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Geometrical structures and vibrational frequencies of the energetically low-lying isomers of SiC₃

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The ground state of the SiC₃ molecule is found to be a closed-shell cyclic C_{2v} symmetry structure which can be described as a four-membered ring with a transannular (cross ring) carbon-carbon bond, $r(\text{C}-\text{C}) = 1.469 \text{ \AA}$. Theoretical studies with a triple-zeta plus double-polarization function (TZ2P) basis set in conjunction with the configuration-interaction technique at the TZ2P self-consistent-field optimized geometries predict this rhomboidal structure to be 4.1 kcal/mol more stable than the linear triplet Si-C-C-C isomer. A second closed-shell rhomboidal C_{2v} symmetry structure with carbon-silicon transannular bonding, $r(\text{Si}-\text{C}) = 1.880 \text{ \AA}$, was located and characterized as a local minimum lying 4.3 kcal/mol above the ground-state rhomboidal structure at this level of theory. Higher-level theoretical methods, including contributions from triple excitations, with larger basis sets will be required to obtain a more definitive set of relative energies.

I. INTRODUCTION

Silicon-containing carbon cluster molecules have been of interest since the electronic absorption spectrum of SiC₂ was first observed in the atmospheres of carbon stars.¹ More recently, SiC and SiC₄ have been detected in interstellar space,² the identification of these species being made through comparison of astronomical data and laboratory spectroscopic experiments. It is very probable that other carbon-silicon cluster molecules are present and their detection is important for an understanding of chemical processes in interstellar environments. Similarly, silicon carbide vapors have been shown to contain various species, in particular SiC, SiC₂, and Si₂C amongst others, at high temperatures.³ The SiC₃ molecule is probably present in interstellar environments and silicon carbide vapors, and our aim is to provide information to aid spectroscopists in its identification.

Experimental and theoretical investigations on the triatomic clusters SiC₂,^{4,5} Si₂C,^{6,7} and Si₃ (Ref. 8) show that the ground states are strongly bent (Si₂C) or cyclic (SiC₂, Si₃) C_{2v} symmetry closed-shell structures (Si₃ has a low-lying D_{3h} symmetry triplet state, $^3A'_2$), in contrast to C₃ which is well known to be linear.^{9,10} The ground-state structures of the series of tetra-atomic carbon-silicon clusters also display this competition between cyclic and linear isomers. The rhombic structure of C₄ is preferred over the linear structure by less than 5 kcal/mol according to most *ab initio* research,¹¹⁻¹⁶ with the latest theoretical studies suggesting that the two isomers are essentially isoenergetic.¹⁷ There is no definitive experimental conclusion to the structural dilemma of the ground state of C₄ since evidence from ESR,^{18,19} uv photoelectron spectra,²⁰ and Fourier transform ir (Ref. 21) supports linear C₄, while Coulomb explosion experiments²² favor the rhombic form.

In contrast, Si₄ strongly prefers a rhombic form.²³ Interestingly, for the mono- and diprotonated systems C₄H⁺ and C₄H₂²⁺ the linear structure lies lowest energetically.²⁴ The mixed carbon-silicon tetra-atomic clusters might be expected to display intermediate structural behavior. Such features are indeed exhibited by Si₂C₂. Theoretical studies show the rhombic structure incorporating a so-called transannular C-C bond to be favored over both the linear Si-C-C-Si structure and the rhomboidal structure incorporating a transannular Si-C bond.^{25,26} The Si₂C₂ molecule involves two distinct rhombic structures, the ground-state isomer and an energetically high-lying isomer, and in a recent article Lammertsma and co-workers²⁷ discuss the concept of bond-stretch isomerism in relation to these two structures.

The present study continues the series of tetra-atomic carbon-silicon clusters, concentrating on a detailed *ab initio* theoretical analysis of the potential-energy hypersurface of SiC₃. In recent work on SiC₃, a linear structure was found to be a local potential-energy minimum; however, no other structural isomers were considered.^{2(b)} In this context for the current research it is important to focus on the various possible conformations of SiC₃, with special emphasis being placed on the linear form and two distinct rhomboidal structures. These structures are predicted to be the most stable energetically at the theoretical levels employed.

II. THEORETICAL METHODS

To determine the ground-state structure of SiC₃ it was necessary to consider a number of possible geometrical isomers. These can be divided into three structural categories: linear, rhomboidal, and structures incorporating three-membered rings. These geometrical isomers are depicted in

^{a)}Contribution CCQC No. 109.

