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Structure and Energetics of the Silicon Carbide Clusters SiC₃ and Si₂C₂

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Abstract

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Keywords

Silicon, Carbides, Ab initio calculations, Atomic and molecular clusters, Wave functions

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Structure and energetics of the silicon carbide clusters SiC₃ and Si₂C₂

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A comprehensive *ab initio* study of the four atom silicon carbide clusters SiC₃ and Si₂C₂ using multiconfigurational self-consistent-field wave functions is presented. In contrast to previous studies the global minimum isomer for SiC₃ is predicted to be a $C_{\infty v}$ linear triplet with a terminal silicon atom. For Si₂C₂ the global minimum is a rhombic structure, in accordance with previous studies, while the linear triplet Si–C–C–Si is just 1.0 kcal mol⁻¹ higher in energy. © 2001 American Institute of Physics. [DOI: 10.1063/1.1380714]

I. INTRODUCTION

Understanding the reactivity of silicon carbide under extreme environments is of current interest. In order to understand the properties of such a material it is useful to study smaller clusters of the bulk material. Information on the nature of bonding and electronic structure can be gained when studying these smaller units at a level of theory that would not be possible for the bulk material. Such calculations then provide a baseline for future calculations on larger species. This is the focus of the present study.

The work presented in this paper has been additionally stimulated by recent experiments performed by the Lineberger group, who are studying silicon carbide clusters of 3 to 10 atoms. Because the recent experiments by Lineberger, Davico, and Schwartz¹ find primarily carbon-dominated species, SiC₃ and Si₂C₂ are considered here. In order to compare fully with the results of the photodetachment experiments it will ultimately be necessary to look at both the neutral and anion species. This paper presents results for the neutral species.

There have been a number of previous studies of SiC₃ and Si₂C₂, all of which used single reference wave functions. Albers, Grev, and Schaefer studied SiC₃ using configuration interaction with single and double excitations (CISD) at Hartree–Fock geometries.² They found the lowest energy isomer to be a singlet rhombic C_{2v} structure with the silicon terminated linear $^3\Sigma_u^-$ structure 4.1 kcal mol⁻¹ higher and a second rhombic C_{2v} structure 4.3 kcal mol⁻¹ higher than the global minimum (Fig. 1). In 1997, Gomei *et al.* conducted a study of SiC_{*n*} clusters.³ They also found a C_{2v} rhombic structure to be the SiC₃ global minimum at the CCSD(T)/aug-cc-pVDZ//MP2/6-31G(d) level of theory with the $^3\Sigma_u^-$ silicon terminated linear isomer 6.9 kcal mol⁻¹ higher. Hunsiker and Jones examined mixed silicon carbide clusters using density functional theory (DFT) and found the SiC₃ global minimum again to be the singlet rhombic structure, with the linear triplet and second rhombic structure just 0.2 and 1.8 kcal mol⁻¹ higher, respectively.⁴

Trucks and Bartlett performed SDTQ–MBPT(4) calculations on Si₂C₂,⁵ and later Fitzgerald and Bartlett performed MBPT(4) calculations.⁶ Both studies found the D_{2h} rhombic

structure to be the global minimum with a silicon terminated linear $^3\Sigma_u^-$ isomer ~12 kcal mol⁻¹ higher (12.3 and 11.9 kcal mol⁻¹, respectively). The second study, however, also located a distorted trapezoid 4.0 kcal mol⁻¹ above the global minimum. Lamertsma *et al.*'s MP2 study of Si₂C₂ located the same rhombic ground state with the distorted trapezoid 10.1 kcal mol⁻¹ and the $^3\Sigma_u^-$ structure 15.5 kcal mol⁻¹ higher than the global minimum.⁷ Hunsiker and Jones' DFT study found the same ordering although the three isomers were found to be closer in energy.⁴ The Hunsiker and Jones results indicate that the distorted trapezoid and $^3\Sigma_u^-$ isomers are just 4.2 kcal mol⁻¹ and 8.3 kcal mol⁻¹ above the global minimum, respectively. Presilla-Márquez *et al.* optimized the rhombic global minimum structure with CCSD(T) and found its energy to be 6.5 kcal mol⁻¹ lower than the distorted trapezoid and 7.7 kcal mol⁻¹ lower than the linear triplet, with single points for the latter two structures calculated using CCSD(T) at the MBPT(2) optimized structures.⁸

Because all of the previous calculations were performed with single reference wave functions, some potentially low-lying states were not studied. In this paper we present the results of a comprehensive *ab initio* study of the SiC₃ and Si₂C₂ systems utilizing a multiconfigurational self-consistent-field (MCSCF) wave function. Energies, equilibrium geometries, and vibrational frequencies are presented for each isomer. We also evaluate the need for the application of a multireference wave function in this investigation.

II. COMPUTATIONAL DETAILS

(a) Basis set. In this investigation the 6-31G(d) basis set⁹ was used for all geometry optimizations. Future calculations on anion structures are planned. Therefore, in the interest of using a consistent basis set throughout, the aug-cc-pVDZ basis^{10–12} was chosen. This basis set includes necessary diffuse functions, yet remains tractable enough to apply to these systems. This basis set was used in calculating single point energies subsequent to geometry optimization.

(b) Wave functions. A fully optimized reaction space (FORS)–MCSCF wave function^{13–15} (also referred to as CASSCF¹⁶) was used as the reference function for all calculations in this study. An active space of 12 electrons in 10

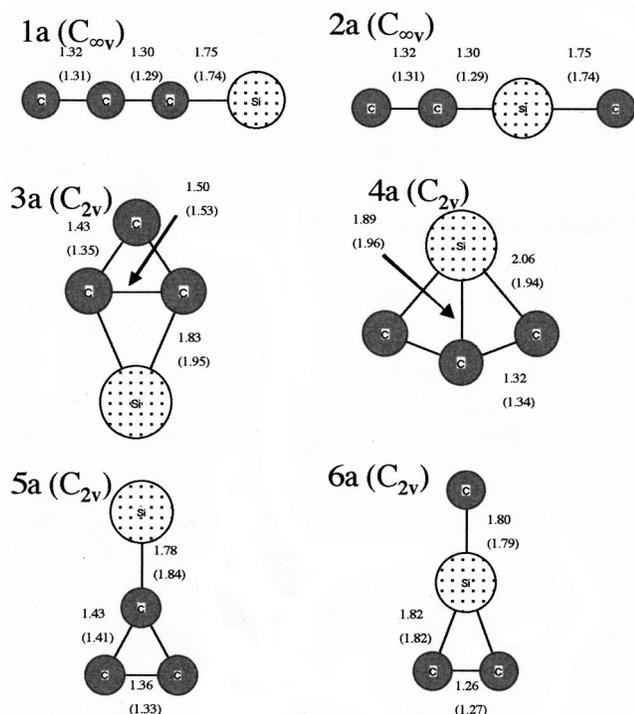


FIG. 1. Optimized MCSCF geometries for the singlet and triplet isomers of SiC_3 . Triplet bond lengths are given in parentheses.

