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Structures and Energies of Disilicon Dicarbide, C_2Si_2

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Abstract: The structures and energies of the binary disilicon dicarbide C_2Si_2 in the lowest singlet and triplet states have been investigated by ab initio MO theory. Full fourth-order Møller–Plesset (MP4) perturbation theory is employed on HF/6-31G*-optimized geometries. Rhombic dicarbide **5s** is the global C_2Si_2 minimum and 8.5 kcal/mol more stable than the rhomboidal structure **6s**, which contains an inverted tricoordinate carbon as well as an inverted tricoordinate silicon. Both cyclic structures are energetically favored over a linear triplet isomer. Whereas the relative energies are very sensitive to electron correlation effects, addition of diffuse functions at the Hartree–Fock level (HF/6-31+G*) has little influence.

Silicon carbide is an important industrial material, known as an abrasive,[1] for applications in high-temperature ceramics[2] and with potential as a semiconductor.[3] Although the common silicon carbides (α- and β-SiC) have alternating tetrahedral silicons and carbons,[4] many dislocations have been recorded.[5,6] The silicons and carbons in binary and ternary systems are often contained in fascinating structures. The Zintl complex $CaAl_2Si_2$ is illustrative,[7] Its $Al_2Si_2^{2-}$ layer has been studied theoretically as a composition of molecular units.[8] $Al_2Si_2^{2-}$ is isoelectronic with Si_4. In contrast to the high-energy small carbon and silicon clusters, there exists little structural information on small carbon silicides. Recognition of bonding patterns in small carbon/silicon clusters is also of significant astrophysical interest, since some are believed to exist in interstellar space. Here we provide an analysis on the C_2Si_2 fragment and will show similarities and differences with the relating C_4 and Si_4 clusters.

The type of bonding in tetraatomic clusters depends on its number of valence electrons and the electronegativity of the elements involved. For example, the 26-electron (26e) A_2B_2 series (e.g., O_2F_2, S_2F_2, and S_4^{2-}) favors C_2 symmetry,[9,10] while a linear structure is preferred by the 18e C_2N_2[9,10] and the strongly ionic 12e triplet C_2Be_2.[11] The "bent" rhombic and linear structures are of similar energy for the 10e lithium carbide C_2Li_2.[12] The 16-valence-electron C_4 shows a slight preference for the rhombic over linear structure,[13] which reverses on mono- and diprotonation to C_4H^+ and to the known $C_4H_2^{2+}$.[14,15] In contrast, the related 16e Si_4 strongly favors a rhombic form,[16] with a tetrahedral arrangement for its 20e tetraanion Si_4^{4-} fragment.[17] Thus, the rhombic form is prevelant in Si_4 and competitive with the linear isomer for C_4. In this study on C_2Si_2 we broaden the scope of possible rhombic structures that display inverted geometries.

Whereas inverted tetracoordinated carbon geometries (folded umbrellas)[18] have attracted significant focus in several very de-

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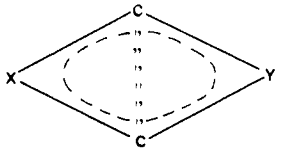
Table I. Total (au) and Relative (kcal/mol) Energies of C_2Si_2 Isomers

			HF/3-21G			HF/6-31G*		
	geometry	state	abs	rel NIMAG[a]	$\langle s^2 \rangle$	abs	rel NIMAG[a]	$\langle s^2 \rangle$
1s	$D_{\infty h}$	$^1\Sigma_g^+$	−649.968 89	−11.2 (0)		−653.379 08	22.3 (0)	
3s	C_{2v}	$^1A_1$	−649.952 53	−1.0 (1)		−653.367 15	29.8 (2)	
4s	C_{2v}	$^1A_1$	−649.843 24	67.6 (1)		−653.296 28	74.3	
5s	D_{2h}	^1A_g	−649.950 99	0.0 (0)		−653.414 67	0.0 (0)	
6s	C_s	$^1A'$	−649.956 32	−3.3 (0)		−653.399 61	9.4 (0)	
7s	D_{2h}	^1A_g	−649.778 94	108.0 (0)		−653.241 60	108.6	
8s	C_{2v}	$^1A_1$	−649.898 56	32.9 (2)		−653.336 13	49.3	
9s	C_2	^1A	−649.911 78	24.6 (1)		−653.356 86	36.3	
1t	$D_{\infty h}$	$^3\Sigma_g^-$	−650.000 63	−31.2 (0)	2.11	−653.414 64	0.0 (0)	2.15
3t	C_{2v}	$^3B_1$	−649.947 92	−1.9 (0)	2.12	−653.366 19	30.4	2.14
5t	D_{2h}	$^3B_{3u}$	−649.841 46	68.7 (0)	2.11	−653.298 11	73.1	2.08
6t	C_s	$^3A''$	−649.963 01	−7.5 (0)	2.14	−653.394 04	13.0	2.16
7t	D_{2h}	^3A_u	−649.832 34	74.5 (2)	2.20	−653.277 53	86.1	2.16
8t	C_{2v}	$^3B_1$	−649.898 88	32.7 (1)	2.05	−653.337 26	48.6	2.06

[a] Indicates the number of imaginary frequencies.

tailed studies on propellanes[19] and bicyclobutanes,[20] such studies on related silicon derivatives are rare.[21] Recently, we reported on rhombic structures with inverted tricoordinate carbons, which are defined as having three ligands on one side of a plane through that carbon, while maintaining planarity.[14,22] These structures contained only elements of the first row of the periodic table (I, X = Y = Be, BH, C, CH$^+$). The specific properties of each rhombic structure proved to be dependent upon its dicarbide-bridging ligands. For example, the well-studied 16-valence-electron rhombic C_4 is the global minimum energy structure with covalent bonding,[14,22] whereas the 12-valence-electron rhombic C_2Be_2 is a high-energy local minimum with significant ionic character.[11,22]



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It is well-known that silicon prefers to form single bonds and that the nature of its double bonds differs from that of normal C=C bonds.[23] Experimental and theoretical studies on the triatomic C_2Si,[24] CSi_2,[25] and Si_3[16,25b,c,26] show a preference for cyclic structures, thereby contrasting C_3,[27] which is linear. Hence, the C_2Si_2 potential energy surface does not a priori resemble that of C_4 nor of Si_4, although some similarities are expected. Indeed, in the only previous study on C_2Si_2, Trucks and Barlett[28] showed that the D_{2h} rhombic form (^1A_g state) is favored over a $D_{\infty d}$ linear isomer ($^3\Sigma_g^+$ state) by 12 kcal/mol, using full fourth-order many-body perturbation theory on a double-ζ plus polarization basis. However, relevant to this study, no other structures were reported by these authors.