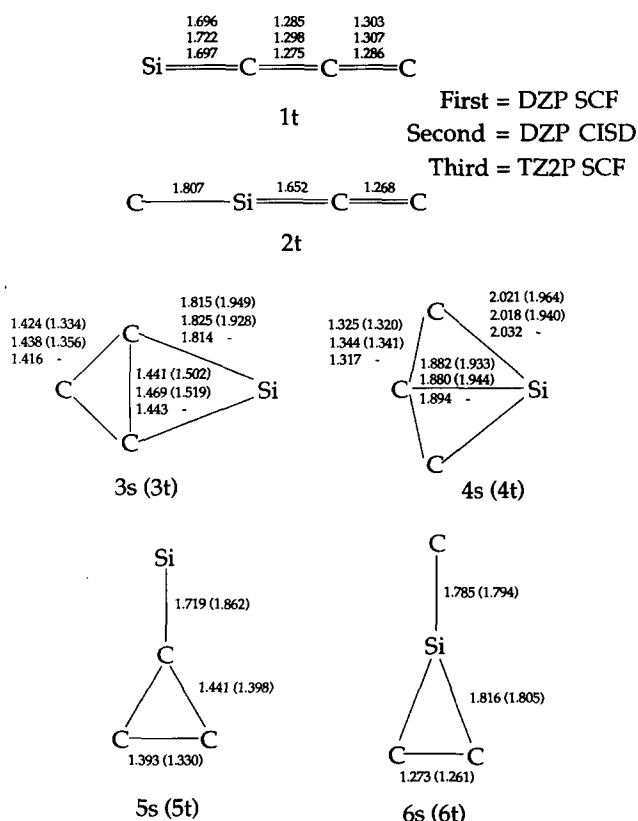


FIG. 1. Optimized geometries for the singlet and triplet isomers of SiC₃ at various levels of theory, with triplet geometries in parentheses where appropriate.

Fig. 1. In accordance with the analogous form of C₄, the lowest-energy linear structure of SiC₃ is expected to be an open-shell $^3\Sigma^-$ state; hence for all isomeric forms closed-shell states and the lowest triplet states were considered.

All structures were determined using the standard Huzinaga–Dunning^{28–30} double-zeta basis set of contracted Gaussians augmented with a set of Cartesian *d*-like functions on each atom. This complete double-zeta plus polarization (DZP) basis set is designated Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d). The polarization function orbital exponents were $\alpha_d(\text{Si}) = 0.5$, $\alpha_d(\text{C}) = 0.75$. When small energy differences are involved results are often very sensitive to the quality of the basis set. Thus a more flexible basis set of triple-zeta plus double-polarization (TZ2P) quality was employed on the important lowest-energy structures. This orbital set involves McLean and Chandler's³¹ 6s5p contraction of Huzinaga's 12s9p primitive set for silicon²⁸ and Dunning's²⁹ 5s3p contraction of Huzinaga's 10s6p set for carbon augmented with two sets of Cartesian *d* functions for each atom with orbital exponents $\alpha_d(\text{Si}) = 1.0, 0.25$ and $\alpha_d(\text{C}) = 1.5, 0.35$. This basis set is designated Si(12s9p2d/6s5p2d), C(10s6p2d/5s3p2d). Investigations by other workers^{5,10,11,25} have shown the importance of including polarization functions in the basis set for studies involving cyclic structures.

The various structures of SiC₃ have been fully optimized within the given symmetry constraints at both the self-consistent field^{32,33} (SCF) and configuration interac-

tion with all single- and double-excitations^{34–36} (CISD) levels of theory using analytic gradient techniques. The CISD wave function, which includes the effects of electron correlation, was determined using the shape-driven graphical unitary-group approach³⁷ utilizing the frozen-core approximation, meaning only the valence electrons have been explicitly correlated. Specifically, the eight lowest occupied molecular orbitals (Si 1s, 2s, 2p; C 1s-like orbitals) were held doubly occupied (frozen cores) and the four highest-lying virtual orbitals (Si 1s*; C 1s*-like orbitals) were deleted (frozen virtuals) in all configurations. Otherwise, all singly and doubly excited configurations relative to the SCF reference have been included. With the TZ2P basis set for the linear $^3\Sigma^-$ state this gives rise to 90 131 configurations in C_{2v} symmetry, and for the two rhomboidal structures in C_{2v} symmetry, namely 3s and 4s (see Fig. 1), there are 72 970 and 72 550 configurations, respectively. The effect of unlinked quadruple excitations on the CISD relative energies is approximated by incorporating the Langhoff and Davidson correction,³⁸ and the subsequent energy differences are labeled CISD + Q. The symmetry-constrained structures were characterized via the determination of all quadratic force constants and harmonic vibrational frequencies using analytic SCF second-derivative techniques.³⁹