orbitals was used for geometry optimization of nonlinear structures and a 12 electrons in 11 orbitals active space was used for geometry optimization of all linear structures. This difference in active space is necessary in order to include all eight π orbitals formed by all combinations of valence p_x and p_y orbitals on silicon and carbon. As will be discussed later, the calculation and inspection of natural orbital occupation numbers (NOONs) for each isomer confirms this choice. For single point energies the larger (12,11) active space was used for all species.

In the case of the linear species studied here, it is impossible to represent the correct singlet wave function without including at least two determinants. Because the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are degenerate π MOs, the correct wave function must include partial and equal occupation of each of these orbitals. This is true of both the $^1\Sigma_g^+$ and $^1\Delta_g$ states of Si_2C_2 and the $^1\Sigma^+$ and $^1\Delta$ states of SiC_3 . Due to these group theoretical considerations, it is necessary to use a multideterminant description in order to construct a qualitatively correct wave function for the linear singlet species. It is straightforward to determine that this is an even-odd phenomenon, that is, at least two configurations will be necessary to construct a wave function for the singlet species of any linear silicon carbide cluster constructed from an even number of atoms. Likewise a similar approach is required when describing a linear triplet silicon carbide cluster containing an odd number of atoms. One can determine this by considering the bonding using a minimal basis model. In the case of four atom clusters there are 16 valence electrons, 10 of which reside in either σ or lone pair orbitals. The remaining six electrons must reside in π orbitals. Since each π

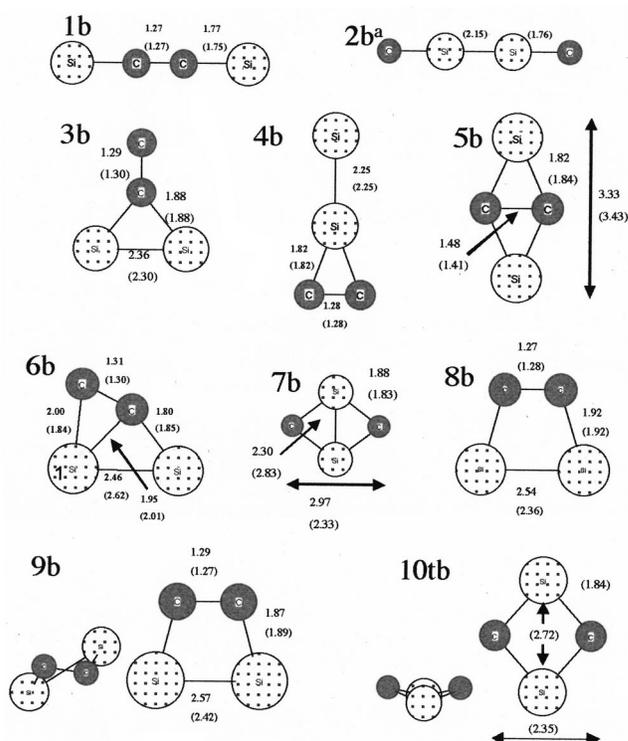


FIG. 2. Optimized MCSCF geometries for the singlet and triplet isomers of Si_2C_2 . Triplet bond lengths are given in parentheses.

orbital is one of a degenerate pair of orbitals, the first four π electrons go in the two fully bonding (no nodes) π orbitals. The next two must go into a degenerate pair of orbitals, so that to construct a correct singlet wave function one must include a combination of $(\pi_{xz}^2 + \pi_{yz}^0)$ and $(\pi_{xz}^0 + \pi_{yz}^2)$. Of course, this applies only to fully unsaturated species.

Generally, for a given spin and symmetry, only the lowest electronic state is considered for each isomer.

(c) Methods. Starting with preliminary Hartree-Fock structures, geometry optimizations were performed using a 12 electrons in 10 orbitals (11 orbitals for linear structures) FORS-MCSCF wave function with the 6-31G(d) basis set.⁹ Unless otherwise stated any discussion of optimized structures or nature of stationary points implies this level of theory. Some structures with very high energies (e.g., structures **2a**, **6a**, **2b** in Figs. 1 and 2) were optimized with only a six electrons in six orbitals active space. Stationary points were characterized by the calculation and diagonalization of the energy second derivative matrix (Hessian). No negative eigenvalues indicates a minimum on the potential energy surface, one negative eigenvalue indicates a transition state, and more than one negative root indicates a higher order saddle point of little chemical interest.

External correlation effects (sometimes referred to as dynamic correlation effects) were included by carrying out second order multiconfigurational quasidegenerate perturbation theory (MCQDPT)¹⁷ calculations at the MCSCF (12,10 or 12,11) optimized geometries. For these single point calculations the aug-cc-pVDZ basis set was used.¹⁰⁻¹²

All calculations were done using the electronic structure code GAMESS.^{18,19}

III. RESULTS AND DISCUSSION

For both the SiC₃ and the Si₂C₂ system all structures considered chemically reasonable and interesting were investigated and optimized. Each isomer was then characterized as a minimum, transition state, or higher order stationary point. Results are presented first for SiC₃ followed by results for Si₂C₂. Each isomer is given an alphanumeric label. The number refers to the geometric structure; an “a” or “b” designates SiC₃ or Si₂C₂, respectively; and “s” and “t” refer to singlet and triplet spin states, respectively.

SiC₃. Six basic structures were optimized and identified as stationary points on the SiC₃ potential energy surface (PES). Geometries are shown in Fig. 1. Vibrational frequencies can be found in Table I. All energies, summarized in Table II, are given in relation to **1ta**, the SiC₃ global minimum, unless otherwise stated.