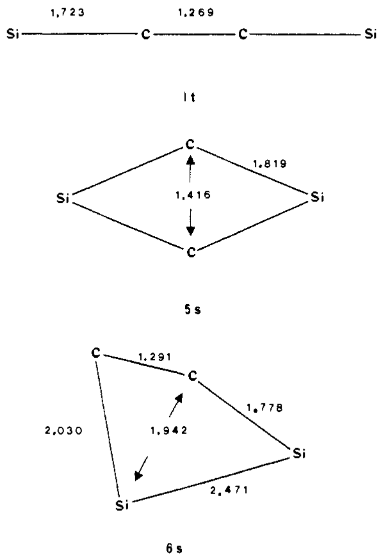

Figure 1. HF/6-31+G* geometries of structures **1t**, **5s**, and **6s**.

The objective of the present study is to provide a comprehensive and detailed survey of the potential energy hypersurface of the binary C_2Si_2 cluster, with emphasis on the special bonding properties of silicon in four-membered ring structures. In this context, we concentrate on the ability of silicon and carbon to adopt inverted tricoordinate geometries in two highly strained ring

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Table II. Total (au) and Relative (kcal/mol) Energies of C_2Si_2 Isomers

		MP2/6-31G*		MP3/6-31G*		MP4/6-31G*		binding
	geometry	abs	rel	abs	rel	abs	rel	energy[b]
1s	$D_{\infty h}$	−653.77004	23.9	−653.79074	20.8	−653.82816	17.1	16.5
3s	C_{2v}	−653.74310	40.8	−653.76642	36.1	−653.80284	33.0	15.7
4s	C_{2v}	−653.68569	76.8					
5s	D_{2h}	−653.80804	0.0	−653.82393	0.0	−653.85545	0.0	17.2
6s	C_s	−653.78954	11.6	−653.80783	10.1	−653.84195	8.5	16.8
7s	D_{2h}	−653.67340	84.5					
8s	C_{2v}	−653.73201	47.7	−653.74864	47.3	−653.78587	43.7	15.3
9s	C_2	−653.75011	36.4	−653.76952	34.1	−653.80542	31.4	15.8
1t	$D_{\infty h}$	−653.78263	16.0	−653.80438	12.3	−653.83724	11.4	16.7
3t	C_{2v}	−653.71856	56.2					
5t	D_{2h}	−653.71529	58.2					
6t	C_s	−653.75461	33.5					
7t	D_{2h}	−653.69165	73.0					
8t	C_{2v}	−653.73296	47.1					
C[a]	K_h	−37.70512		−37.7191		−37.72415		
Si[a]	K_h	−288.87203		−288.8839		−288.88765		

[a] See ref 44. [b] Binding energy in electronvolts.

structures, which are both energetically favored over a linear isomer.

Methods

The ab initio calculations were performed with the GAUSSIAN 82 and GAUSSIAN 86 series of programs.[29] All geometries were fully optimized with minimization of the Hartree–Fock (HF) energy within each assumed symmetry.[30] Singlets were treated by the spin-restricted (RHF) theory,[31] while the spin-unrestricted (UHF) theory[32] was used for triplets. Singlet structures are indicated by s and triplets by t. All geometries were obtained with the 3-21G basis[33] and characterized by analysis of the harmonic vibrational frequencies, obtained from diagonalization of force constant matrices. Minima on the potential energy surface have no imaginary frequencies, and saddle points do have one. Subsequently, most geometries were further optimized with 6-31G*,[34] which has polarization functions for both carbon and silicon. Because of the carbon–silicon electronegativity differences, the "best" structures (**5s**, **6s**, and **1t**) were also optimized with the 6-31+G* basis,[35] which has an extra set of diffuse p functions on both C and Si; this basis set describes anionic structures well.[30] A limited number of structures was then subjected to 6-31G* frequencies analyses,[36] because of observed geometrical changes. This was not possible for all species due to cpu and disk-space limitations. For all geometries we have searched for the singlet and triplet electronic ground states. No attempts have been made to explore the various excited states, although numerous "orbital switchings" were encountered. Population analyses are based on the Mulliken method.[37] Valence-electron correlation effects were evaluated by single-point Møller–Plesset perturbation theory at fourth order, which includes contributions of single, double, triple, and quadruple substitutions.[38] These calculations are denoted MP4/6-31G*//HF/6-31G*, the // symbol meaning "at the geometry of". For some higher energy triplet structures electron correlation effects were only determined at MP2/6-31G*. Frozen-core MP2 perturbation theory was also applied to HF/6-31+G*-optimized structures.

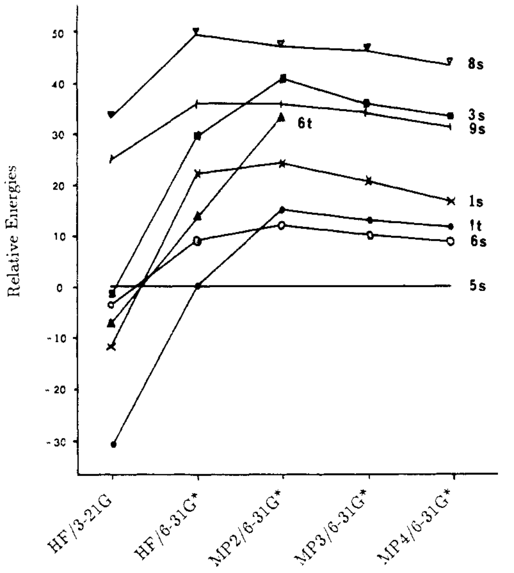

Figure 2. Plot of relative energies (kcal/mol) vs basis set. All energies are relative to **5s**.

