

A comparative *ab initio* study of the Si_2C_4 , Si_3C_3 , and Si_4C_2 clusters

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Various structural possibilities for the Si_2C_4 and Si_4C_2 clusters are investigated by employing a basis set of triple-zeta plus polarization quality; electron correlation is generally accounted for by second-order Möller–Plesset and, in certain instances, by higher-order perturbation (CASPT2) approaches. The building-up principle recently suggested from an analysis of Si_3C_3 clusters is found to be fully operative for Si_2C_4 and Si_4C_2 clusters. A comparison of the structure and stability of various geometrical arrangements in the series C_6 , Si_2C_4 , Si_3C_3 , Si_4C_2 , and Si_6 shows that linear and planar structures become rapidly less stable if carbons are replaced by silicons and that the three-dimensional bipyramidal forms become less favorable as soon as silicons are exchanged by carbons in the parent Si_6 structure. The effects can be rationalized in qualitative terms based on differences in silicon and carbon bonding.

I. INTRODUCTION

The discovery of the structure of C_{60} (Refs. 1 and 2) inspired numerous scientists and renewed the interest in cluster research. As a result, silicon^{3–9} and carbon^{10–15} elemental clusters became of great interest, in particular, since their occurrence is important in combustion processes and in catalytic research. In order to understand the building-up mechanisms and the nature of chemical bonding in large clusters, it seems necessary to have also a closer look at small clusters. Such systems can very effectively be investigated by *ab initio* calculations whose accuracy can be very high for systems up to $n=10$, for example. While many recent publications^{3–15} deal with elementary carbon and silicon clusters such as the C_6 and Si_6 , much less information seems to be available for the “mixed” silicon–carbon cluster systems, however, although silicon carbide has long been known for its potential as a material of technical interest for wide-band-gap semiconductor applications. Recent *ab initio* studies are focusing on Si_2C (Ref. 16) and SiC_2 (Ref. 17) and the four atomic species Si_2C_2 (Refs. 18–20), Si_3C (Ref. 21), and SiC_3 (Ref. 22).

The present work is part of an investigation of larger mixed silicon–carbon clusters. In a previous publication,^{23,24} the relationship between various Si_3C_3 structures was discussed and rules for the building-up principle of mixed SiC clusters could be extracted. The most important was that strong CC bonds are favored over CSi bonds, while SiSi bonds are much less important for the arrangement of atoms in the cluster and that in addition multicenter bonding plays an important role. As a result three-dimensional Si_3C_3 structures were favored over linear or planar arrangements.

It is the goal of the present work to expand this study to further systems of similar type, namely to Si_2C_4 and Si_4C_2 which can be looked upon as resulting from Si_3C_3 by substitution of a carbon by a silicon or vice versa. At the same time these clusters form the link between Si_3C_3 and Si_6 on one side and C_6 on the other. It will be of interest to see whether

the carbon-rich compound shows a behavior close to C_6 and whether Si_4C_2 can be more closely related to Si_6 than Si_3C_3 . Thus the first part of the present paper will deal with the lowest-energy structures of the various Si_2C_4 and Si_4C_2 isomers. Special emphasis will be given to the bonding properties, in particular, to the relationship between structure and stability in light of our previously determined rules for a possible building-up principle for carbon silicon clusters. The second part will focus on the comparison between the structures for Si_6 , Si_4C_2 , Si_3C_3 , Si_2C_4 , and C_6 , and relate structural differences to basic differences in bonding features.

The study can also be useful for certain lattice aspects in thin films of α -SiC. Studies of amorphous silicon–carbide based on some rough estimates and preliminary results by one of the authors²⁵ have suggested that the underlying lattice of α -SiC turns from diamondlike to graphitic-type for concentrations of C slightly above 50%. The information on bonding features in carbon-rich or silicon-rich clusters may be instrumental in understanding such effects.

II. TECHNICAL DETAILS

The Hartree–Fock method was employed as a starting point for determining the various stationary points on the multidimensional Si_2C_4 and Si_4C_2 potential surface. Various initial structures were chosen (primarily on the basis of several geometries of the C_6 , Si_6 , and Si_3C_3 isomers) and a complete geometry optimization within a given symmetry group was then carried out until the structure corresponding to a stationary point was found. All such stationary points were tested with respect to their character and stability by a further optimization procedure under C_1 symmetry and by a vibrational analysis checking for possible imaginary values. Altogether a total of sixteen stationary points are studied.

The atomic basis set includes cartesian Gaussian functions of both, double-zeta (DZP) and triple-zeta (TZP) quality²⁶ augmented with d polarization functions. The d ex-

ponents are the same as in the previous work on Si_3C_3 , namely $d(\text{Si})=0.4$ and $d(\text{C})=0.8$. The contraction scheme in the TZP basis is $(19s, 8p, 1d) \rightarrow [8s, 3p, 1d]$ for silicon and $(9s, 5p, 1d) \rightarrow [5s, 3p, 1d]$ for carbon in accordance with the values given by Schaefer *et al.*¹⁶ From prior experience it is known that basis sets of TZP quality tend to underestimate bond lengths in self-consistent field (SCF) calculations while DZP basis sets give quite realistic structural values due to a fortunate cancellation between atomic orbital (AO) basis set deficiencies and the neglect of electron correlation. For this reason the geometry optimizations are undertaken in the DZP basis (which is also more economical) while energy differences between the various structures are determined by single-point calculations employing the more flexible TZP basis. Comparison of DZP and TZP results also give an indication of the AO basis set convergence. In the previous study of Si_3C_3 , geometry optimization was also undertaken for the low-energy structures using the MP2 treatment in combination with a TZP basis; the differences in bond lengths and bond angles relative to the less expensive SCF/DZP geometries was less than 1%, however, so that optimization at the SCF level seems to yield sufficient accuracy for the structural data.