Linear. There are two possible linear (*C_{∞v}*) SiC₃ isomers, for which ¹Σ⁺, ¹Δ, and ³Σ⁻ states can be calculated. These linear isomers differ in the location of the Si, either terminal (**1a**) or internal (**2a**). Since unsaturation at C is preferred, and silylenes are more stable than carbenes, **1a** is likely to be lower in energy than **2a**.

2a. The FORS(12,11)/6-31G(d) energy of the ³Σ⁻ state of isomer **2a** is very high (86 kcal mol⁻¹) at the FORS(6,6) geometry [FORS(12,11)/6-31G(d)/FORS(6,6)/6-31G(d)]. The energies of the ¹Σ⁺ and ¹Δ states are 101 kcal mol⁻¹ and 104 kcal mol⁻¹, respectively, at the triplet geometry using the same level of theory described above. Because of the high energies of these species, they are not discussed further.

1a. More important than isomer **2a**, from an energetic point of view, is the silicon terminated linear isomer **1a**. The ³Σ⁻ state, **1ta**, is a minimum on the FORS(12,11)/6-31G(d) potential energy surface. In fact, it is the global minimum among all SiC₃ isomers at the MCQDPT(12,11)/aug-cc-pVDZ//MCSCF(12,11)/6-31G(d) level of theory. Examination of natural orbitals and bond lengths indicates a strong double bond between each pair of carbons. The internal C–C bond (1.29 Å) is slightly shorter than the terminal C–C bond (1.31 Å).²⁰ The C–Si bond length of 1.74 Å is comparable to the double bond length of 1.69 Å in silene.²¹

In the ³Σ⁻ state the unpaired electrons are in degenerate π orbitals. These orbitals have a node between the two central carbons, and bonding interaction between the terminal carbon and its nearest neighbor carbon and between the terminal silicon and its nearest neighbor carbon.

Examination of NOONs reveals considerable electron density outside those orbitals which would be occupied in the Hartree-Fock (HF) reference (for the sake of brevity, in subsequent discussions we will refer to this as “outside the HF reference”). The first two such orbitals are degenerate π orbitals with two nodes and bonding interactions between the two middle carbons. The corresponding NOONs are both 0.097. It is likely that this makes a contribution to the strength of this central C–C bond. The remaining two active orbitals are a degenerate pair of completely antibonding π orbitals. The corresponding NOONs are both 0.044. Thus the total deviation from the HF reference is 0.282 electrons.

Hund’s rule predicts the triplet to be lower in energy

TABLE I. SiC₃ vibrational frequencies.

Vibration	Symmetry	Intensity Debye ² amu ⁻¹ Å ⁻²	Frequency cm ⁻¹
1sa-delta			
1,4 bend	π	0.05	153(2×)
1,3 bend	π	0.14	397(2×)
Si–C stretch	σ	0.31	612
1,3 C–C stretch	σ	1.99	1350
C–C stretch	σ	4.70	1982
1sa-sigma			
1,4 bend	π	0.04	150(2×)
1,3 bend	π	0.14	382(2×)
Si–C stretch	σ	0.45	613
1,3 C–C stretch	σ	2.45	1342
C–C stretch	σ	4.19	1959
1ta			
1,4 bend	π	0.08	160(2×)
1,3 bend	π	0.15	410(2×)
Si–C stretch	σ	0.10	619
1,3 C–C stretch	σ	0.66	1369
C–C stretch	σ	5.04	2055
3sa			
Out-of-plane bend	<i>b</i> ₂	0.11	316
In-plane bend	<i>b</i> ₁	0.89	509
Breathing	<i>a</i> ₁	1.28	720
Symmetric Si–C stretch	<i>a</i> ₁	1.51	984
In-plane ring distortion	<i>b</i> ₁	0.06	1120
Symmetric C–C stretch	<i>a</i> ₁	5.63	1504
3ta			
In-plane ring distortion	<i>b</i> ₁	0.84	272
Out-of-plane bend	<i>b</i> ₂	0.00	395
Symmetric Si–C stretch	<i>a</i> ₁	1.24	502
Breathing	<i>a</i> ₁	0.13	747
Asymmetric C–C stretch	<i>b</i> ₁	0.01	1255
Symmetric C–C stretch	<i>a</i> ₁	0.23	1651
4sa			
Out-of-plane bend	<i>b</i> ₂	0.58	279
In-plane ring distortion	<i>b</i> ₁	0.00	420
Symmetric Si–C stretch	<i>a</i> ₁	0.51	538
Transannular Si–C stretch	<i>a</i> ₁	1.08	852
Symmetric C–C stretch	<i>a</i> ₁	0.10	1254
Asymmetric C–C stretch	<i>b</i> ₁	4.72	1603
4ta			
In-plane ring distortion	<i>b</i> ₁	2.69	363
Out-of-plane bend	<i>b</i> ₂	0.09	479
Symmetric C–Si stretch	<i>a</i> ₁	1.60	674
Transannular C–Si stretch	<i>a</i> ₁	0.47	755
Breathing	<i>a</i> ₁	0.19	1234
Asymmetric C–Si stretch	<i>b</i> ₁	1.57	1380
5sa			
In-plane rocking	<i>b</i> ₁	2.56	373 <i>i</i>
Out-of-plane bend	<i>b</i> ₂	0.09	257
Asymmetric C–C stretch	<i>b</i> ₁	1.81	527
C–Si stretch	<i>a</i> ₁	0.00	559
C–C–C bend	<i>a</i> ₁	0.08	1254
C ₃ ring breathing	<i>a</i> ₁	1.31	1508
5ta			
Asymmetric C–C stretch	<i>b</i> ₁	82.03	1475 <i>i</i>
In-plane rocking	<i>b</i> ₁	0.02	115
Out-of-plane bend	<i>b</i> ₂	0.04	326
C–Si stretch	<i>a</i> ₁	0.90	536
C–C–C in-plane bend	<i>a</i> ₁	0.96	1124
C ₃ ring breathing	<i>a</i> ₁	0.08	1685

TABLE II. SiC₃ relative energies (kcal mol⁻¹).