Table III. Total (au) and Relative (kcal/mol) Energies of C_2Si_2 Isomers

		HF/6-31+G*		MP2/6-31+G*	
	geometry	abs	rel	abs	rel
5s	D_{2h}	−653.41879	0.0	−653.81636	0.0
6s	C_s	−653.40562	8.3	−653.80024	10.1
1t	$D_{\infty h}$	−653.42042	−1.0	−653.79172	15.5

Results and Discussion

The geometries of all investigated 6-31G* singlet and triplet C_2Si_2 linear, three- and four-membered (including tetrahedral) ring structures are displayed throughout the text (3-21G values are in given in parentheses) and discussed in detail with emphasis on the bonding properties of the most stable species. Figure 1 displays the HF/6-31+G* geometries of **1t**, **5s**, and **6s**. All Hartree–Fock (HF/3-21G and HF/6-31G*) and correlated (MP2, MP3, and MP4(SDTQ)/6-31G*) energies of C_2Si_2-optimized isomers are listed in Tables I and II, respectively, with some graphically displayed in Figure 2. The tables also list the C_2Si_2 relative energies and electronic states. Table III lists the HF and MP2/6-31+G* energies for **1t**, **5s**, and **6s**. The harmonic

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Table IV. 3-21G and 6-31G* Harmonic Frequencies of C_2Si_2 Isomers

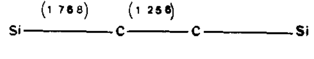
geometries		frequencies												ZPE
								3-21G						
1s	$D_{\infty h}$	150	(π_u)	164	(π_u)	483	(π_g)	501	(σ_g)	564	(π_g)	899	(σ_u)	2037	(σ_g)	6.9
3s	C_{2v}	153i	(b_2)	299	(b_1)	343	(a_1)	543	(b_2)	638	(a_1)	1953	(a_1)			5.4
4s	C_{2v}	89i	(b_2)	155	(b_2)	164	(b_1)	347	(a_1)	791	(a_1)	1763	(a_1)			4.6
5s	D_{2h}	225	(b_{3u})	267	(b_{2u})	499	(a_g)	963	(b_{3g})	1003	(b_{1u})	1109	(a_g)			5.8
6s	C_s	176	(a′)	309	(a′)	315	(a″)	584	(a′)	686	(a′)	1786	(a′)			5.5
7s	D_{2h}	292	(b_{3u})	407	(b_{1u})	452	(b_{3g})	489	(a_g)	578	(b_{2u})	737	(a_g)			4.2
8s	C_{2v}	582i	(b_2)	275i	(a_2)	333	(a_1)	389	(b_2)	625	(a_1)	2091	(a_1)			4.9
9s	C_2	460i	(b)	269	(a)	309	(a)	517	(b)	665	(a)	1913	(a)			5.3
1t	$D_{\infty h}$	154	(π_u)	490	(σ_g)	519	(π_g)	860	(σ_u)	2060	(σ_g)					6.8
3t	C_{2v}	215	(b_2)	281	(a_1)	394	(b_1)	637	(a_1)	841	(b_2)	1586	(a_1)			5.7
5t	D_{2h}	297	(b_{3u})	376	(b_{2u})	453	(a_g)	707	(b_{1u})	749	(a_g)	813	(b_{3g})			4.9
6t	C_s	132	(a′)	376	(a″)	439	(a′)	640	(a′)	669	(a′)	1527	(a′)			5.4
7t	D_{2h}	641i	(b_{2u})	154i	(b_{3u})	433	(a_g)	666	(b_{3g})	894	(b_{1u})	708	(a_g)			3.6
8t	C_{2v}	776i	(a_2)	81	(b_2)	291	(a_1)	483	(b_2)	655	(a_1)	2105	(a_1)			5.2
								6-31G*						
1s	$D_{\infty h}$	125	(π_u)	158	(π_u)	340	(π_g)	468	(π_g)	528	(σ_g)	980	(σ_u)	1982	(σ_g)	6.6
3s	C_{2v}	256i	(b_2)	35i	(b_1)	403	(a_1)	537	(b_2)	659	(a_1)	1938	(a_1)			5.1
5s	D_{2h}	240	(b_{3u})	374	(b_{2u})	567	(a_g)	1050	(b_{3g})	1070	(b_{1u})	1255	(a_g)			6.5
6s	C_s	272	(a″)	340	(a′)	492	(a′)	676	(a′)	759	(a′)	1733	(a′)			6.1
1t	$D_{\infty h}$	140	(π_u)	401	(π_g)	519	(σ_g)	959	(σ_u)	2011	(σ_g)					6.5