Correlation effects are included by second-order Møller–Plesset (MP2) perturbation treatment employing the TZP basis. In addition, for the lowest-energy structures the influence of electron correlation was studied using more sophisticated correlation treatments, i.e., single point calculations were carried out with MP3 and MP4. In this case a split valence basis 6-31G* was chosen employing the GAUSSIAN 90 program package;²⁷ this choice enables the comparison with prior results, in particular, those obtained by Raghavachari for Si_6 in a similar treatment.⁸ The influence of multi-reference effects for the energy of the lowest structures was investigated by employing a single-point complete active space self-consistent field (CASSCF) calculation followed by second-order perturbation theory (CASPT2) (Refs. 28 and 29) using the MOLCAS program package (Ref. 30). The bulk of all calculations was carried out with the TURBOMOLE direct SCF program.^{31,32}

III. EQUILIBRIUM STRUCTURES AND BONDING PROPERTIES OF Si_2C_4 AND Si_4C_2 CLUSTERS

The equilibrium geometries obtained for the low-energy Si_2C_4 and Si_4C_2 isomers are given in Figs. 1–3; bond lengths and bond angles are indicated. For the geometrically complicated structures the Cartesian coordinates are listed in Table I. Some of the relevant structures of Si_3C_3 are also contained in the Figs. 1–3 for comparison. The relative stabilities of the Si_2C_4 and Si_4C_2 isomers are given in Tables II and III, respectively. The population analysis according to the Mulliken scheme³³ and that of Roby–Davidson–Heinzmann–Ahlrichs^{34–36} (RDHA) is shown in Tables IV (Si_2C_4) and V (Si_4C_2). The latter scheme has the advantage that it accounts also for multicenter bonding effects, which were found to be important in Si_3C_3 clusters. For this reason the RDHA analysis is generally preferred over the Mulliken analysis; if multicenter bonding is important, the charges on the nuclei $q(A)$ in the RDHA

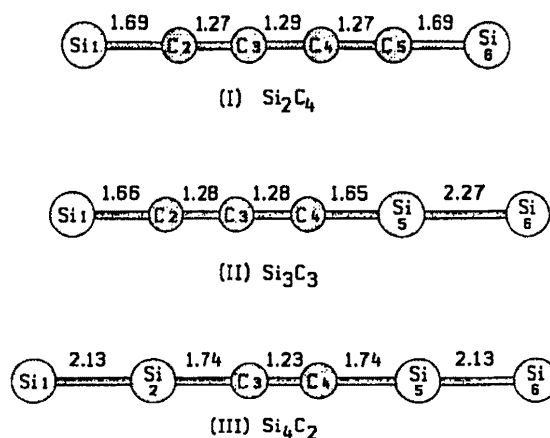


FIG. 1. Equilibrium geometries of the linear structures of Si_2C_4 , Si_3C_3 , and Si_4C_2 . Distances are in Å.

analysis are generally smaller than in the Mulliken procedure which distributes the charge only between two centers. The *s*-, *p*-, and *d*-type atomic population, on the other hand, are only available in the latter analysis and because it is a helpful measure for estimating *d*-type contribution in the bonding, the values of the Mulliken analysis are also given.

The infrared frequencies for the various vibrational modes in the harmonic approximation as obtained from analytic second-order derivative techniques at the SCF level and the corresponding infrared intensities derived from the computed SCF dipole moment are listed in Tables VI and VII. These frequencies might be helpful in an experimental search for the infrared spectra of such clusters. In addition, they serve to detect differences in zero-point energies of the various structures.

A. The Si_2C_4 Isomers

The lowest-energy Si_2C_4 isomer (structure I) is the linear arrangement of nuclei (Fig. 1) in the $^3\Sigma_g^-$ electronic state whose orbital occupation is $1\pi_u^4 3\sigma_u^2 4\sigma_g^2 1\pi_g^4 2\pi_u^2$ if valence electrons are listed only. Three strong carbon bonds are formed and the silicon atoms are in the terminal positions; this outer position is generally preferred by the second-row atom included in linear chains with first- and second-row constituents. A certain parallel thus exists to the C_6 cluster in which the cumulene isomer is also very low in energy.

The next Si_2C_4 structure in the energy ordering (about 10 kcal above the ground state) is found to possess a chairlike geometry (structure IV in Fig. 2). It results from a gradient optimization procedure starting from a pyramidal arrangement of the atoms and resembles the hexagonal chair structure of C_6 found by Raghavachari. On the other hand, in contrast to Si_2C_4 , the latter C_6 structure is about 30 kcal/mole above the planar ring structure of C_6 so that the finding that structure IV is a low-energy structure in Si_2C_4 underlines the tendency towards three-dimensional structures observed for the mixed carbon-silicon Si_3C_3 clusters. Structure IV is characterized by two very strong CC bonds of triple bond character judged on the basis of the shared electron numbers (SEN) numbers in the population analysis (Table IV) and