Isomer	State	MCQDPT/aug-cc pVDZ //FORS(12,10/11)/6-31G(d)	
		MCQDPT/6-31G(d) //FORS(12,10/11)/6-31G(d)	(zero point corrected energies in parentheses)
1sa	¹ Δ	6.6	10.6(10.4)
1sa	¹ Σ ⁺	10.0	9.3(9.0)
1ta	³ Σ ⁻	0.0	0.0(0.0)
2sa	¹ Δ	94.1	
2sa	¹ Σ ⁺	97.9	
2ta	³ Σ ⁻	79.5	
3sa	A ₁	0.7	4.4(4.3)
3ta	³ B ₂	20.4	26.2(25.7)
4sa	A ₁	6.8	7.8(7.4)
4ta	³ B ₂	12.7	5.9(5.4)
5sa	A ₁	28.1	25.2(24.7)
5ta	³ A ₂	30.1	30.8(28.8)
6sa	A ₁	103.4	
6ta	³ A ₂	82.1	

than the singlet, and our results are consistent with that prediction. However, since singlet configurations, ¹Σ⁺ and ¹Δ, have energies within 11 kcal mol⁻¹ of the triplet state, it is important to consider these two singlet states. In the ³Σ⁻ state, the two unpaired electrons are in degenerate π orbitals, π_x and π_y. To generate a singlet spin state the electrons must be paired, and will occupy a degenerate pair of π orbitals. Therefore, one must use a minimum of two determinants to correctly describe the qualitative nature of the singlet states. Conceptually, the ¹Σ⁺ state can be characterized by the orbital occupation (π_x⁰π_y² + π_x²π_y⁰), the two dominant determinants. The ¹Δ state consists of two degenerate states (π_x⁰π_y² - π_x²π_y⁰) and π_x¹π_y¹ such that in the latter the electrons are singlet coupled. The ¹Σ⁺ and ¹Δ energies are 9.3 kcal mol⁻¹ and 10.6 kcal mol⁻¹, respectively, above the ³Σ⁻ global minimum at the MCQDPT/aug-cc-pVDZ//CASSCF/6-31G(d) level. All subsequent SiC₃ energies are likewise given in reference to the above-mentioned global minimum (**1ta** ³Σ⁻). The geometries of the linear singlets differ only slightly from the geometry of the triplet.

Four membered ring. Isomers **3a** and **4a** (Fig. 1) have very similar four membered ring structures. Conceptually, they can be interconverted simply by lengthening the transannular C–C bond while simultaneously shortening the transannular carbon–silicon bond. The bond stretch isomerism of these two species has been examined in depth in a previous study.²²

3a. Both singlet and triplet states were examined for isomer **3a**. The ¹A₁ structure is lower in energy than the ³B₂ structure by 21.9 kcal mol⁻¹. The transannular C–C bond is slightly shorter in the ¹A₁ structure (1.46 Å) than in the ³B₂ structure (1.53 Å). The two equivalent C–C bonds are slightly longer in the singlet (1.42 Å) than in the triplet (1.35 Å), while the two equivalent C–Si bonds are shorter in the singlet (1.82 Å) than in the triplet (1.95 Å). Relative energies (Table II) for **3sa** and **3ta** are 4.4 kcal mol⁻¹ and 26.2 kcal mol⁻¹ above the global minimum, respectively.

4a. Structure **4a** is related to **3a** by a lengthening of the C–C bond, and a corresponding shortening of the Si–C tran-

sannular bond. In **4ta** the singly occupied orbitals are *b*₁ and *a*₂ giving a ³B₂ state.

It has been proposed² that **4a** can be viewed as a silicon atom complexed to a linear C₃ unit. While the C–C–C bond angles of 154.9° and 138.1° for **4sa** and **4ta**, respectively, may suggest this, examination of natural orbitals, and the corresponding density matrix over active MCSCF orbitals gives no indication of this type of bonding situation. For both the ¹A₁ and ³B₂ states silicon participates in σ bonding with each of the three carbons, with the majority of the remaining electron density around silicon located in a lone pair orbital. There is a bonding π orbital on the C₃ unit that has no bonding overlap with the π orbital or the σ lone pair orbital on silicon.

The C–C bonds are intermediate between single and double bonds in both **4sa** and **4ta**. The transannular C–Si bond length in **4sa** indicates single bonding, while peripheral C–Si bond lengths indicate weak single bonding.²³ In **4ta**, however, the three C–Si bonds are almost equivalent, with the transannular bond only 0.02 Å longer than the peripheral C–Si bonds. The MCSCF bond order analysis²⁴ is consistent with this picture. The three C–Si bond orders are virtually identical for **4ta** (0.691, 0.691, and 0.684), while in **4sa** the transannular Si–C bond is a bit stronger than the peripheral Si–C bonds (0.736, 0.595, and 0.595).

4sa and **4ta** are very close in energy, 7.8 and 5.9 kcal mol⁻¹ above the global minimum, respectively.

Three membered ring structures. Two C_{2v} structures containing one three membered ring were examined. Isomer **5a** (Fig. 1) consists of a ring of three carbons with a silicon bonded to one of the vertices. Isomer **6a** has a ring containing two carbons and one silicon with an exocyclic carbon bonded to the silicon.

5a and 6a. Both the ¹A₁ and ³A₂ states of isomer **6a** are very high in energy (¹A₁ 103.4 kcal, ³A₂ 82.1 kcal) at the MCQDPT(12,10)/6-31G(d) level. Thus, this isomer was not examined extensively for quantitative information on energetics. Clearly it is not relevant in a search for the most stable isomers, those isomers most likely to be observed experimentally; however, when seeking to understand the characteristics of the most stable clusters, it is helpful to contrast these with the properties of the least stable structures. Note that isomer **5a** maximizes C–C bonding while minimizing Si–C bonding. Isomer **6a** represents the three-membered ring structure with the maximum possible number of Si–C bonds and the minimum possible number of C–C bonds (one). Since silicon avoids multiple bonding, it is not surprising that the π bond in **6a** is located almost completely between the two equivalent carbons of the ring, whereas in isomer **5a**, the analogous π bond is much more delocalized throughout the ring. In **5a** the ¹A₁ energy is 25.2 kcal mol⁻¹, while that of the triplet is 30.8 kcal mol⁻¹.

SiC₃ relative energies. The lowest energy isomer is predicted to be the ³Σ⁻ state of the linear molecule with a terminal silicon atom (Si–C–C–C). The ¹Σ⁺ and ¹Δ states are both within 11 kcal mol⁻¹ of the global minimum, 9.3 and 10.6 kcal mol⁻¹ respectively. The linear isomer with an internal silicon atom is found to be much higher in energy. The second lowest energy structure, rhombic **3sa**, with a sili-

con at the vertex of the long axis, is 4.4 kcal mol⁻¹ above the global minimum. The previous CISD study by Alberts, Grev, and Schaefer² predicts the reverse order of the two lowest isomers. This may be due to the multiconfigurational nature of these clusters, since these earlier calculations were done using single reference wave functions. The occupation numbers in the orbitals outside the HF reference for **3sa** are all greater than 0.05, with the largest being 0.076. Those for **1ta** are (2×) 0.097 and (2×) 0.044. The singlet and triplet states of isomer **4a**, **4sa**, and **4ta**, are also quite low in energy at 7.8 and 5.9 kcal mol⁻¹, respectively (see Table II).