Structural optimizations and harmonic vibrational frequency analyses were performed for all the isomeric forms at the SCF/DZP level and refined energetic predictions were obtained from single-point CISD/DZP calculations at SCF/DZP geometries. Since the predicted geometries and relative energies of molecular clusters may exhibit a strong dependence on the level of theory adopted, the three lowest-lying isomers, 1t, 3s, and 4s (see Fig. 1), were subject to geometry optimizations at SCF/TZ2P and CISD/DZP levels, and CISD/TZ2P single-point energies were determined at SCF/TZ2P geometries. The structural parameters of the isomers 3t and 4t were also optimized at the CISD/DZP level of theory.

The leading coefficient in the CI expansion for the various structures has a range $C_0 = 0.92$ to 0.93 , while the range for the second configuration is $C_1 = -0.04$ to -0.06 , strongly suggesting these isomers can be suitably described with single-reference-based methods.

III. RESULTS AND DISCUSSION

In Fig. 1 we report the optimized geometries of all the isomeric forms in both singlet and triplet electronic states at various levels of theory. Total energies for all the isomers are reported in Table I with relative energies in Table II. Dipole moments, harmonic vibrational frequencies, and infrared intensities are given in Table III. The following discussion places emphasis on the bonding properties of the most-stable species. Singlet structures are indicated by *s* and triplets by *t*.

A. Linear structures

The most important linear isomer on energetic grounds contains a terminal silicon atom, Si–C–C–C,

TABLE I. Total energies^a (hartrees) of optimized geometrical structures for SiC₃.

		SCF DZP	CISD ^b DZP	CISD + Q ^c DZP	SCF TZ2P	CISD TZ2P	CISD + Q TZ2P
1 <i>t</i>	³ Σ [−]	−0.299 02	−0.675 86 (−0.675 17)	−0.729 79 (−0.728 51)	−0.337 48	(−0.749 40)	(−0.810 20)
2 <i>t</i>	³ Σ [−]	−0.194 81	(−0.558 98)	(−0.611 28)			
3 <i>s</i>	¹ A ₁	−0.304 68	−0.691 56 (−0.690 87)	−0.745 59 (−0.744 19)	−0.342 29	(−0.757 35)	(−0.816 67)
3 <i>t</i>	³ B ₁	−0.271 48	−0.650 72	−0.704 22			
4 <i>s</i>	¹ A ₁	−0.291 56	−0.674 43	−0.729 46	−0.335 41	(−0.748 84)	(−0.809 83)
4 <i>t</i>	³ B ₁	−0.256 62	−0.652 89	−0.711 58			
5 <i>s</i>	¹ A ₁	−0.252 08	(−0.638 27)	(−0.694 34)			
5 <i>t</i>	³ A ₂	−0.257 71	(−0.634 28)	(−0.686 00)			
6 <i>s</i>	¹ A ₁	−0.144 04	(−0.528 23)	(−0.586 53)			
6 <i>t</i>	³ A ₂	−0.196 09	(−0.569 12)	(−0.622 66)			

^aAdd −402 hartrees.^bValues in parentheses are absolute energies obtained at SCF optimized geometries with the same basis set.^cUnless in parentheses, the energies were evaluated at the CISD/DZP stationary point geometries.

showing the preference of silicon not to partake in multiple bonding.^{40,41} The ³Σ[−] electronic state, 1*t*, is favored over the ¹Σ⁺ and ¹Δ states for linear SiC₃ via Hund's rules, and displays strong C–C and Si–C bonding as expected for a cumulene-like valence structure. The C–C bond lengths are intermediate between that of a normal C–C double bond (1.35 Å in ethylene) and a normal triple bond (1.21 Å in acetylene), and are nearly identical to those found by Bernholdt, Magers, and Bartlett¹⁷ for linear C₄, *r*(C–C) = 1.288, 1.300 Å (SCF/DZP). The Si–C bond length at the SCF/DZP level, 1.696 Å, is slightly shorter than both the suggested prototypical double-bond value, 1.71 Å,⁴² and the value found by Lammertsma and Güner in linear Si₂C₂, *r*(Si–C) = 1.721 Å with a 6-31G* basis set at the SCF level.^{25(a)} An increase in the basis set from DZP to TZ2P at the SCF level leads to a reduction in