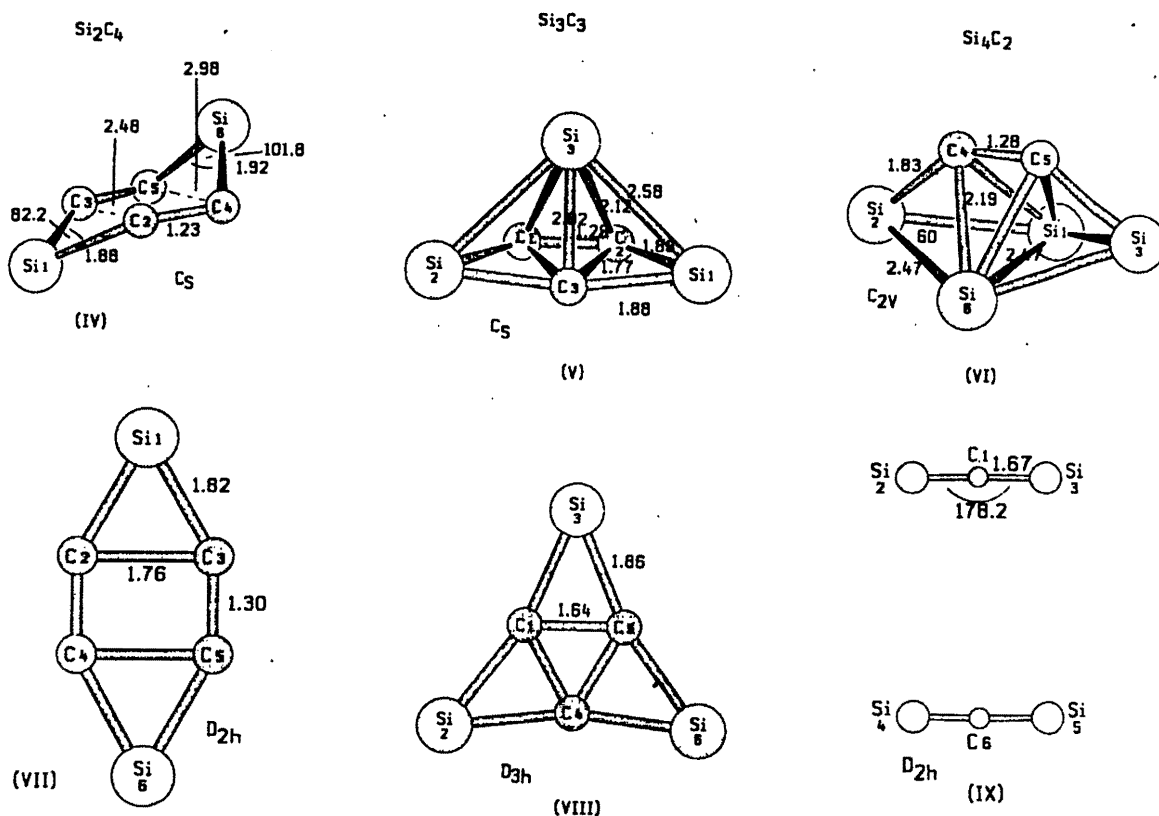


FIG. 2. Equilibrium geometries of energetically low-lying structures of Si_2C_4 , Si_3C_3 , and Si_4C_2 obtained if the geometry optimization was started from a "pyramidlike" (upper part) or "planar-hexagonal" geometry. Distances are in Å; angles are given in degrees. Bond lengths and angles which can be deduced easily from the symmetry are not given explicitly. The Cartesian coordinate of the more complicated structures (IV,VI) are given in Table I and, therefore, only some characteristic internal coordinates are included in the figure for these species.

four SiC bonds with SEN numbers of 1.32 for Si(1)C(2) and Si(1)C(3) and 1.18 for the other two bonds connecting Si(6) with the carbons C(4) and C(5). The lengths of the SiC bonds of 1.92 and 1.88 Å is also in line with what is known for SiC single bonds: Trucks and Bartlett¹⁸ give a SiC bond distance of 1.88 Å for the rhombic Si_2C_2 ground state and similar values are obtained for Si_2C (Ref. 16) and SiC_2 (Ref. 17); the bond strength in diatomic SiC with a $^3\Pi$ ground state is larger³⁷ and leads to a shorter bond of 1.75 Å. The SEN numbers and the interatomic distance indicate weak bonding (SiC distance of 2.5 Å) between Si(6) and C(2) and C(3) as well as a small three-center bridging of C(2)C(3) by Si(6). The Si(1)C(4) separation is 3 Å and, hence, the corresponding SEN are only 0.02. A significant charge transfer from silicon to the carbons is observed so that the system shows considerable ionic character. The tight CC bonding is also seen from Table VI; this structure has the highest frequency for the vibrational modes involving CC bonds of all three-dimensional Si_2C_4 isomers studied. The frequency $\nu_1=2089\text{ cm}^{-1}$ corresponds to the two symmetric CC vibrations in phase, $\nu_2=2044\text{ cm}^{-1}$ is the out-of-phase counterpart with very low intensity.

The next structure in the energetic ordering is the planar structure VII. It is found to lie only about 10 kcal/mol above structure IV and due to its strained character it is more influenced by electron correlation effects than structure IV. This

is quite obvious from Table VIII which shows correlation effects estimated by MP2, MP3, MP4 SDTQ, and CASPT2 techniques. For the more favorable structure IV, the correlation correction is only about 16 kcal/mol (MP2) and seems to remain fairly constant if higher-order terms are considered. Electron correlation for structure VII is of the order of 40 kcal/mol (MP2) and is obviously not yet converged if the corresponding data for MP2 and MP4 SDTQ are considered (Table VIII). However, the CASPT2T treatment gives similar results as the MP4 treatment. Structure VII is obtained by starting the geometry optimization from the equivalent planar C_6 hexagon in which two carbons on opposite sites are replaced by silicons. In contrast to the situation in Si_3C_3 , in which the planar structures are only transition states, this planar Si_2C_4 is a local minimum on the energy surface, i.e., it possesses no imaginary vibrational frequencies (Table VI). The C_4 rectangle is the basis for the bonding properties. The two short CC bonds of 1.30 Å are somewhat stronger than a double bond (SEN=2.32), each of the two longer CC bonds of 1.76 Å (SEN=0.96) is bridged by a silicon atom leading to four SiC bonds of 1.82 Å (SEN=1.75). Besides the two strong CC and the SiC bonds, multicenter CCSi effects also stabilize this structure. Charge transfer between silicon and carbon does not take place. For this reason the CC (in-plane and out-of-plane) stretching modes cannot be observed (Table VI) and the only infrared mode of sizeable intensity is