Somewhat intermediate in energy, at 25.2 and 30.8 kcal mol⁻¹ are **5sa** and **5ta**. In the context of trends observed in this system this is most likely due to ring strain and Si–C multiple bonding.

High energy structures include singlet and triplet **6a** and **2a**, all at least 80 kcal mol⁻¹ above the global minimum. Isomer **6a** has the maximum number of Si–C bonds, with very little C–C bonding, and an exocyclic carbene. Isomer **2a** forces silicon to participate in π bonding, and also has an additional C–Si bond instead of a C–C bond, and a terminal carbene carbon.

Si₂C₂. Ten basic structures were optimized and identified as stationary points on the Si₂C₂ PES. Singlet and lowest energy triplet configurations were examined for all isomers when possible. Geometries are shown in Fig. 2. Vibrational frequencies are presented in Table III.

D_{∞h} structures. Two (linear) *D_{∞h}* isomers of Si₂C₂ have been considered. Isomer **1b** has two terminal silicon atoms, while in isomer **2b** the carbon atoms are terminal. Both isomers have ³Σ_g⁻, ¹Σ_g⁺, and ¹Δ states to be considered.

1b. The ³Σ_g⁻ configuration of isomer **1b**, **1tb**, has an energy of 1.0 kcal mol⁻¹ relative to the rhombic global minimum. Before the addition of dynamic correlation via MC-QDPT2, the ³Σ_g⁻ state is lowest in energy; however, as is frequently the case, the addition of external correlation preferentially stabilizes the singlet with respect to the triplet.

A C–C bond length of 1.28 Å in **1tb** indicates that there is a double bond interaction between these two atoms.²⁰ The silicon–carbon bond length of 1.77 Å also indicates a double bond.²¹ The Mayer bond order analysis is consistent with this picture.^{19,24,25}

The ¹Σ_g⁺ and ¹Δ states of **1b**, **1sb-Σ** and **1sb-Δ**, are just 8.9 and 5.8 kcal mol⁻¹ above the global minimum, respectively. Since Si₂C₂ and SiC₃ are isovalent, the electron occupations for linear singlet species are quite similar. The ¹Δ state can be described schematically as having ($\pi_x^0\pi_y^2 - \pi_x^2\pi_y^0$) and $\pi_x^1\pi_y^1$ occupation in the HOMO and LUMO π orbitals, while **1sb-Σ** can be described by ($\pi_x^0\pi_y^2 + \pi_x^2\pi_y^0$).

Bond lengths in **1sb-Σ** and **1sb-Δ** are quite similar to those in **1tb**; the C–C bonds are the same length, 1.27 Å, while the C–Si bonds are slightly longer in the ¹Σ_g⁺ and ¹Δ states (Fig. 2). Thus, bonds again appear to be double bonds.

2b. The calculated states of isomer **2b** are all significantly higher in energy (≈200 kcal mol⁻¹) than isomer **1b**. Thus, these states were not studied extensively. It is worthwhile to briefly consider the qualitative differences between **1b** and **2b**. Especially significant is the observation that in **2b** the silicons are forced to multiple bond with each other. This

is highly unfavorable; the C–C multiple bonds in **1b** are preferred.

D_{2h} structures. The two *D_{2h}* structures considered in this investigation each consist of four membered rings of alternating silicons and carbons (Fig. 2). Isomer **5b** has a transannular C–C bond, and a long Si–Si distance. In isomer **7b**, the Si–Si bond is short, while the C–C bond distance is much longer than that of **5b**.

5b. The ¹A_g state of rhombic structure **5b** is a minimum on the PES.

The C–C bond in ¹A_g (**5sb**) is intermediate between typical single and double bond lengths at 1.48 Å. In agreement with this, the Mayer bond order analysis indicates a C–C bond order of 1.45. The HOMO is a σ bonding orbital, between the two carbons, with additional electron density extending outside the ring from the two carbons. The HOMO-1 is a π bonding orbital with Mulliken populations indicating that approximately 80% of the electron density is located on the carbons. Additionally, there is a low lying σ orbital that is bonding throughout the molecule. These are the only orbitals contributing to C–C bonding in this molecule. Si–C bond distances are 1.82 Å, with bond orders of 1.061. The Si–Si distance is 3.33 Å. Examination of NOONs shows 0.19 electrons outside the RHF reference for **5b** ¹A_g.

The lowest triplet state of isomer **5b**, ³B_{1g}, is 43.0 kcal mol⁻¹ above the ¹A₁ state, the Si₂C₂ global minimum. ³B_{1g} is also a minimum on the FORS(12,10)/6-31G(d) PES. The C–C bond distance is slightly shorter than that of the singlet, 1.44 Å (¹A₁ = 1.48 Å), while the Si–C bond distance is slightly longer at 1.86 Å compared to 1.82 Å in ¹A₁.

7b. Relative to **5b** the second *D_{2h}* isomer, **7b**, has a longer C–C distance and a shorter Si–Si distance. Both the ¹A_g and the lowest triplet, ³A_u, are rather high in energy; 76.8 and 47.3 kcal mol⁻¹ higher than the global minimum, respectively (Table IV).

The **7b** ¹A_g state (**7sb**) is a minimum on the PES. It is interesting to compare the **7b** ¹A_g π bonding MO with the analogous **5b** ¹A_g π MO. In **5b** ¹A_g this orbital is located primarily between the two carbons; in **7b** ¹A_g, the electron density is almost equally distributed among all atoms.

Now consider the ³A_u state of isomer **7b**, **7tb**. Not only is **7tb** much lower in energy than **7sb**, there is also a significant change in geometry. The Si–Si bond distance is more than 0.5 Å longer in **7tb** than **7sb** (¹A_g 2.304, ³B_{1g} 2.835 Å) while the C–C distance is more than 0.5 Å shorter in the triplet than the singlet (¹A_g 2.967, ³B_{1g} 2.329 Å). Examination of molecular orbitals shows σ bonding between the carbons of **7tb**, whereas there is virtually no C–C σ bonding in **7sb**.