Table V. 6-31G* Valence-Electron Configurations for C_2Si_2 Isomers

1s	$D_{\infty h}$	${}^1\sigma_g{}^+$	$(5\sigma_g)^2(5\sigma_u)^2(6\sigma_g)^2(3\pi_u)^2(6\sigma_u)^2(4\pi_u)^2(7\sigma_g)^2(3\pi_g)^2$
3s	C_{2v}	${}^1A_1$	$(7a_1)^2(8a_1)^2(5b_2)^2(9a_1)^2(10a_1)^2(2b_1)^2(6b_2)^2(11a_1)^2$
4s	C_{2v}	${}^1A_1$	$(8a_1)^2(9a_1)^2(4b_2)^2(10a_1)^2(3b_1)^2(11a_1)^2(12a_1)^2(5b_2)^2$
5s	D_{2h}	${}^1A_g$	$(5a_g)^2(4b_{1u})^2(3b_{2u})^2(6a_g)^2(2b_{3u})^2(5b_{1u})^2(2b_{3g})^2(7a_g)^2$
6s	C_s	${}^1A'$	$(11a')^2(12a')^2(13a')^2(14a')^2(3a'')^2(15a')^2(16a')^2(17a')^2$
7s	D_{2h}	${}^1A_g$	$(5a_g)^2(3b_{2u})^2(4b_{1u})^2(6a_g)^2(2b_{3g})^2(2b_{3u})^2(4b_{1u})^2(7a_g)^2$
8s	C_{2v}	${}^1A_1$	$(6a_1)^2(7a_1)^2(6b_2)^2(8a_1)^2(2b_1)^2(9a_1)^2(7b_2)^2(10a_1)^2$
9s	C_2	${}^1A$	$(7a)^2(8a)^2(7b)^2(8b)^2(9a)^2(10a)^2(9b)^2(11a)^2$
1t	$D_{\infty h}$	${}^3\sigma_g{}^-$	$(5\sigma_g)^2(5\sigma_u)^2(6\sigma_g)^2(2\pi_u)^4(6\sigma_u)^2(7\sigma_g)^2(2\pi_g)^2$
3t	C_{2v}	${}^3B_1$	$(7a_1)^2(8a_1)^2(5b_2)_2(9a_1)^2(2b_1)^2(10a_1)^2(6b_2)^2(11a_1)^1(3b_1)^1$
5t	D_{2h}	${}^3B_{3u}$	$(5a_g)^2(4b_{1u})^2(3b_{2u})^2(6a_g)^2(2b_{3u})^2(5b_{1u})^1(2b_{3g})^2(7a_g)^2(2b_{2g})^1$
6t	C_3	${}^3A''$	$(11a')^2(12a')^2(13a')^2(14a')^2(3a'')^2(15a')(16a')^2(17a')^1$- $(4a'')^1$
7t	D_{2h}	${}^3A_u$	$(5a_g)^2(3b_{2u})^2(4b_{1u})^2(2b_{3u})^2(6a_g)^2(2b_{3g})^2(5b_{1u})^1(7a_g)^2(1b_{1g})^1$
8t	C_{2v}	${}^3B_1$	$(6a_1)^2(7a_1)^2(6b_2)^2(8a_1)^2(2b_1)^2(9a_1)^2(7b_2)^2(10a_1)^1(3b_1)^1$

frequencies and zero-point vibrational energies for each structure are listed in Table IV. The valence-electron configurations for all isomers are given Table V. The 6-31G* geometrical data are used throughout the text unless otherwise noted,

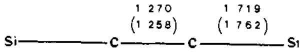
Geometries. Linear Structures. The linear isomer of main interest contains two terminal silicons, The triplet form **1t** ($D_{\infty h}$) is the most favored electronic configuration for this structure and is a minimum at the HF/6-31G* potential energy surface. Its calculated 6-31G* (3-21G) C–C bond length of 1.267 (1.256) Å is only 0.009 Å shorter than that in linear C_4 (same level).[13d,14] The C–Si bond lengths of 1.721 (1,766) Å are those of a typical C=Si double bond.[23a,39] It is apparent, also from the molecular orbitals, that **1t** represent a cumulene-like molecule in which the silicons participate in multiple bonding.



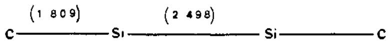
1T

It can be argued that, because of differences in carbon and silicon electronegativities, more diffuse functions (in particular on silicon) are required to adequately describe this linear structure. The relevance for investigating structure **1t** with the standard 6-31+G* basis (which has a set of extra diffuse p functions on both C and Si) is underlined by the CSi_2 species. Grev and Schaefer[25d] showed that optimization of linear CSi_2 with a "double" d-polarized (DZ+2P) basis set resulted in a bent (C_{2v}) structure. However, our HF/6-31+G* optimizations of both cis and trans distorted linear C_2Si_2 forms resulted in the linear $D_{\infty h}$ structure **1t**, with bond lengths (C–C = 1.269 Å; Si–Si = 1.723 Å) virtually the same as those at 6-31G* (Δd = 0.003 Å). Both C–C and C–Si bond lengths are shorter than those reported by Trucks and Bartlett.[28] They obtained C–C = 1,283 (1.290) Å and C–Si = 1.742 (1.759) Å with the DZ+P basis and with the fourth-order many-body perturbation theory, MBPT(4), given in parentheses. The C–Si bonds in **1t** are longer than both the 1.672–1.705 Å calculated for linear C_2Si[24] and the 1.684 Å (DZ+P) in vinylidenesilene.[40]

The geometry of the singlet structure **1s** is virtually the same as that of triplet **1t**, with bond differences of ca. 0.003 Å. We have not explored other than these ${}^1\Sigma_g{}^+$ and ${}^3\Sigma_g{}^-$ states for structure **1**.[28,41] Both **1s** and **1t** are 6-31G* minima. A 3-21G-optimized linear C_2Si_2 isomer **2t**, which has two terminal C's, was not further considered because of its high relative 3-21G energy and large spin contamination.[42]



1 S



2 T

Three-Membered Ring Structures. The only viable C_2Si_2 three-membered ring structure is isomer **3**, which contains a C-ring substituted carbon. The (ring) C–Si bond length of 1,869 (1.898) Å for singlet **3s** is typical for a single bond. Also the Si–Si bond distance of 2,375 (2.542) Å is indicative of single bonding.[23b] This apparent single bonding of the silicons in the cyclic structure **3s** is supported by the molecular orbital framework, which shows Si-free electron pairs. In contrast, the exocyclic carbon is strongly bonded with a C–C bond length of only 1.279 (1.276) Å, which

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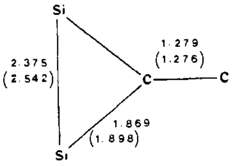
(39) (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676. (c) Gordon, M. S. *Ibid.* **1982**, *104*, 4352. (d) Schaefer, H. F., III *Acc. Chem. Res.* **1982**, *15*, 283.

(40) Frenking, G.; Remington, R. B.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 2169.