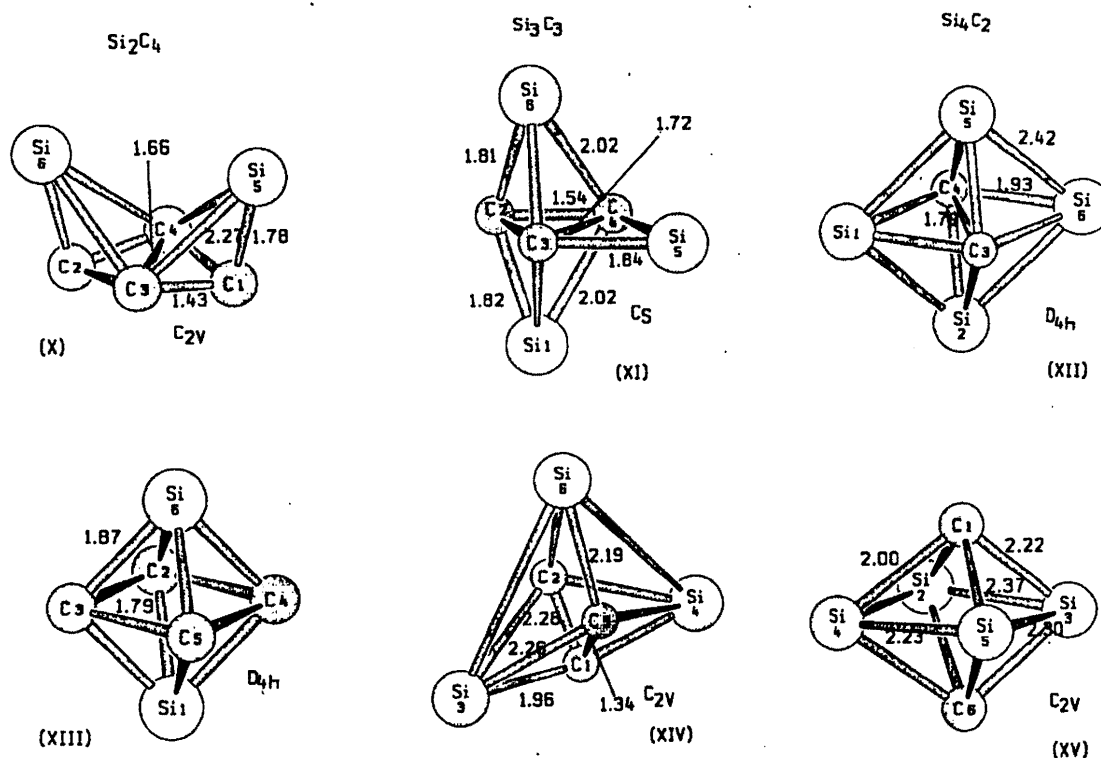


FIG. 3. Equilibrium geometries of "octahedrallike" and "bipyramidlike" structures of Si_2C_4 , Si_3C_3 , and Si_4C_2 obtained by starting the geometry optimization from Si_6 ground state structure; distances are in Å. The Cartesian coordinates of structures X and XI are given in Table I and, therefore, only some characteristic internal coordinates are displayed in the figure. Bond lengths and angles which can be deduced easily from the symmetry, are not given explicitly.

ν_3 (894 cm^{-1}) which involves in-plane motion and is composed of diagonal CC movement and silicon displacement.

If an out-of-plane distortion is induced in the planar structure, the two silicon atoms move above and below the CCCC plane and the distorted chair of structure IV results from structure VII as indicated schematically in Fig. 4. The shortening of bond lengths from 1.30 to 1.23 Å (almost triple bond) in structure IV becomes energetically favorable (SEN from 2.32 to 3.02) and the corresponding expansion of the C(2)C(3) and C(5)C(4) in structure IV is compensated by the SiC and the three-center bonds as well as the ionic character as discussed earlier. The further step to the pyramidlike structure of Si_3C_3 is also obvious from Fig. 4.

Structures X and XIII are considerable higher in energy than all those discussed so far. Structure X is the result of a geometry optimization starting from a nuclei arrangement closely related to the lowest Si_6 isomer. It lies about 70 kcal/mol above the Si_2C_4 ground state. Two triangles C(1)C(3)C(4) and C(2)C(3)C(4) with a bond of 1.43 Å are connected at their C(3)C(4) baseline of 1.66 Å and each triangle can be looked upon as the base of a pyramid with a silicon on top. The reason from the smaller stability is obvious from Table IV: the CC bonds in the triangle are weaker than in structures IV or VII and the number of strong SiC bonds (two vs four) is also smaller than in compound VII. The highest six infrared frequencies between 1074 and 1591 cm^{-1} (Table VI) involve mostly carbon displacements.

TABLE I. Cartesian coordinates for the more complicated structures of Si_2C_4 and Si_4C_2 displayed in Figs. 2 and 3. The values are given in a.u. The numbering of atoms and structures is according to Figs. 2 and 3.

Structure	Center	x	y	z
Si_2C_4 IV	Si(1)	+1.500 739	+2.826 884	0.000 000
	C(2)	+1.201 076	+0.527 027	-2.820 000
	C(3)	+1.201 076	+0.527 027	+2.820 000
	C(4)	-0.772 883	-0.612 057	-2.340 000
	C(5)	-0.772 883	-0.612 057	+2.340 000
	Si(6)	-2.343 015	-2.765 070	0.000 000
X	C(1)	+2.146 287	0.000 000	-1.886 912
	C(2)	-2.146 287	0.000 000	-1.886 912
	C(3)	0.000 000	+1.567 203	-1.392 753
	C(4)	0.000 000	-1.567 203	-1.392 753
	Si(5)	+2.857 094	0.000 000	+1.402 569
	Si(6)	-2.857 094	0.000 000	+1.402 569
Si_4C_2 VI	Si(1)	+0.990 121	-2.340 418	0.000 000
	+Si(2)	-0.049 643	+0.002 472	+3.905 911
	Si(3)	-0.049 643	+0.002 472	-3.905 911
	C(4)	-2.203 900	+0.001 592	+1.205 541
	C(5)	-2.203 900	+0.001 592	-1.205 541
	Si(6)	+0.994 188	+2.334 111	0.000 000
XV	C(1)	+2.608 056	0.000 000	-0.321 978
	Si(2)	0.000 000	-2.068 866	+2.241 179
	Si(3)	0.000 000	-2.087 754	-2.103 483
	Si(4)	0.000 000	+2.068 866	+2.241 179
	Si(5)	0.000 000	+2.087 754	-2.103 483
	C(6)	-2.608 056	0.000 000	-0.321 978

TABLE II. Relative stabilities ΔE (in kcal/mol) and total binding energies ΔE_B (in kcal/mol) of the different Si₂C₄ isomers at the SCF and MP2 level. The relative stabilities are given with respect to isomer IV. The numbering is according to Figs. 1–3. The symmetry (sym.) and the electronic configuration of the different species is also given.