The ³B_{1g} state is a transition state on the PES. When this structure is distorted along the imaginary normal mode, subsequent optimization leads to the ³A₂ state of C_{2v} symmetry (**10tb**).

C_{2v} structures. Four C_{2v} structures have been studied (Fig. 2). Two of these (**3b**, **4b**) consist of three-membered rings with an exocyclic carbon or silicon. The third C_{2v}

TABLE III. Si₂C₂ vibrational frequencies.

Vibration	Symmetry	Intensity Debye ² amu ⁻¹ Å ⁻²	Frequency cm ⁻¹	Vibration	Symmetry	Intensity Debye ² amu ⁻¹ Å ⁻²	Frequency cm ⁻¹
1sb-sigma				Si-Si stretch	<i>a'</i>	0.06	358
Symmetric bend	π_g	0.01	128(2×)	Peripheral C-C-Si bend	<i>a'</i>	0.08	484
Asymmetric bend	π_u	0.00	344(2×)	Transannular C-Si stretch	<i>a'</i>	1.31	627
Symmetric C-Si stretch	σ_g^+	0.00	460	Breathing	<i>a'</i>	0.98	735
Asymmetric C-Si stretch	σ_u^+	3.82	898	C-C stretch	<i>a'</i>	0.52	1676
C-C stretch	σ_g^+	0.00	1782	6tb			
1sb-delta				Si-C-Si bend	<i>a'</i>	0.11	173
Symmetric bend	π_g	0.12	130(2×)	Out-of-plane bend	<i>a''</i>	0.01	341
Asymmetric bend	π_u	0.00	357(2×)	Transannular C-Si stretch	<i>a'</i>	1.25	527
Symmetric C-Si stretch	σ_g^+	0.00	467	Si ₂ -C ₄ stretch	<i>a'</i>	0.21	593
Asymmetric C-Si stretch	σ_u^+	2.88	893	Si ₁ -C ₃ stretch	<i>a'</i>	1.21	747
C-C stretch	σ_g^+	0.00	1800	C-C stretch	<i>a'</i>	0.49	1619
1tb				7sb			
Symmetric bend	π_g	0.00	137(2×)	Out-of-plane bend	<i>b_{2u}</i>	3.00	177
Asymmetric bend	π_u	0.00	371(2×)	Si-C symmetric stretch	<i>b_{1u}</i>	0.01	537
Symmetric C-Si stretch	σ_g^+	0.00	474	Si-Si stretch	<i>a_g</i>	0.00	570
Asymmetric C-Si stretch	σ_u^+	0.21	922	In-plane ring distortion	<i>b_{2g}</i>	0.00	600
C-C stretch	σ_g^+	0.00	1860	Si-C asymmetric stretch	<i>b_{3u}</i>	0.78	715
3sb				Breathing	<i>a_g</i>	0.00	803
In-plane distortion	<i>b₁</i>	0.04	224 <i>i</i>	7tb			
Out-of-plane bend	<i>b₂</i>	0.04	86	Out-of-plane bend (to 10tb)	<i>b_{2u}</i>	0.06	261 <i>i</i>
Si-C-Si bend in plane	<i>a₁</i>	0.55	418	Si-Si stretch	<i>a_g</i>	0.00	404
C-Si asymmetric stretch	<i>b₁</i>	0.29	528	Si-C asymmetric stretch	<i>b_{3u}</i>	0.49	519
Ring breathing	<i>a₁</i>	1.68	647	In-plane ring distortion	<i>b_{2g}</i>	0.00	625
C-C stretch	<i>a₁</i>	14.24	1881	Si-C symmetric stretch	<i>b_{1u}</i>	0.59	752
3tb				Breathing	<i>a_g</i>	0.00	794
In-plane distortion	<i>b₁</i>	0.07	47	8sb			
Out-of-plane bend	<i>b₂</i>	0.00	233	In-plane distortion to 6sb	<i>b₁</i>	0.02	445 <i>i</i>
Si-C-Si bend	<i>a₁</i>	0.59	386	Out-of-plane twist to 9sb	<i>a₂</i>	0.00	330 <i>i</i>
Asymmetric C-Si stretch	<i>b₁</i>	0.76	397	Si-Si stretch	<i>a₁</i>	0.03	316
Ring breathing	<i>a₁</i>	1.30	643	C-Si asymmetric stretch	<i>b₁</i>	0.63	557
C-C stretch	<i>a₁</i>	10.64	1759	C-Si symmetric stretch	<i>a₁</i>	3.89	722
4sb				C-C stretch	<i>a₁</i>	1.43	1909
Out-of-plane bend	<i>b₂</i>	0.00	77 <i>i</i>	8tb			
In-plane distortion	<i>b₁</i>	0.59	126	In-plane distortion to 6tb	<i>b₁</i>	2109.50	1333 <i>i</i>
Asymmetric C-Si stretch	<i>b₁</i>	1.37	361	Out-of-plane twist to 9tb	<i>a₂</i>	38.51	919 <i>i</i>
Si-Si stretch	<i>a₁</i>	0.57	412	Si-Si stretch	<i>a₁</i>	0.27	625
Symmetric C-Si stretch	<i>a₁</i>	6.20	892	Out-of-plane twist	<i>a₂</i>	23.43	705
C-Si-C bend	<i>a₁</i>	1.81	1783	C-Si asymmetric stretch	<i>b₁</i>	705.41	937
4tb				C-C stretch	<i>a₁</i>	1.83	1813
In-plane distortion	<i>b₁</i>	0.39	126	9sb			
Out-of-plane bend	<i>b₂</i>	0.28	136	C-Si asymmetric stretch	<i>b</i>	0.58	272 <i>i</i>
C-Si asymmetric stretch	<i>b₁</i>	1.53	345	Si-Si stretch	<i>a</i>	0.04	287
Si-Si stretch	<i>a₁</i>	0.02	394	Twist	<i>a</i>	0.18	305
C-Si symmetric stretch	<i>b₁</i>	9.24	895	C-Si asymmetric stretch	<i>b</i>	1.04	623
C-Si-C bend	<i>a₁</i>	0.80	1803	C-Si symmetric stretch	<i>a</i>	2.71	709
5sb				C-C stretch	<i>a</i>	0.21	1721
Out-of-plane bend	<i>b_{2u}</i>	0.13	224	9tb			
In-plane ring distortion	<i>b_{1u}</i>	1.34	424	C-Si asymmetric stretch	<i>b</i>	0.06	142 <i>i</i>
Breathing	<i>a_g</i>	0.00	543	Twist	<i>a</i>	0.15	296
C-C stretch	<i>a_g</i>	0.00	1013	Si-Si stretch	<i>a</i>	0.08	342
C-Si asymmetric stretch	<i>b_{2g}</i>	0.00	1026	C-Si asymmetric stretch	<i>b</i>	0.31	459
C-Si symmetric stretch	<i>b_{3u}</i>	9.74	1066	C-Si symmetric stretch	<i>a</i>	2.30	725
5tb				C-C stretch	<i>a</i>	0.11	1713
Out-of-plane bend	<i>b_{2u}</i>	0.04	269	10sb			
In-plane ring distortion	<i>b_{1u}</i>	0.29	411	Symmetric butterfly bend	<i>a₁</i>	0.23	262
Breathing	<i>b_{3u}</i>	6.03	474	C-C stretch	<i>a₁</i>	0.29	419
C-Si symmetric stretch	<i>b_{3u}</i>	33.35	623	C-Si asymmetric stretch	<i>b₁</i>	0.45	573
C-C stretch	<i>a_g</i>	0.97	1150	C-Si asymmetric stretch	<i>a₂</i>	0.00	702
Si-C asymmetric stretch	<i>b_{2g}</i>	0.01	2686	C-Si symmetric stretch	<i>a₁</i>	0.34	762
6sb				Breathing	<i>a₁</i>	0.03	806
Out-of-plane bend	<i>a''</i>	0.22	244				