(41) The ${}^1\Sigma_g{}^+$ state of structure **1s** is significantly mixed with the ${}^1\Delta_g$ state.[28] This is also evident from the nondegeneracy of both the π_u and π_g harmonic frequencies (see Table IV). No separation of states has been attempted. For a rigorous discussion on the mixing of these states, see ref 28. The energy difference between **1t** and bf **1s** of 22.3 (6-31G*) and 5.7 (MP4/6-31G*) kcal/mol is similar to that of 29.0 (DZ+P) and 6.5 (MBPT-DZ+P) kcal/mol calculated by Trucks and Bartlett[28] for the pure ${}^1\Sigma_g{}^+$ and ${}^3\Sigma_g{}^-$ states.

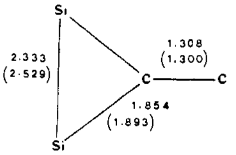
(42) The 3-21G energy for **2t** ($D_{\infty h}$) is −649.779 16, which is 107.8 kcal/mol less stable than **5s**. Although **2t** has one imaginary frequency, its ${}^3\Sigma_u{}^+$ state shows high-spin contamination ($\langle s^2 \rangle$ = 4.80, also evident in the harmonic frequencies), which may be expected for forcing linearity ($D_{\infty h}$) of doubly bonded silicons. Other electronic states for **2t** have not been investigated.



3 S

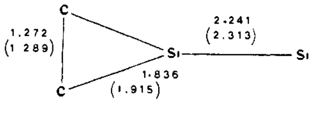
is shorter than that of a typical C=C double bond. Whereas **3s** is a transition structure at 3-21G, it has a second but very small 6-31G* imaginary frequency of $35i$ cm^{-1} (b_1). The normal mode of the imaginary frequency at $256i(b_2)$ cm^{-1} suggests **3s** to be a transition for the degenerate rearrangement of rhomboidal **6s**. This is supported by the long C–Si bond distance of 2.027 Å for **6s** (see later).

The energetically less favored triplet structure **3t** (a 3-21G minimum) is virtually the same as that of the singlet isomer; the C–C bond is only 0.027 Å elongated and the Si–Si shortened 0.042 Å at 6-31G*.



3 T

The high-energy, singlet ring structure **4s** has an exocyclic silicon bonded to the tricoordinate ring Si. The bond length of



4 S

2.241 (2.313) Å is indicative of double bonding between the silicons, The ring carbons are separated by only 1,273 (1.289) Å, which is even shorter than a double bond length, whereas the C–Si distance of 1.836 (1.915) Å is typical for a single bond.[23b] The C_2Si ring bond lengths of **4s** are remarkably similar to those of the unsubstituted C_2Si ring structure.[24f–j] At 3-21G **4s** is a transition structure, with the normal mode of its imaginary b_2 frequency indicating a degenerate C–Si exchange.

Four-Membered Ring Structures. Because most clusters can be regarded as compositions of smaller cyclic components (C_4,[13,14,22] C_6,[43] and Si_{4-10}[16] are exemplary) and silicon shows a preference for divalent bonding, we carefully studied an array of four-membered ring structures.

Rhombic Dicarbide. Equilibrium singlet structure **5s** has bonding properties similar to those of our previously reported rhombic structures with inverted tricoordinate carbons.[13,14,22] The C–Si bond length of 1.818 (1.892) Å at 6-31G* (3-21G) is only slightly less than that of a single bond, e.g., 1.883 (3-21G*)[44a]–1.857[44b] (DZ+P) Å in methylsilane, while the distance between the two inverted carbons is 1.415 (1.425) Å short! The dependency of the C–C interaction[13,14,22] and Si bonding[23a] on the calculational level (3-21G vs 6-31G*) has been noted before. However, addition of diffuse functions to the d-polarized 6-31G* basis set does not further influence the geometrical parameters; i.e., C–C = 1.417 Å and C–Si = 1.819 Å. Trucks and Bartlett calculate longer bond lengths both with a double-ζ basis (C–C = 1.432 Å, C–Si = 1.875 Å) and at correlated levels (DZ+P-D-MBPT(4), C–C = 1.464 Å, C–Si = 1.857 Å).[28] Elongation of the transannular interaction between inverted carbons at post-Hartree–Fock levels is expected; a similar observation has been made for propellanes.

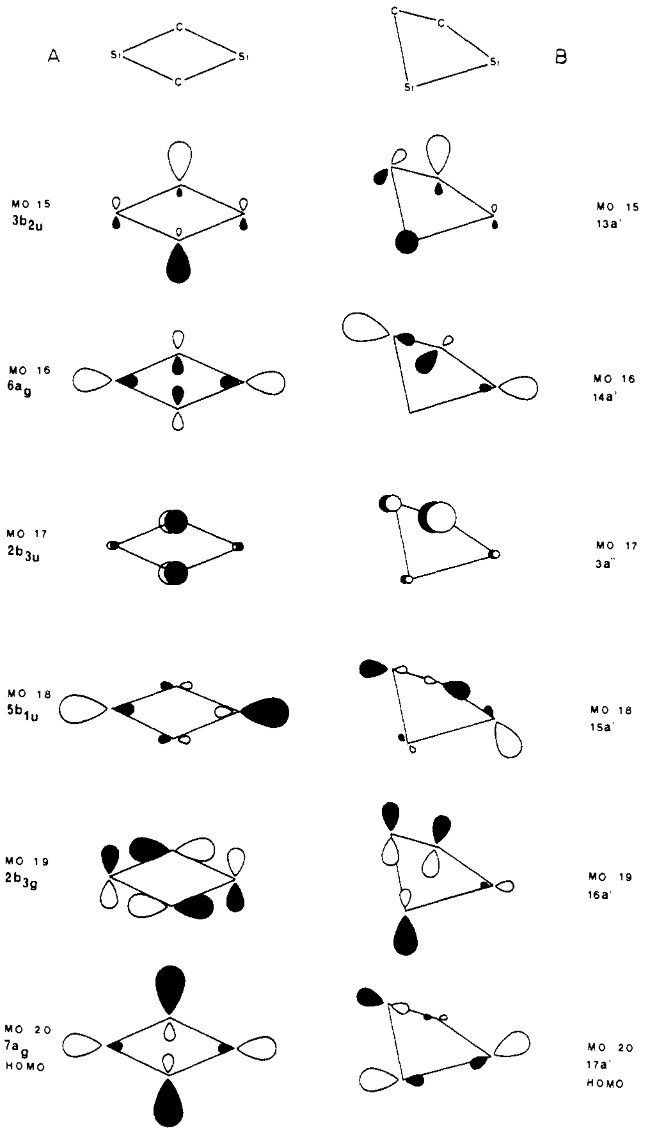
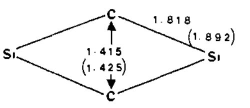
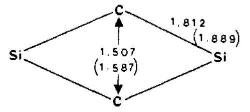


Figure 3. Six highest occupied MO's for (a) rhombic **5s** and (b) rhomboidal **6s**.