Isomer	Sym.	Electronic configuration	$\Delta E(\text{SCF})^a$	$\Delta E(\text{SCF})^b$	$\Delta E(\text{MP2})^b$	$\Delta E_B(\text{SCF})^b$
I	$D_{\infty h}$	$9\sigma_g^2 8\sigma_u^2 2\pi_g^4 2\pi_u^4 3\pi_u^2$	-729.043 15 ^c	-729.132 92 ^c	d	438.7
(³ Σ_g^-)			-10.3	-9.1		
IV	C_s	$17a'^2 9a''^2$	0.0	0.0	0.0	429.6
VII	D_{2h}	$8a_g^2 3b_{1g}^2 2b_{2g}^2 1b_{3g}^2 2b_{1u}^2 4b_{2u}^2 6b_{3u}^2$	51.5	50.5	7.8	397.3
X	C_{2v}	$11a_1^2 2a_2^2 9b_1^2 4b_2^2$	125.6	125.7	63.9	322.6
XIII	D_{4h}	$7a_1^2 1b_{1g}^2 2b_{2g}^2 2e_g^4 4a_{2u}^2 4e_u^4$	255.7	249.1	147.0	198.7

^aPerformed with DZP basis set (Ref. 26).

^bPerformed with TZP basis set (Ref. 26).

^cTotal energy in hartree.

^dNot calculated; the corresponding 6-31G* value can be seen from Table VIII.

Structure XIII is an octahedral structure with carbons arranged in a fairly loosely bound square (1.79 Å) corresponding to SEN numbers of approximately 1.0. Multicenter effects and charge transfers are visible just as in structure X. Structure XIII is energetically much higher than the other isomers, but obviously it is a local minimum on the Si₂C₄ surface.

The most interesting structures among the Si₂C₄ variety are certainly the linear arrangement (I), the distorted chair (IV) with its ionic contribution to the bonding and the planar hexagon (VII). All are related to relatively low-energy structures of C₆. Their direct relation to the Si₃C₃ structures is seen in Figs. 1–3. In the linear chain the σ_u -type vibration of the carbon chain at $\nu_2=1993 \text{ cm}^{-1}$ show the highest intensity; the most intense infrared vibration in the distorted chair (IV) corresponds to $\nu_3=695 \text{ cm}^{-1}$ and involves carbon and silicon displacements. In the planar hexagon only one vibrational mode ($\nu_3=894 \text{ cm}^{-1}$) is noticeably infrared active while the intensity is distorted over a number of modes in structure X with C_{2v} symmetry. All frequencies result from SCF calculations and are thus only rough estimates (within about 10%).

B. The Si₄C₂ Isomers

The silicon-rich isomers Si₄C₂ are expected to be more closely related to Si₆ than to C₆. Under this assumption it is

likely that three-dimensional structures are preferred over planar or linear arrangements of nuclei. Furthermore, we remember that the formation of a strong CC bond is a driving force in the structural arrangement of mixed carbon–silicon clusters and note, that a maximum of one CC bond is possible in the Si₄C₂ isomers. In other words, carbon triangles found as important features in the the structure of Si₃C₃ or Si₂C₄ isomers or carbon quadrangles presented in Si₂C₄ structures cannot form a decisive substructure in the silicon-rich Si₄C₂ compounds.

There are two low-lying extrema on the Si₄C₂ surface: structures VI and XII (Figs. 2 and 3). Only the first of these represents a true minimum as seen from Table VII. In structure VI the CC bond is found to be 1.28 Å, which is between a typical double (1.35 Å in ethene) and triple (1.21 Å in ethine) bond; the SEN number of 2.55 (Table V) supports this interpretation. The SiC bonds are somewhat shorter than a typical single SiC bond [1.88 Å in rhombic Si₂C₂ (Ref. 18)], and show SEN numbers of 1.72. The SiSi distances are 2.47 Å [with the exception of Si(2)Si(3)] and indicate single bonding (SEN=1.15 or 1.19). A similar value of 2.46 Å was obtained by Raghavachari⁸ for the tetrahedron structure of Si₄, whereas the ground state of Si₄ possessing a planar D_{2h} symmetry shows shorter SiSi bonds [2.3 and 2.4 Å (Ref. 8)]. As shown schematically in Fig. 5, structure XII can be viewed either as derived from a Si₄ tetrahedron by capping

TABLE III. Relative stabilities ΔE (in kcal/mol) and total binding energies ΔE_B (in kcal/mol) of the different Si₄C₂ isomers at the SCF and MP2 level. The numbering is according to Figs. 1–3. The symmetry (sym.) and the electronic configuration of the different species is also given. The relative stabilities on the SCF and MP2 level are given with respect to isomer VI.

Isomer	Sym.	Electronic configuration	$\Delta E(\text{SCF})^a$	$\Delta E(\text{SCF})^b$	$\Delta E(\text{MP2})^b$	$\Delta E_B(\text{SCF})^b$
VI	C_{2v}	$15a_1^2 3a_2^2 7b_1^2 9b_2^2$	-1231.203 54	-1231.329 11	-1231.969 96	357.2
XII	D_{4h}	$7a_1^2 1a_2^2 4b_1^2 2b_2^2 2e_g^4 3a_{2u}^2 1b_{2u}^2 6e_u^4$	+19.0	+20.8	+3.5	353.7
IX ^c	C_1	$34a^2$	+38.0	+42.1	+90.1	315.1
III (³ Σ_g^-)	$D_{\infty h}$	$11\sigma_g^2 10\sigma_u^2 3\pi_g^4 3\pi_u^4 4\pi_u^2$	+106.0	+108.3	d	248.9
XV	C_{2v}	$14a_1^2 3a_2^2 6b_1^2 11b_2^2$	+173.5	+179.4	+137.0	+177.7

^aPerformed with the DZP basis set (Ref. 26).