TABLE IV. Si₂C₂ relative energies (kcal mol⁻¹).

Isomer	State	MCQDPT/6-31G(d)	MCQDPT(12,11)/aug-cc-pVDZ
		//FORS(12,10/11)/6-31G(d)	//FORS(12,10/11)/6-31G(d) (zero point corrected energies in parentheses)
1sb-delta	¹ Δ	6.2	5.8(5.6)
1sb-sigma	¹ Σ ⁺ _g	9.2	8.9(8.6)
1tb	³ Σ ⁻ _g	1.0	1.0(1.0)
3sb	¹ A ₁	34.8	26.4(25.4)
3tb	³ B ₂	33.4	28.2(27.0)
4sb	¹ A ₁	68.2	70.2(69.2)
4tb	³ A ₂	58.8	44.8(43.9)
5sb	¹ A _g	0.0	0.0(0.0)
5tb	³ B _{1g}	51.4	43.0(44.9)
6sb	¹ A'	6.0	4.2(4.0)
6tb	³ A''	24.8	15.0(14.6)
7sb	¹ A _g	82.2	76.8(75.5)
7tb	³ A _u	55.6	47.3(45.6)
8sb	¹ A ₁	46.4	33.5(32.4)
8tb	³ B ₂	35.5	25.5(25.2)
9sb	¹ A	40.8	23.0(22.1)
9tb	³ B	23.5	21.6(20.6)
10tb	³ A ₂	52.2	47.1(46.0)

structure (**10b**) is a butterfly shaped four membered ring generated from **7b** ³B_{1g} by following the normal mode with the imaginary frequency, as discussed above. The fourth (**8b**) is a trapezoidal planar structure.

3b. The lowest energy C_{2v} structure is isomer **3b**. The ¹A₁ state is slightly lower in energy than the ³B₂ state, by 1.8 kcal mol⁻¹ (Table IV). In both **3sb** and **3tb** Si–Si and Si–C bond lengths are very close to typical single bond lengths.²¹ The Mayer bond order analysis indicates that the Si–Si bond orders for the singlet and triplet are 1.145 and 1.269, while the Si–C bond orders are 0.815 and 0.803, respectively. For both states there is very strong bonding between the carbons. C–C bond lengths of 1.29 Å for the ¹A₁ structure and 1.30 Å for the ³B₂ structure indicate strong double bonding. Examination of natural orbitals is consistent with this: There are two π bonding orbitals between the carbons, one of them perpendicular to the plane of the molecule and the other in the plane of the molecule. The NOONs in the singlet are 1.940 and 1.914; in the triplet they are 1.938 and 1.925, respectively. The π bond perpendicular to the plane is very localized between the two carbons such that it is analogous to the bonding observed in the linear species where there are two degenerate π bonds. Of course, in this case the two orbitals are not degenerate. The singlet and the triplet are 26.4 and 28.2 kcal mol⁻¹ above the global minimum.

4b. Isomer **4b** consists of a three-membered ring with an exocyclic silicon bonded to the silicon vertex. There is very little difference between the ¹A₁ structure, **4sb**, and that of ³A₂, **4tb**. The largest difference in bond lengths is 0.06 Å; bond angles are the same to within 1°. The bonding is quite similar. The bond lengths indicate strong double bonding between the carbons, Si–C bonding slightly stronger than single, and a Si–Si bond intermediate between single and double bonding.

The lowest energy state for this isomer is ³A₂, in which the two unpaired electrons reside in the b₁ Si–Si π bonding

orbital and a b₂ π orbital that is primarily localized on the exocyclic silicon. Strictly speaking, this b₂ orbital is antibonding between the cyclic silicon and the two carbons; however, there is so little electron density on the carbons that there is little antibonding character. **4tb** and **4sb** are 44.8 and 70.2 kcal mol⁻¹ above the global minimum, respectively.

10b. The butterfly C_{2v} isomer, **10tb**, is closely related to its D_{2h} precursor **7tb**. In **10tb** the molecular plane of **7tb** is broken.

Although the transannular C–C distance is 2.35 Å, natural orbitals indicate that the carbons participate in both σ bonding and banana shaped, π like bonding, both with diradical character on the carbons. Lone pairs are located on the silicons.

Attempts to isolate the singlet with this geometry (**10sb**) were not successful. Optimizations starting from the triplet geometry in attempt to find an isomer **10sb** all lead back to the global minimum structure **5sb**.

8b. Isomers **8sb** and **8tb** are trapezoidal structures. Although the singlet and triplet are only 33.5 and 25.5 kcal mol⁻¹ above the global minimum, both structures have two imaginary frequencies. For isomer **8sb**, the modes corresponding to the two imaginary frequencies lead to isomers **6sb** and **9sb**. For isomer **8tb**, the two imaginary frequencies connect this structure to isomers **6tb** and **9tb**. Both **9sb** and **9tb** are C₂ transition states on the PES.