Inspection of the molecular orbital framework confirms that the HOMO (a_g, MO No. 20) displays σ-deficient bonding (Figure 3a), reminiscent of C_4 and others.[22] However, the main difference with C_4 is that there is no four-center–two-electron (4c–2e) π MO but rather direct π overlap (b_{3u}, MO No. 17, Figure 3a) between the two carbons (as in C_2Be_2). Indeed the C–C bond length in **5s** is shorter than that in rhombic C_4 by 0.042 Å.[13d,14,22] Also the 6-31G* Mulliken overlap populations of 0.233 for **5s**, as compared to −0.063 for C_4,[22] are indicative for enhanced C–C bonding in **5s**. The reluctance of silicon to participate in aromatic bonding may be attributed to the carbon–silicon electronegativity difference and the larger polarizability of silicon.



5 S



5 T

Comparison of **5s** with silacyclopropyne SiC_2, which has C–Si and C–C bond lengths of 1.835 and 1.256 Å (DZ+P), respectively,[24h] shows, aside from the expected elongation of the C–C bond, a shortened C–Si bond length. Similarly, **5s** may be compared with 3-silacyclopropenylidene (by substituting the two hydrogens for a silicon), which has C–Si and C–C bond lengths of 1.806 and 1.343 Å (DZ+P), respectively.[40] The C–C double

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(43) Raghavachari, K.; Whiteside, R. A.; Pople, J. A. *J. Chem. Phys.* **1986**, *85*, 6623.

(44) (a) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (b) Kilb, R. W.; Pierce, L. *J. Chem. Phys.* **1957**, *27*, 108.

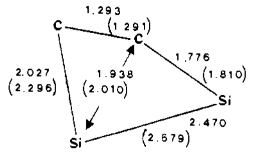
(45) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*; Carnegie-Mellon University: Pittsburgh, PA, 1983.

bond in the latter is considered to be relatively weak; structure **5s** has a 0.074 Å (6-31+G*) larger C–C separation.

The triplet structure **5t** shows a slightly shorter C–C bond distance of 1.507 (1.587) Å at 6-31G* (3-21G) than **5s**, with C–Si bond lengths of 1.812 (1.889) Å. The orbital pattern is similar to that observed for **5s**.

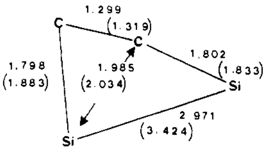
Since Ritchie found a 6.2° bending (RHF/6-31G*) for the 14e rhombic lithium carbide C_2Li_2[12a] (with an even larger bending angle for its dianion),[12b] we also conducted a search for a nonplanar "butterfly" structure. However, 6-31G* optimization of a bent C_2Si_2 structure within C_s symmetry (see also later) gave planar **5s**. A related 3-21G triplet structure (C_{2v}) was not further investigated because of its unfavorable energetics and spin contamination ($\langle s^2 \rangle = 2.88$).

Rhomboidal Silicon Carbide. The question arises as to whether rhomboidal C_2Si_2 structures can be formed with an inverted tricoordinate Si. Structure **6** may represent such a case, carrying both an inverted carbon and an inverted silicon. Alternatively, **6** may be viewed as a C_2Si molecule with Si complexed side-on; triangular C_2Si appears to be slightly more stable than its linear isomer.[24f-j] Both singlet and triplet **6** are 3-21G and 6-31G* minimum energy structures. The **6s** C–C bond length of 1.293 Å (6-31G*) is marginally longer than that in both triangular (by 0.037 Å) and linear C_2Si (by 0.020 Å); the latter calculated with the DZ+P basis by Grev and Schaefer.[24h] The C–Si distances in rhomboidal **6s** vary significantly from 1.775 to 1.938 (for the transannular distance) to 2.027 Å and range from weak double to weak single bonding, respectively. The reported DZ+P C–Si bond length is 1.676 Å for linear C_2Si and 1.835 Å for the cyclic isomer.[24h] The Si–Si bond length of 2.470 Å in **6s** indicates a weak single bond. Expectedly, geometry **6s** is strongly dependent on the calculational level: Polarization functions cause strong reduction of the ring C–Si and Si–Si bond lengths of the inverted Si. However, additional diffuse p functions (HF/6-31+G*) do not alter the geometry further, the bond length changes being ≤0.003 Å.



6 S

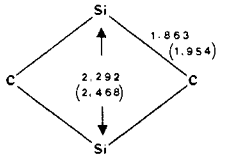
Inspection of the molecular orbital framework gives a clearer picture of the bonding properties in **6s** than the bond distances. The six highest 6-31G* MO's for **6s** (C_s) are shown in Figure 3b. For reasons of comparison all corresponding orbitals (same level) for rhombic **5s** (D_{2h}) are also displayed (Figure 3a). MO No. 17 (a″) for **6s** is a 4c-2e π orbital, similar to that found for rhombic C_4, but with the main overlap between the carbons; for **5s** (MO No. 17, b_{3u}) this is even more extreme. The remaining orbitals shown for **6s** have a′ symmetry and are subject to mixing. For example, the antibonding combination of the C and Si lone pairs (compare b_{1u} (MO No. 18) in **5s**) is mixed with a σ-ring (all $p_{x,y}$) bonding combination (compare b_{3g} (MO No. 19) in **5s**) resulting in the **6s** MO's No. 18 and No. 20 (see Figure 3a). MO No. 16 represents the bonding combination of the C and Si lone pairs (compare a_g (MO No. 16) in **5s**). Although the HOMO-1 (MO No. 19) for **6s** shows σ-deficient character between the transannular atoms, this is masked by the substantial participation of the second carbon's p orbital, which in part results from distortion from D_{2h} symmetry. Finally, the Mulliken (6-31G*) overlap population for the transannular C–Si bond of 0.113 is substantially smaller than those for the other bonds, i.e., 0.459 for the 2.027-Å C–Si bond and 0.694 for the 1.775-Å C–Si bond. Hence, the analysis suggests that 6s is a rhomboidal structure with both inverted carbon and silicon atoms.