the C–C bond lengths by 0.010 and 0.007 Å with the Si–C bond distance remaining almost constant. Reoptimization at the CISD/DZP level of theory has the effect of increasing the bond lengths relative to SCF/DZP as expected for the inclusion of electron correlation. Subsequent vibrational analysis at the SCF/DZP level of theory shows the ³Σ[−] state to be a local minimum on the SiC₃ potential-energy surface.

At the SCF/DZP level a symmetry-broken wave function^{43,44} was found for this linear ³Σ[−] state involving localization of the π molecular orbitals. Upon geometry optimization, the symmetry broken structure is very close to that reported for the symmetrized solution and the energy is only 0.2 kcal/mol lower. Furthermore, the CISD/DZP structure using the symmetry-broken SCF wave function as a reference function is 1.6 kcal/mol above the corre-

TABLE II. Relative energies of optimized geometrical structures for SiC₃. Energy differences are in kcal/mol.

		SCF DZP	CISD ^a DZP	CISD + Q DZP	SCF TZ2P	CISD TZ2P	CISD + Q TZ2P
1 <i>t</i>	³ Σ [−]	3.6	9.9	9.9	3.0	(5.0)	(4.1)
2 <i>t</i>	³ Σ [−]	68.9	(82.8)	(83.4)			
3 <i>s</i>	¹ A ₁	0.0	0.0	0.0	0.0	(0.0)	(0.0)
3 <i>t</i>	³ B ₁	20.8	25.6	26.0			
4 <i>s</i>	¹ A ₁	8.2	10.7	10.1	4.3	(5.3)	(4.3)
4 <i>t</i>	³ B ₁	30.2	24.3	21.3			
5 <i>s</i>	¹ A ₁	33.0	(33.0)	(31.3)			
5 <i>t</i>	³ A ₂	29.5	(35.5)	(36.5)			
6 <i>s</i>	¹ A ₁	100.8	(102.1)	(98.9)			
6 <i>t</i>	³ A ₂	68.1	(76.4)	(76.3)			

^aValues in parentheses are relative energies obtained at SCF optimized geometries with the same basis set.

TABLE III. SCF dipole moments (D), harmonic vibrational frequencies (cm⁻¹), and, in parentheses, infrared intensities (km/mol) for the isomeric forms of SiC₃.

		μ	ω_1 a_1 or σ^+	ω_2 a_1 or σ^+	ω_3 a_1 or σ^+	ω_4 b_1 or π	ω_5 b_2 or π	ω_6 b_2
1 <i>t</i>	DZP	4.74	2033 (5.5)	1285 (55)	681 (24)	474 (14)	171 (0.1)	...
1 <i>t</i>	CISD	4.72						
1 <i>t</i>	TZ2P	4.80	2037 (18)	1275 (75)	659 (30)	456 (10)	164 (0.0)	...
2 <i>t</i>	DZP	1.46	2053 (1486)	988 (85)	627 (11)	166 (23)	96 (49)	...
3 <i>s</i>	DZP	4.25	1550 (296)	1172 (114)	767 (79)	335 (2.3)	1118 (1.9)	393 (55)
3 <i>s</i>	CISD	4.21						
3 <i>s</i>	TZ2P	4.22	1514 (304)	1129 (96)	757 (80)	315 (4.7)	1095 (1.2)	388 (55)
3 <i>t</i>	DZP	0.58	1782 (0.7)	998 (14)	541 (58)	419 (1.3)	1328 (0.2)	220 (54)
4 <i>s</i>	DZP	2.27	1277 (1.3)	859 (49)	588 (35)	341 (31)	1623 (84)	439 (1.1)
4 <i>s</i>	CISD	2.28						
4 <i>s</i>	TZ2P	2.14	1262 (1.8)	849 (44)	575 (39)	308 (37)	1622 (83)	419 (1.3)
4 <i>t</i>	DZP	1.82	1326 (2.0)	753 (44)	617 (69)	510 (7.6)	1662 (2275)	371 <i>i</i> (—)
5 <i>s</i>	DZP	5.78	1573 (191)	1203 (512)	632 (1.6)	253 (6.5)	805 (0.4)	152 <i>i</i> (—)
5 <i>t</i>	DZP	2.90	1750 (5.2)	1274 (17)	529 (40)	356 (3.0)	2830 (3210)	181 (0.2)
6 <i>s</i>	DZP	0.19	1867 (34)	1022 (74)	694 (77)	193 (78)	236 (11)	127 (45)
6 <i>t</i>	DZP	0.72	1937 (49)	979 (176)	652 (48)	126 (64)	162 (14)	79 (86)