Isomer **9sb** (23.0 kcal mol⁻¹ above the global minimum) has one imaginary frequency at 271i cm⁻¹. Distortion along this normal mode followed by optimization of the geometry leads to isomer **6sb**.

For **9tb**, distortion along the mode with imaginary frequency 142i cm⁻¹, followed by geometry optimization produces isomer **6tb**. **9tb** is 21.6 kcal mol⁻¹ higher than the global minimum **5sb**.

C_s structures. **6b**. Isomer **6b** is a distorted trapezoidal structure with C_s symmetry. Both the singlet and the triplet

are minima on the MCSCF/6-31G(d) potential energy surface.

6sb is 4.2 kcal mol⁻¹ higher than the global minimum. The Si–Si bond distance is 2.455 Å compared with 2.342 Å in disilane,²⁶ indicating a weak bond. On the other hand, qualitative examination of natural orbitals reveals five orbitals with some amount of bonding interaction between the two silicons, and one with antibonding character. MCSCF bond order analysis indicates a Si–Si bond order of 0.819, and Edmiston–Ruedenberg energy localized orbitals²⁷ indicate weak Si–Si interaction. The $4c-2e-\pi$ bond is mostly localized on the two carbon atoms, with Mulliken populations of 1.083 on the central carbon and 0.520 on the other carbon atom. The populations on the silicons are 0.226 and 0.113. Between each carbon atom and silicon-1 there is nearly a single bond; the third C–Si bond is much stronger, with a bond order of 1.406. The C–C MCSCF bond order is 1.547.

6tb is higher in energy than **6sb**, 15.0 kcal mol⁻¹ above the global minimum. The Si–Si distance is 2.62 Å in **6tb** compared to 2.46 Å in **6sb**. The transannular C–Si bond is slightly longer in **6tb** than that in **6sb**, while the peripheral carbon distance to the same silicon is shorter by 0.06 Å. The Si–Si bond length here is much shorter than the 2.971 Å obtained in a previous study that employed UHF with the 6-31G* basis set.⁷

Si₂C₂ relative energies. The lowest energy isomer is predicted to be **5sb**, just 1.0 kcal mol⁻¹ lower than the $^3\Sigma_g^-$ state of **1b**, **1tb**. Although the relative ordering of these two isomers is in agreement with most previous studies,⁵⁻⁷ we find them to be much closer in energy than the 11.9 kcal mol⁻¹ found by Fitzgerald and Bartlett (MP4/DZP) or the 15.5 kcal mol⁻¹ found by Lammertsma and Güner [MP2/6-31G(d)]. As with SiC₃ the linear singlets are also quite low in energy. The $^1\Sigma_g^+$ state has a relative energy of 8.9 kcal mol⁻¹, while the $^1\Delta_g$ state has an energy of only 5.8 kcal mol⁻¹ at the $^1\Sigma_g^+$ geometry. Also very low in energy is the distorted trapezoid structure **6b**; the singlet is only 4.2 kcal mol⁻¹ and the triplet is 15.0 kcal mol⁻¹ above the global minimum.

A number of structures have somewhat higher energy, ~20–30 kcal mol⁻¹. These have some C–C bonding, but suffer either from some degree of ring strain associated with the incorporation of a three-membered ring, or from some C–Si bonding at the expense of C–C bonding. Very high energy isomers (>40 kcal mol⁻¹) allow very little C–C bonding, **7b**, or suffer from a great deal of ring strain, as in **4b** where Si–C–C bond angles are 69° and the C–Si–C bond angle is 41°.

IV. WAVE FUNCTIONS

Now consider the importance of using MCSCF wave functions for these compounds. The unsaturated nature of these molecules, combined with the presence of a large number of negative virtual orbital energies at the Hartree–Fock level suggests the need for a multireference wave function.

Since our primary interest is in predicting the lowest energy structures, and characterizing these and other struc-

tures which might be observed experimentally, we will focus on those isomers whose energy is ≤ 10 kcal mol⁻¹ above the global minimum. Within these isomers we will focus on those orbitals which would be unoccupied by a single reference wave function. We will refer to these orbitals as “unoccupied” orbitals, although clearly they are not completely unoccupied in an MCSCF wave function. These low energy isomers all have at least one “unoccupied” natural orbital occupation number (U–NOON) greater than 0.07. **1ta** has two U–NOONs of 0.097, with total electron density outside the Hartree–Fock configuration of 0.281 e^- . **1sa-Σ** and **1sa-Δ** both have U–NOONs above 0.1 and total electron density in “unoccupied” orbitals of more than 0.3. It has been suggested previously²⁸⁻³¹ that an occupation number for a virtual orbital of 0.1 or as low as 0.07 indicates that a single determinant wave function is suspect.

The situation is similar for Si₂C₂. The wave function of the rhombic structure **5sb** is the most dominated by the Hartree–Fock configuration. Its largest U–NOON is 0.070, with 0.189 e^- total electron density outside the RHF reference. The linear species more clearly require a multiconfigurational representation. **1tb** has two U–NOONs of 0.117 and total electron density in “unoccupied” orbitals is 0.339. **1sb-Σ** has two U–NOONs of 0.170 and total electron density in “unoccupied” orbitals of 0.463, nearly half an electron.

These occupation numbers indicate that a multireference wave function is most appropriate. This may explain the difference between relative energies found in this study and those in previous studies.

V. CONCLUSIONS

A comprehensive study of singlet and triplet isomers of SiC₃ and Si₂C₂ has been presented, including examination of structures, bonding, relative energies, and vibrational modes. The SiC₃ global minimum is predicted to be a silicon terminated $^3\Sigma^-$ structure, **1ta**, with a singlet rhombic structure, **3sa**, 4.4 kcal mol⁻¹ higher. This is in contrast to previous predictions that the rhombic structure is the global minimum. The Si₂C₂ global minimum is predicted to be a singlet rhombic structure, **5sb**, with a $^3\Sigma_u^-$ silicon terminated linear isomer, **1tb**, 1.0 kcal mol⁻¹ higher in energy. Although the rhombic structure has previously been predicted to be the global minimum, we find the $^3\Sigma_u^-$ structure to be much lower in energy than had previously been expected.

It has also been determined that the use of a multireference wave function is important for studying these systems.

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