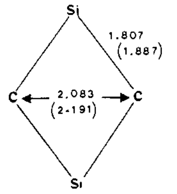
6 T

Triplet **6t** shows distinct differences with its singlet structure. Most importantly, there is hardly Si–Si bonding at 6-31G* (2.971 Å); the Mulliken overlap population is 0.065. This and the C–Si bond length of 1.802 Å suggest a C_2Si ring substituted with a Si on a carbon. In fact, the 6-31G* ring C–Si bond lengths of 1.798 and 1.985 Å vary only little from the 1.835 Å (DZ+P) reported for cyclic C_2Si.[24h] However, a rhomboidal **6t** structure at higher (correlated) levels cannot be excluded a priori; the strong molecular contraction at 6-31G* from 3-21G with a Si–Si bond reduction of 0.458 Å(!) must be noted.

Rhombic Disilicide. Structure **7** (D_{2h}) represents a disilicide with two inverted tricoordinate silicons. We must ask ourselves whether the bonding nature of singlet **7s** is reminiscent to that of rhombic structures with inverted tricoordinate carbons. In light of the Si reluctance to participate in multiple bonding,[23a,39a] a structure with lone pairs on the silicons may be preferred. However, the equilibrium Si_4 structure was shown to be rhombic with two inverted tricoordinate silicons separated by 2.40 Å (the ring Si–Si bond lengths are 2.30 Å (also 6-31G*)).[16] For structure **7s** a shorter Si–Si distance of 2.292 (2.468) Å is calculated at 6-31G* (3-21G), which compares with a Si–Si double bond.[23a] However, the Mulliken overlap population between the silicons is only 0.038. Similar to rhombic C_4 also for **7s**, the HOMO displays nonbonding σ character. Although the **7s** C–Si bond lengths of 1.863 (1.955) Å are only 0.045 (0.063) Å longer than those for **5s** and similar to typical C–Si single bonds, MO No. 18 represents a 4c-2e π interaction with a C–Si Mulliken (6-31G*) overlap population of 0.638. It appears that **7s** has indeed two inverted tricoordinate silicons and benefits from "aromatic" stabilization in a similar fashion as discussed before for C_4 and others. As noted for other rhombic structures, **7s** too displays strong geometrical contraction upon addition of polarization functions (6-31G*).



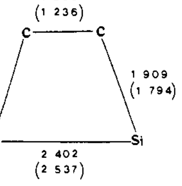
7 S



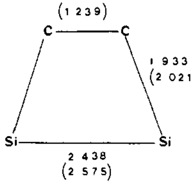
7 T

The triplet structure **7t** (D_{2h}) differs substantially from the singlet form with its long 6-31G* Si–Si and C–C separations of 2.953 and 2.083 Å, respectively (d_{C-Si} = 1.887 Å). Moreover, **7t** has two imaginary 3-21G frequencies, with normal modes indicating deformations to **3t** (641*i* cm^{-1} (b_{2u})) and an out of plane bending (154*i* cm^{-1} (b_{3u})).

Trapezoidal Structures. Singlet trapezoid **8s**, with triple C–C bond character (1.238 Å), has two imaginary 3-21G harmonic frequencies and therefore is a stationary point of higher order, which we document for completeness. The normal mode of the b_2 frequency of 582*i* cm^{-1} indicates an in-plane deformation to the rhomboidal structure **6s**. The a_2 frequency of 275*i* cm^{-1} suggests a distortion to nonplanarity.



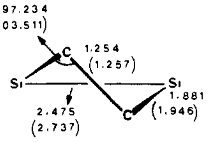
8 T



8 S

The triplet trapezoid **8t** is a 3-21G transition structure. Its imaginary a_2 frequency of 775*i* cm^{-1} indicates an out-of-plane distortion. The bonding characteristics are quite similar to those of the singlet structure with C–C, C–Si, and Si–Si bond lengths of 1.233, 1.909, and 2.402 Å, respectively.

Nonplanar Structures. Finally, the nonplanar four-membered C_2Si_2 ring structure **9** was investigated. The singlet tetrahedral-like or asymmetric butterfly form **9s** is a transition structure. Its 6-31G* bond lengths of 2.475, 1.881, and 1.254 Å compare with single Si–Si and C–Si bonds and a triple C–C bond distance, respectively. The deformation from planarity (defined as the dihedral angle X-C-C-Si, where X bisects the two C–C–Si planes) equals 28.5° (26.2°, 3-21G). The imaginary 460*i* cm^{-1} (b) frequency (3-21G) suggests **9s** to be a transition for the degenerate C-exchange in **6s**.



9S

Although a nonplanar triplet structure **9t** was suggested by analysis of the normal mode of the reaction coordinate (a_2) of structure **8t** (see above), no such species was found despite numerous attempts.