sponding structure using the symmetrized SCF wave function as a reference, and with a TZ2P basis no SCF symmetry-broken solution was found. More detailed investigation of the symmetry-broken solution was, therefore, not warranted.

The linear $^3\Sigma^-$ isomer with an internal Si atom, 2*t*, lies a full 73.6 kcal/mol above 1*t* at the CISD + Q/DZP level due to increased Si–C π bonding at the expense of C–C π bonds. Curiously, 2*t* shows significant differences in the two Si–C bond distances, one being significantly longer, and the other significantly shorter, than normal double-bond lengths, whereas in 1*t* all bond distances are shorter than normal double-bond lengths. The geometry is suggestive of a linear :Si=C=C: molecule datively bonded to a carbon 3P atom through the silicon lone pair. This structure, too, is a local minimum.

B. Four-membered ring structures

The cyclic structures 3 and 4 in Fig. 1 are consistent with a four-membered ring description. The 1A_1 state of structure 3, designated 3*s*, involves a transannular C–C distance of 1.441 Å, indicative of significant across the ring C–C bonding. These so-called inverted tricoordinate sp^2 hybridized carbon atoms have been reported for rhombic C₄ (Refs. 11–17) and Si₂C₂ (Refs. 25–27), and are defined as having three ligands on one side of a plane through that carbon while maintaining planarity.^{25,27} Isomer 3*s* involves two π bonding electrons (b_1 orbital) delocalized over the ring, hence all the bonds display some degree of multiple-bond character as exemplified by the bond lengths. With a TZ2P basis in conjunction with the SCF method the peripheral C–C bonds contract relative to DZP by 0.008 Å, and at the correlated level bond lengths increase by 0.010–

0.028 Å for this isomer. The SCF vibrational analysis of 3*s* shows this 1A_1 rhomboidal isomer to be a minimum on the potential-energy hypersurface.

The 3B_1 state associated with structure 3, namely 3*t*, is generated from 3*s* by the single electronic excitation $5a_1 \rightarrow 2b_1$. The $5a_1$ orbital is transannular C–C bonding and peripheral C–C antibonding in character. The doubly occupied $1b_1$ orbital is almost exclusively in the C₃ fragment in the triplet, 3*t* whereas in the singlet, 3*s*, it is largely delocalized around the whole SiC₃ ring. The $2b_1$ orbital is an out-of-phase combination of out-of-plane p orbitals on Si (mainly) and the unique carbon. Consideration of these orbital characters leads to the observed bond-length changes upon excitation. That is, shortening of the peripheral C–C bonds and lengthening of the transannular C–C and peripheral Si–C bonds. This 3B_1 state is found to be a local minimum lying 26.0 kcal/mol above the 1A_1 state at the CISD + Q/DZP level of theory.

Structure 4 also corresponds to a four-membered ring incorporating what may be termed inverted tricoordinate silicon and carbon atoms. Alternatively, structure 4 may be viewed as a linear C₃ molecule with silicon complexed to the central carbon atom. This electronic interaction can be viewed as bonding from C₃ to silicon through a π molecular orbital located mainly on the central carbon, reinforced by bonding from silicon to an empty π orbital of C₃ located on the terminal carbons. The 1A_1 state of structure 4, designated 4*s*, involves two π bonding electrons (b_1) delocalized almost completely over the C₃ unit, resulting in strong peripheral C–C bonding, $r(\text{C–C}) = 1.325$ Å. The transannular Si–C distance, 1.882 Å, is within the realm of Si–C single-bond lengths;⁴⁵ however, the peripheral Si–C distances are rather long, 2.021 Å, and the CCC angle is

found to be 152.3°, hence the argument for complexation. Isomer 4s has rather similar bonding characteristics to Lammertsma's structure 6s of Si₂C₂.^{25(a)} Extension of the basis set to TZ2P results in C–C bond-length contraction accompanied by increases in the Si–C distances. Inclusion of electron correlation increases the C–C bond lengths and slightly reduces the Si–C bond lengths relative to SCF/DZP. Structure 4s is found to be a local minimum on the potential-energy surface lying 10.1 kcal/mol above the isomer 3s at the CISD + Q/DZP level of theory.