^bPerformed with the TZP basis set (Ref. 26).

^cStructure IX represents two SiCSi fragments, see Fig. 2.

^dNot calculated; the corresponding 6-31G* value can be seen from Table IX. For the lowest-energy structure VI the total energy is also given (in hartree).

TABLE IV. Calculated atomic (partial) charges $q(A)$ obtained according to the Mulliken and the Roby–Davidson–Heinzmann–Ahlrichs method of population analysis for the silicon and carbon atoms in the Si₂C₄ cluster structures. In the Mulliken analyses the m , n , and r values of the s -, p -, and d -orbital occupation numbers are reported. Bonding features are expressed by the shared electron numbers SEN. Multicenter bonding effects are indicated by the occurrence of either three-center or four-center SEN values.

No. ^a	Atom	Mulliken		Roby–Davidson–Heinzmann–Ahlrichs		
		$q(A)$	$s^m p^n d^r$ ^b	$q(A)$	SEN _{two-center}	SEN _{multicenter}
I	Si(1)	+0.37	5.86 7.66 0.10	+0.19	C(2)C(3) 2.50	
	C(2)	-0.48	3.35 3.10 0.02	-0.29	C(3)C(4) 2.12	
	C(3)	+0.11	3.24 2.59 0.05	+0.10	Si(1)C(2) 2.34	
IV	Si(1)	+0.63	5.74 7.48 0.15	+0.46	C(2)C(4) 3.02	Si(1)C(3)C(4) 0.23
	Si(6)	+0.60	5.76 7.48 0.14	+0.65	Si(1)C(2) 1.32	Si(2)C(4)C(5) 0.10
	C(2)	-0.40	3.39 2.98 0.03	-0.30	Si(6)C(4) 1.18	
	C(4)	-0.22	3.49 2.69 0.04	-0.25	Si(6)C(2) 0.24 Si(1)C(4) 0.02	
VII	Si(1)	+0.36	5.77 7.70 0.17	-0.01	C(2)C(4) 2.32	C(2)C(3)C(4) 0.24
	C(2)	-0.18	3.45 2.69 0.04	+0.00	C(2)C(3) 0.96	Si(1)C(2)C(3) 0.46
					C(3)C(4) 0.26	C(2)C(3)C(4)C(5) 0.27
					Si(1)C(2) 1.75	
X	C(1)	-0.25	3.50 2.69 0.13	-0.26	C(1)C(3) 1.76	C(1)C(3)C(4) 0.51
	C(3)	-0.23	3.51 2.65 0.17	-0.09	C(3)C(4) 0.96	C(1)C(3)Si(5) 0.37
	Si(5)	+0.48	5.84 7.55 0.13	+0.35	Si(5)C(1) 1.75	C(3)C(4)Si(5) 0.16
					C(3)Si(5) 0.74 Si(5)Si(6) 0.36	C(3)Si(5)Si(6) 0.19 C(1)C(3)C(4)Si(5) 0.21
XIII	Si(1)	+0.48	5.60 7.64 0.28	+0.54	C(2)C(3) 1.03	C(1)C(3)Si(5) 0.39
	C(2)	-0.24	3.71 2.49 0.04	-0.27	Si(1)C(2) 1.33	C(2)Si(1)Si(6) 0.17
					Si(1)Si(6) 0.22	C(1)C(3)Si(5)Si(6) 0.14

^aThe numbering of the atomic centers is according to Figs. 1–3.

^bThe corresponding population numbers of the atoms in their ground state are C: $s^4 p^2 d^0$ and Si: $s^6 p^8 d^0$.

TABLE V. Calculated atomic (partial) charges $q(A)$ obtained according to the Mulliken and the Roby–Davidson–Heinzmann–Ahlrichs method of population analysis for the silicon and carbon atoms in the Si₄C₂ cluster structures. In the Mulliken analyses the m , n , and r values of the s -, p -, and d -orbital occupation numbers are reported. Bonding features are expressed by the shared electron numbers SEN. Multicenter bonding effects are indicated by the occurrence of either three-center or four-center SEN values.

No. ^a	Atom	Mulliken		Roby–Davidson–Heinzmann–Ahlrichs		
		$q(A)$	$s^m p^n d^r$ ^b	$q(A)$	SEN _{two-center}	SEN _{multicenter}
VI	Si(1)	+0.00	5.81 8.06 0.12	+0.07	C(4)C(5) 2.55	Si(1)C(4)C(5) 0.43
	Si(2)	+0.26	5.84 7.76 0.14	+0.00	Si(2)C(4) 1.72	Si(1)Si(3)C(4) 0.35
	C(4)	-0.26	3.46 2.75 0.04	-0.10	Si(1)C(4) 0.84 Si(1)Si(2) 1.19 Si(1)Si(6) 1.15	Si(1)C(4)Si(6) 0.13 Si(1)C(4)C(5)Si(6) 0.12 Si(1)Si(3)C(4)Si(6) 0.14
XII	Si(1)	+0.28	5.81 7.72 0.18	+0.16	C(3)C(4) 0.98	Si(1)C(3)C(4) 0.31
	C(3)	-0.57	3.63 2.90 0.04	-0.32	Si(1)C(3) 1.40 Si(1)Si(2) 1.05	Si(1)Si(2)C(3) 0.39 Si(1)C(3)C(4)Si(6) 0.22
XV	C(1)	-0.53	3.75 2.75 0.03	-0.50	C(1)Si(5) 1.34	C(1)Si(3)Si(5) 0.42
	Si(3)	+0.28	5.74 7.83 0.15	+0.29	C(1)Si(3) 1.00	C(1)Si(3)Si(6) 0.36
	Si(5)	+0.25	5.67 7.87 0.20	+0.21	Si(3)Si(4) 1.49 Si(3)Si(5) 1.46 Si(5)Si(6) 1.20	C(1)Si(3)Si(4) 0.28 Si(3)Si(4)Si(5)Si(6) 0.17
III	Si(1)	+0.18	5.84 7.91 0.06	+0.02	Si(1)Si(2) 2.23	
	Si(2)	-0.02	5.32 8.59 0.09	+0.04	Si(2)C(3) 1.85	
	C(3)	-0.17	3.35 2.79 0.02	-0.06	C(3)C(4) 2.87	

^aThe numbering of the atomic centers is according to Figs. 1–3.

