(57) DZP SCF frequencies (in cm^{-1}) for $^3B_2$ cyclopropyne are the following: a_1 sym C−H str, 3240; a_1 C≡C str, 1919; a_1 CH_2 scissor, 1639; a_1 sym C−C str, 1108; a_2 CH_2 twist, 895; b_1 asym C−H str, 3323; b_1 CH_2 rock, 1171; b_2 CH_2 wag, 1142; b_2 asym C−C str, 773.

(58) DZP SCF frequencies (in cm^{-1}) for $^3B_2$ for salicyclopropyne are the following: a_1 sym Si−H str, 2387; a_1 C=C str, 1709; a_1 SiH_2 scissor, 1086; a_1 sym Si−C str, 771; a_2 SiH_2 twist, 557; b_1 asym SiH str, 2385; b_1 SiH_2 rock, 716; b_2 asym Si−C str, 783; b_2 SiH_2 wag, 692.

In both cases the geometries of the triplet states (Tables 1 and 2) are primarily characterized by a lengthening of the carbon−carbon multiple bond. In cyclopropyne the DZP CISD bond length is 1.300 Å, which matches the double-bond length in cyclopropene (1.296 Å). In silacyclopropyne at the same level of theory, the bond length is 1.320 Å, which is somewhat shorter than the double-bond length for silacyclopropenylidene (**5**) at the same level of theory (1.353 Å). Both triplet species are thus characterized as diradicals with carbon−carbon double bonds.

V. Conclusions

State-of-the-art *ab initio* methods have been used to characterize the recently-detected molecule silacyclopropyne (**6**). The DZP CCSD(T) frequencies of **6** and **7** support Maier's identification of **6** by matrix isolation infrared spectroscopy. High-quality equilibrium geometries and relative energies have been reported for SiC_2H_2 isomers **5**, **6**, and **7**, and additionally the lowest-lying triplet state of **5** has been characterized as a potential energy minimum lying near 40 kcal mol^{-1} above the singlet. Because the experimental detection of **6** contradicted previous theoretical predictions, we have reinvestigated the parent cyclopropyne (**4**) using a wide range of highly-accurate *ab initio* methods. Although **6** is described reasonably well by a single electronic configuration, two configurations are required to obtain an acceptable zeroth-order wave function for **4**. At no level of theory does cyclopropyne become a minimum on the C_3H_2 surface: the very reliable CCSD(T) method predicts two imaginary vibrational frequencies, while methods which add the second configuration to the reference wave function (e.g. TC-CISD) predict only one imaginary frequency, the ring-opening b_2 C−C stretch. Geometries and relative energies have been determined for C_3H_2 isomers **1**, **3**, and **4**, and the singlet−triplet gap for **4** is determined to be 10 kcal mol^{-1}, much smaller than the singlet−triplet gap for **6**. Structures **6** and **4** both exhibit weak triple bonds, but this bond appears somewhat stronger in **4**. The existence of silacyclopropyne as an isolable chemical species, in contradistinction with cyclopropyne, is explained as primarily due to the very high relative energy of the cumulated π network of silapropadienylidene (**7**).

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Supporting Information Available: Tables of energies, bond lengths, and bond angles for **1** and **3**−**7** and harmonic vibrational frequencies and IR intensities for **6** (8 pages). See any current masthead page for ordering and Internet access instructions.

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