The ³B₁ state associated with structure 4, namely 4t, is generated from 4s by the single electronic excitation 3b₂ → 1a₂. This state is characterized as a transition state with one imaginary b₂ vibrational frequency, 371i cm⁻¹, lying above structure 4s by 22.0, 13.6, and 11.2 kcal/mol with SCF, CISD, and CISD + Q methods, respectively. Electron correlation has a surprisingly large effect. The second b₂ vibrational mode of 4t, 1662 cm⁻¹, has an unphysically large ir intensity of 2275 km/mol. These features are strongly suggestive of the onset of symmetry breaking.^{43,44} Following the imaginary b₂ mode a C_s symmetry structure (³A'') was located, involving localization of the open-shell orbitals, and characterized as a minimum lying 9.4 kcal/mol below the C_{2v} symmetry structure, 4t. The differences in C–C and C–Si bond lengths for the C_s isomer are 0.136 and 0.248 Å, respectively, at the SCF level. However, the CISD/DZP structure of the C_s isomer, derived from the symmetry-broken SCF reference function, lies 3.7 kcal/mol above the CISD/DZP structure of the C_{2v} isomer using the symmetrized SCF wave function as a reference. The differences in C–C and C–Si bond lengths for the C_s isomer at the CISD level are 0.062 and 0.220 Å, respectively, smaller than at the SCF level. Further, upon small b₂ symmetry perturbations the CISD + Q/DZP energy of 4t rises from its C_{2v} stationary point value, hence, at the correlated level 4t is no longer a transition state. These arguments suggest that the prediction of 4t as a transition state is an artifact of the SCF method for this state.

C. Three-membered ring structures

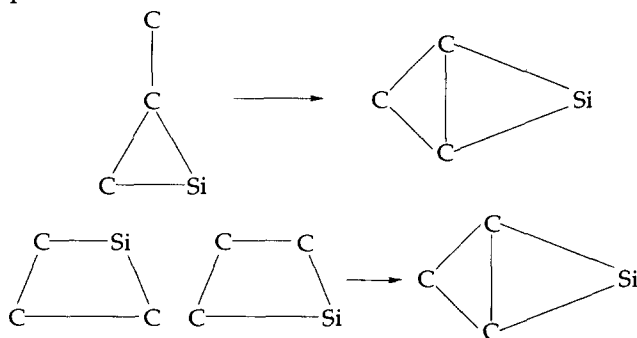
In terms of energetic behavior the most favorable three-membered ring structure is the ¹A₁ state of structure 5 in Fig. 1 with the silicon atom exocyclic to the ring. This isomer involves two π electrons (b₁) delocalized over the C₃ ring with little Si participation, leading to significant multiple bonding in the ring. The short Si–C distance is suggestive of bonding between silicon and the C₃ ring enhanced by electron donation from a C₃ ring b₂ orbital to silicon. The SCF vibrational analysis shows that this ¹A₁ structure is a transition state with a single imaginary frequency, 152i cm⁻¹ (b₂), corresponding to the SiCC bending mode. Isomer 5s may be considered to be a transition state for the degenerate rearrangement of rhomboidal isomer 3s.

The ³A₂ state associated with structure 5, designated 5t, is generated from 5s by the electronic excitation 2b₂ → 2b₁. The 2b₂ orbital, as described above, is Si–C bonding while the 2b₁ orbital is an out-of-plane π orbital

located mainly on Si, with some unique C–C bonding character. Therefore, the significant increase in the Si–C bond length upon excitation is predictable. This state is characterized as a local minimum with an unphysically large asymmetric C–C stretching frequency, 2830 cm⁻¹, that is indicative of the onset of symmetry breaking.^{43,44} However, as this is an energetically high-lying state, such problems were not pursued further in this research.

The high-energy singlet structure 6s with exocyclic carbon atom has ring bond lengths similar to those predicted for unsubstituted cyclic SiC₂ at the SCF/DZP level.⁵ Isomer 6s involves two π electrons principally localized between the carbons of the SiC₂ ring leading to strong C–C bonding. The exocyclic Si–C bond, as in 5s, is enhanced by overlap between an SiC₂ ring b₂ orbital and a carbon orbital of appropriate symmetry. The ³A₂ state (6t) associated with structure 6, generated from 6s by the single electronic excitation 2b₂ → 2b₁, has a geometrical structure similar to the ¹A₁ state. The isomers 6s and 6t are vibrationally characterized as energetically high-lying local minima.