Relative Energies. Basis Set Dependency. The calculated relative C_2Si_2 energies show a strong Hartree–Fock basis set dependence at both the singlet and triplet hypersurfaces. Comparing the split valence 3-21G with the polarized 6-31G* basis set shows that in particular rhombic **5s** is significantly more stabilized than all other structures at the higher level. Thus, while **1t**, **1s**, **6t**, **6s**, and **3s** (in decreasing order) are all energetically favored over **5s** at 3-21G, they are less stable than **5s** at 6-31G*, the corresponding 3-21G–6-31G* energy changes relative to **5s** being 31.2, 33.6, 20.5, 12.8, and 30.8 kcal/mol, respectively. While linear **1t** is the most stable 3-21G isomer, rhombic **5s** is the preferred species at 6-31G*, although at this level the energy difference between **5s** and **1t** is only 0.01 kcal/mol. Addition of a set of diffuse p functions to the 6-31G* basis (HF/6-31+G*) has a minor overall effect, although it reverses the stability order by favoring **1t** over **5s** by 1.0 kcal/mol, and gives a **1t** – **6s** energy difference of 9.3 kcal/mol. Clearly, of all structures considered in this study, inclusion of polarization functions favors rhombic **5s** most and to a lesser degree also the rhomboidal structure(s) **6s** (and **6t**) in particular with respect to linear triplet **1t**.

Electron Correlation Effects. Inclusion of electron correlation at 6-31G* results in a totally different post-Hartree–Fock relative stability order. As expected, the relative energies of singlets are lowered significantly with respect to triplet configurations. The changes in relative energies between singlet structures are minor except for **3s**, which shows a comparatively large "destabilization" at the MP2 level.

At MP4, with single, double, triple, and quadruple substitutions, rhombic **5s** is the global energy minimum and more stable than linear triplet **1t** by as much as 11.4 kcal/mol (11.5 after scaled (0.9) zero-point energy correction). This energy difference compares well with the 12.3 kcal/mol reported by Trucks and Bartlett.[28] At MP4/6-31G* the rhomboidal structure **6s** represents the "second best" C_2Si_2 structure! Structure **6s** is only 8.5 kcal/mol less stable than **5s** and is favored over linear **1t** by 2.9 kcal/mol! Although the HF/6-31G* energy difference between singlet and triplet linear **1** was substantial (22.3 kcal/mol), this reduces to only 5.7 kcal/mol at MP4/6-31G*; a value of 6.5 kcal/mol (MBPT/DZ) is reported by Trucks and Bartlett.[28] The singlet form of rhomboidal **6** is similarly favored; the small HF/6-31G* energy difference of 3.5 kcal/mol with **1t** enhances to 21.9 kcal/mol in favor of **6s** at the correlated MP2/6-31G* level. The three-membered ring structure **3s** is 33.0 kcal/mol higher in energy than **5s** and may represent a degenerate C-exchange for rhomboidal **6s** with a barrier of 24.5 kcal/mol (all MP4/6-31G*). Similarly, structure **9s** could represent a degenerate nonplanar C-exchange for **6s** with a barrier of 22.9 kcal/mol (same level). Expectedly, as the added diffuse functions did not have any significant structural nor energetic effect, also the relative MP2/6-31+G* values are similar to those at 6-31G*.

Effect of Silicon Coordination. The C_2Si_2 structures containing silicons with higher coordination numbers are energetically not competitive with the more stable isomers discussed above. This is illustrated by the rhombic structures **5s**, **6s**, and **7s** and the three-membered ring isomer **4s**. Rhombic disilicide **7s**, with its two inverted tricoordinate silicons, is 108.6 kcal/mol (HF/6-31G*) less stable than rhombic dicarbide **5s**, which has two inverted carbons. This energy difference reduces to 84.5 kcal/mol at the correlated MP2 level. In contrast, the discussed rhomboidal **6s**, having one inverted silicon, is only 8.5 kcal/mol less stable than **5s** as it benefits from strong C–C bonding in its periphery. The three-membered ring structure **4s** has a double-bonded tricoordinate silicon and is clearly one of the energetically less favorable structures, having a large energy difference with **5s** of 74.3 kcal/mol.

The structures **5**–**7** also reveal distinctly different singlet–triplet splittings. Singlet rhombic dicarbide **5s** is favored over its triplet isomer **5t** by 73.1 (HF/6-31G*), and 58.2 kcal/mol (MP2/6-31G*). The energy difference between the favored singlet rhomboidal **6s** and its triplet form is much smaller and amounts to 21.9 kcal/mol (MP2/6-31G*). For rhombic disilicide the higher order triplet structure **7t** is energetically preferred over the singlet **7s** form by 22.6 (HF/6-31G*) and 11.5 (MP2/6-31G*) kcal/mol. This suggests that with increasing silicon coordination the singlet–triplet energy difference reduces or even reverses in favor of the triplet form.[18a]

Binding Energy. The total binding energy for the ground-state disilicon dicarbide structure **5s** can be calculated as the difference in energy between this structure and the sum of the four atoms of which it is composed,[34] two carbons and two silicons. At the MP4/6-31G* level, with zero-point energy corrections, a binding energy of 16.9 eV is obtained. Taking into account that MP4/6-31G* recovers only ca. 90% of the binding energy for carbon and ca. 80–85% of that for silicon (as suggested by Raghavachari),[7a,16] a scaled binding energy for C_2Si_2 (**5s**) of ca. 19.4 eV results.

Conclusion

The global C_2Si_2 minimum on the MP4/6-31G* potential energy hypersurface is the rhombic dicarbide structure **5s** with two inverted tricoordinate carbons. The only 8.5 kcal/mol higher energy rhomboidal structure **6s** has both an inverted tricoordinate carbon and silicon as is evident from a MO analysis. The linear triplet **1t** is less stable than rhombic **5s** by 11.4 kcal/mol but favored over its singlet **1s** form by only 5.7 kcal/mol. All these structures and even the high-energy rhombic disilicide **7s** with its two inverted tricoordinate silicons are HF/6-31G* minima.

Disilicon dicarbide has major similarities with the related C_4 and Si_4 but is inherently more complex. Thus, the energy difference of the rhombic C_2Si_2 global minimum structure with its linear isomer is larger than that for C_4; there is no linear Si_4. That rhomboidal structure **6s**, with its mixed C/Si bonding characteristics, is the second best C_2Si_2 structure can be of importance to the bonding properties of binary clusters in general.

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