^bThe corresponding population numbers of the atoms in their ground state are C: $s^4 p^2 d^0$ and Si: $s^6 p^8 d^0$.

TABLE VI. Calculated harmonic vibrational frequencies (in cm⁻¹); total and relative IR intensities (in km/mol) of various Si₂C₄ isomers. The numbering of the structures is according to Figs. 1–3. Imaginary wave numbers indicate that the structure represents a saddle point on the energy surface.

I	Freq. ^a (sym.)	49(π_u)	188(π_g)	396(π_u)	449(σ_g)	487(π_g)	806(σ_u)	1357(σ_g)	1993(σ_u)	2216(σ_g)			
	IR _{tot} ^b (IR _{rel}) ^c	0(0)	0(0)	7(2)	0(0)	0(0)	157(47)	0(0)	330(100)	0(0)			
IV	Freq. ^a (sym.)	106(a')	205(a'')	260(a')	279(a')	332(a'')	499(a')	572(a'')	619(a'')	652(a')	695(a')	2044(a'')	2089(a')
	IR _{tot} ^b (IR _{rel}) ^c	9(3)	1(0)	4(1)	9(3)	0(0)	68(24)	35(13)	212(74)	58(20)	284(100)	10(4)	61(21)
VII	Freq. ^a (sym.)	155(b_{1u})	303(a_u)	367(b_{2u})	434(b_{2g})	475(b_{3u})	558(a_g)	730(b_{1g})	832(a_g)	894(b_{3u})	1418(b_{2u})	1873(a_g)	
	IR _{tot} ^b (IR _{rel}) ^c	12(8)	0(0)	10(6)	0(0)	51(32)	0(0)	0(0)	0(0)	155(100)	0(0)	0(0)	
X	Freq. ^a (sym.)	279(a_1)	403(a_2)	457(b_1)	694(a_1)	776(b_2)	1053(b_1)	1074(b_2)	1120(a_1)	1271(a_1)	1417(a_2)	1490(a_1)	1591(b_1)
	IR _{tot} ^b (IR _{rel}) ^c	0(0)	0(0)	165(41)	30(7)	403(100)	191(47)	328(81)	98(24)	181(45)	0(0)	70(17)	159(39)
XIII	Freq. ^a (sym.)	$i475(e_u)$		437(a_g)	512(b_{1g})	555(b_{1u})	605(e_u)	606(a_{2u})	836(a_{1g})	1016(b_{2g})		1160(e_g)	
	IR _{tot} ^b (IR _{rel}) ^c			0(0)	0(0)	0(0)	44(37)	120(100)	0(0)	0(0)		0(0)	

^aHarmonic vibrational frequency in cm⁻¹. The calculation was performed with the TZP basis set.^bTotal intensities in km/mol.^cRelative intensities. The relative intensities are taken with respect to the most intense line of each cluster whose intensity is set to 100.TABLE VII. Calculated harmonic vibrational frequencies (in cm⁻¹); total and relative IR intensities (in km/mol) of various Si₄C₂ isomers. The numbering of the structures is according to Figs. 1–3. Imaginary wave numbers indicate that the structure represents a saddle point on the energy surface.

VI	Freq. ^a (sym.)	172(a')	181(a')	307(a'')	365(a')	391(a'')	401(a')	430(a')	500(a'')	579(a'')	609(a')	829(a'')	1774(a')
	IR _{tot} ^b	9	3	0	13	39	16	3	0	56	25	140	2
	IR _{rel} ^c	6	3	0	9	27	11	2	0	40	18	100	2
XII	Freq. ^a (sym.)	$i206(b_{2u})$	202(b_{1u})	203(b_{3u})	433(a_g)	435(b_{2g})	485(b_{2u})	529(a_g)	668(b_{3g})	671(b_{1g})	762(a_g)	801(b_{1u})	804(b_{3u})
	IR _{tot} ^b	0	4	4	0	0	50	0	0	0	0	211	210
	IR _{rel} ^c	0	2	2	0	0	24	0	0	0	0	100	99
XV	Freq. ^a (sym.)	$i827(b_2)$	$i267(a_2)$	205(b_2)	226(b_1)	240(a_1)	347(b_2)	453(a_2)	513(a_1)	582(a_1)	641(a_1)	722(b_1)	749(a_1)
	IR _{tot} ^b	0	0	1	38	92	11	0	1	15	19	7	4
	IR _{rel} ^c	0	0	1	41	100	12	0	1	17	21	7	5
IX	Freq. ^a (sym.)	$i29(b_g)$	$i27(a_u)$	$i26(a_u)$	9(a_g)	61(b_u)	71(a_g)	79(b_u)	87(a_g)	643(b_u)	644(a_g)	1516(b_g)	1527(a_u)
	IR _{tot} ^b	0 ^c	0	0	0	42	0	34	0	0	0	0	1825
	IR _{rel} ^c	0	0	0	0	2	0	2	0	0	0	0	100

^aHarmonic vibrational frequency in cm⁻¹ as calculated with the TZP basis set (Ref. 26).^bTotal intensities in km/mol.^cRelative intensities. The relative intensities are taken with respect to the most intense line in each cluster whose intensity is set to 100.

TABLE VIII. Relative stabilities (in kcal/mol) and total energies (in a.u.) for the isomers I, IV, and VII using various methods. The energies of structure IV and VII are given with respect to isomer I.