Geometrical searches were conducted for several further structures; however, despite numerous attempts these species collapsed to structures discussed above. For example:



while nonplanar staggered ring structures collapsed to planar rhomboidal structures.

D. Relative energies

From an examination of the total and relative energies of the various isomers of SiC₃ reported in Tables I and II it is clear that there are three energetically low-lying isomers; 1t, 3s, and 4s. At the SCF/DZP level of theory the lowest-energy isomer of SiC₃ is rhomboidal structure 3s, involving transannular C–C bonding. This structure is only 3.6 kcal/mol more favorable than the linear isomer 1t and 8.2 kcal/mol below rhomboidal structure 4s. Upon inclusion of the zero-point vibrational energy correction, these SCF energy differences are reduced by less than 0.3 kcal/mol. The relative energies highlight the competition of cyclic vs linear structures as has been reported for Si₂C₂,^{25,26} C₄,^{11–17} SiC₂,⁵ and Si₂C.⁷ Interestingly, at the SCF level with a DZ basis set 1t is 39.1 kcal/mol more stable than 3s; however, addition of polarization functions to the basis set reverses this relative ordering. An analogous reversal of isomer stability was noted for the linear triplet and singlet rhombic structures of SiC₂ upon addition of polarization functions to the basis set at the SCF level.^{25(a)}

Inclusion of electron correlation lowers the energies of singlets relative to triplets, and the stability of singlet $3s$ over triplet $1t$ is increased from 3.6 kcal/mol (SCF) to 9.9 kcal/mol at the CISD/DZP level. This relative energy is unaffected by the addition of Davidson's correction for unlinked quadruple excitations. The energy difference between singlet structures is less affected by electron correlation, and the stability of $3s$ relative to $4s$ changes from 8.2 kcal/mol (SCF) to 10.1 kcal/mol at the CISD + Q/DZP level of theory. According to Ritchie, King, and Young,¹² the rhombic form of C_4 is favored over the linear triplet by 1.2 kcal/mol at the CISD/DZP level, reducing to 0.4 kcal/mol upon addition of the Davidson correction. The energy difference between the $3s$ and $1t$ isomers of SiC₃ (9.9 kcal/mol) is significantly greater than that for C_4 at the CISD + Q/DZP level of theory.

With the CISD/TZ2P method isomer $3s$ is below $1t$ and $4s$ by 5.1 and 5.3 kcal/mol, respectively, and inclusion of the Davidson correction lowers these values by 1.0 kcal/mol. Therefore, at the CISD level, increasing the basis set from DZP to TZ2P results in lower $3s-1t$, $4s$ energy differences by over 5.0 kcal/mol. This effect suggests the requirement of basis sets larger than even TZ2P for this system. Interestingly, the SCF-CISD increase in relative energies is less significant with the TZ2P basis set than with DZP.

In the investigation of C_4 , Bartlett and co-workers¹⁷ show the important contribution of triple excitations in stabilizing the rhombic form relative to the linear triplet. A similar effect might be expected for SiC₃ in stabilizing $3s$ over $1t$. The effect of increasing the size of the basis set is in the opposite direction. Thus the actual $3s-1t$ isomeric energy difference may be close to our CISD + Q/TZ2P value of about 4 kcal/mol. For a more precise determination of these relative energies, more highly correlated theoretical methods with larger basis sets than TZ2P are required. However, we do not expect our qualitative results for SiC₃ will change.

Energetic predictions at the CISD + Q/DZP level show isomers $3t$ and $4t$ to lie 26.0 and 21.3 kcal/mol above $3s$, respectively. These values are within the realms of uv excitation energies, and hence these triplet excited states may be accessible experimentally. The remaining three-membered ring structures are much higher energetically; 31.3, 36.5, 98.9, and 76.3 kcal/mol for $5s$, $5t$, $6s$, and $6t$, respectively, from CISD + Q/DZP single-point energy determinations at SCF/DZP optimized geometries. Isomer $2t$ is 83.4 kcal/mol above $3s$ at this correlated level of theory.

Lammertsma and Güner^{25(a)} report analogous results for Si₂C₂. A rhombic structure with relatively short transannular C-C distance is found to be the global minimum at the MP4/6-31G* level of theory, being 8.5 kcal/mol below the rhomboidal structure with transannular Si-C bonding and 11.4 kcal/mol below the linear triplet structure. Thus there is a close correspondence between the SiC₃ and Si₂C₂ results. Once again, it would be interesting to test the reliability of the Si₂C₂ results with higher theoretical levels and larger basis sets.

E. Discussion

Our conclusion that the ground state of SiC₃ at the theoretical levels employed is a closed-shell 1A_1 rhomboidal structure fits this molecule into the series of tetra-atomic clusters ranging from C_4 through Si₂C₂ to Si₄ (Si₃C remains to be studied). This result should not be too surprising, given the qualitative conclusions of the previous structural investigations of C_4 ,¹¹⁻¹⁷ Si₂C₂,^{25(a),26} and Si₄,²³ and the reluctance of silicon to form multiple bonds.^{40,41} It is well known that Si-C and C-C σ bonds are nearly identical in strength; however, Si-C π bonds have only about 60% of the analogous C-C π bond energy.^{46,47} This suggests that silicon would preferentially form σ bonds to carbon and let the carbons partake in π bonding. It has already been discussed that linear and rhombic forms of C_4 (Refs. 11-17) are effectively isoenergetic, hence, based on the above arguments, replacing a carbon atom by a silicon atom in C_4 should stabilize the cyclic structure $3s$ relative to the linear structure $1t$. The reasoning is that the rhomboidal structure involves effectively divalent silicon with a nonbonding electron pair and incorporates two Si-C σ bonds while the linear structure contains an Si-C double bond with both σ and π contributions. Similar arguments can be used to explain the stability of cyclic over linear SiC₂.⁵

The energetically unfavorable three-membered ring structures obviously suffer from more ring strain destabilization than four-membered ring structures. Isomer $5s$ with an exocyclic silicon atom is predicted to lie 31.3 kcal/mol above the ground state $3s$, while isomer $6s$ with silicon incorporated in the ring involves tricoordinate silicon as well as Si-C π bonding and is 98.9 kcal/mol less stable than the global minimum. In close analogy with our SiC₃ predictions, Pople and co-workers¹¹ predict an isomer of C_4 incorporating a three-membered ring to lie 29.5 kcal/mol above the rhombic form at the MP4/6-31G* level.

From the point of view of rotational spectroscopy, it is fortunate that the largest magnitude dipole moments are associated with the lowest-energy structures. Comparing the two distinct linear structures, $1t$ and $2t$, and the two distinct three-membered ring structures, $5s$ and $6s$, the energetically lowest isomer of each pair involves silicon at the terminus and thus has the larger magnitude dipole moment, which might be expected from electronegativity differences. The more-stable four-membered ring structure, $3s$, also involves a larger magnitude dipole moment than structure $4s$ (4.2 D for $3s$, 2.3 D for $4s$ at CISD/DZP).

IV. CONCLUSION

The ground state of SiC₃ is found to be the rhomboidal structure $3s$ with short distance between bridgehead carbon atoms lying about 4 kcal/mol below both the linear triplet isomer $1t$ and the rhomboidal structure $4s$ with inverted tricoordinate carbon and silicon atoms. However, basis sets larger than TZ2P in conjunction with higher theoretical levels will be required for more precise energy differences. The values reported, though, are consistent with previous theoretical results on the series of carbon-

silicon tetra-atomic clusters, C₄,^{11–17} Si₂C₂,^{25(a),26} and Si₄.²³ Thus the competition between the lowest-lying cyclic and linear structures appears to favor the cyclic form as the number of silicon atoms in the system increases. In fact, linear Si₄ is a transition state with an imaginary π_g degenerate bending mode lying 79 kcal/mol above the rhombic ground state.²³ As one descends group IV of the periodic table the stability of cyclic forms appears to increase relative to linear forms. Pacchioni and Koutecký⁴⁸ have suggested that the third row system Ge₄ has a planar rhombic ground state. It will be of interest to test this qualitative model on the Si₃C molecule. The dipole moment of SiC₃ is found to be rather large, 4.2 D for the lowest-energy isomer 3s at the CISD/DZP level of theory, and this result in conjunction with the structural and vibrational information reported herein should aid the spectroscopist in the search for SiC₃ in interstellar environments as well as in the laboratory.

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