Isomer	SCF ^a	MP2 ^a	MP3 ^a	MP4 ^a	CASPT2 ^b
I	-729.0878	-729.7022	-729.7197	-729.77793	-729.89284
	0.0	0.0	0.0	0.0	0.0
IV	+24.9	+9.3	+10.1	+9.6	+11.3
VII	+53.7	+12.6	+27.5	+19.4	+18.5

^aPerformed with 6-31G* AO basis set.^bPerformed with the ANO basis set {Si:(17s,12p,5d)→[6s,5p,2d]; C:(14s,9p,4d)→[5s,4p,2d]} as proposed by Widmark *et al.* (Ref. 38). The CASPT2 calculations were performed on top of a CASSCF calculation including twelve electrons in the active space. All valence electrons (24) were correlated. The nondiagonal zero-order Hamiltonian (Refs. 28 and 29) was used in all calculations.

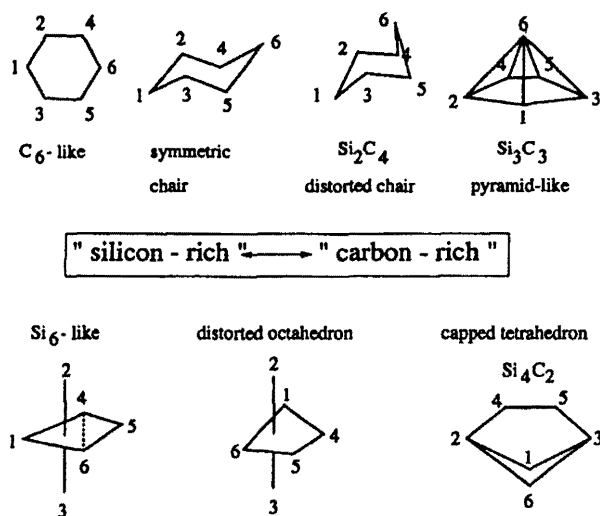


FIG. 4. Schematic illustration of the relation between the C_6 , Si_2C_4 , Si_3C_3 , Si_4C_2 , and Si_6 ground state geometries.

one edge with a C_2 bridge, or alternatively by capping the planar Si_4 ground state structure with a C_2 bridge also resulting in the three-dimensional structure. The highest frequency (Table VII) corresponding to a CC stretch vibration shows no intensity so that the first (and strongest) line is expected around $\nu_2 = 829 \text{ cm}^{-1}$; it involves CSi and CC displacements. Structure XII is obtained from a Si_6 equivalent geometry, but optimization of this structure without the D_{4h} geometry constraint finally leads to structure VI. This is shown schematically in the lower part of Fig. 4. With the D_{4h} constraint it is about 8 kcal above structure VI (Table VII). It possesses eight SiC bonds (SEN=1.40) and four SiSi linkages (SEN=1.05) but only one single CC bond (SEN=0.98). Obviously, the very strong CC bond (SEN=2.55) plus the two strong Si(2)C(4)=Si(3)C(5) bonds with SEN=1.72 in structure VI compensate the larger number of weaker bonds in structure XII and make structure VI the lowest in energy.

In Si_4C_2 planar structures are obviously not stable; this is in accordance with the results for Si_3C_3 . A planar arrangement decomposes into two SiCSi entities as indicated in Fig. 2 (structure IX). Obviously the SiSi linkage is not strong enough to form a real bond and, hence, the system shows a driving force either to form a three-dimensional Si_4C_2 arrangement or to split into fragments.

Finally, the octahedron XV is also only a stationary point on the surface, but lies very high above the ground state isomer. Such arrangement of nuclei is very unfavorable (Table III) for CC bonding and has thus the tendency to drive towards lower-energy structures.

The linear structure of Si_4C_2 (Fig. 2) is very unstable which is understandable because even though there exists one strong CC bond only two CSi bonds are possible. This is an unfavorable situation compared to the three-dimensional structures possessing also only one strong CC but more CSi bonds and possibly additional multibonding effects not present in the linear structure.

IV. COMPARISON OF STRUCTURE AND STABILITY OF CARBON-RICH AND SILICON-RICH CLUSTERS

In comparing the relative energies of the various isomers in the sequence C_6 , Si_2C_4 , Si_3C_3 , Si_4C_2 , and Si_6 various trends are apparent. First of all, the linear and planar arrangements of nuclei which form the most stable C_6 isomers, become energetically much less favorable if carbon atoms in C_6 are subsequently replaced by silicon atoms. This trend is easily seen in Fig. 6 for the linear and hexagonal structures: In C_6 , the linear structures and the regular hexagon (D_{6h}) are almost isoenergetic³⁹ and lie only a few kcal/mol above the absolute minimum (predicted to be a C_6 ring of D_{3h} symmetry³⁹). They become progressively less stable if carbons are replaced by silicons (the linear Si_2C_4 is not entirely in line but this behavior can also be explained on the basis of the electronic structure). In Si_4C_2 , for example, the optimal planar structure decomposes into two Si_2C fragments; the linear arrangement of nuclei represents a local minimum but lies more than 100 kcal/mol above the ground state energy. For Si_6 , neither planar nor linear structures are known. This tendency can be understood from the fact that carbon atoms are more likely to form multiple bonds than silicon atoms and that multiple bonds are favorable for linear and planar geometrical arrangements.

All linear isomers of low energy are in a $^3\Sigma^-$ triplet state resulting from the π^2 electronic configuration. Si_2C_4 still has a line of four carbons with the silicons placed symmetrically at the terminal position. The linear isomer of Si_3C_3 is asymmetric (Fig. 1) in the sense that one of the silicons is relatively loosely attached to the symmetric SiCCCSi frame. Finally, in Si_4C_2 the optimal linear arrangement possesses fewer CSi bonds than the three-dimensional structures and therefore it corresponds to a relatively high-lying local minimum on the potential hypersurface. Linear Si_6 chains are not known; linear Si_4 has been calculated to lie 79 kcal/mol above the lowest-energy Si_4 structure.⁸

Among the ring structures C_6 is able to form a hexagon (D_{6h} or D_{3h} symmetry);¹² in Si_2C_4 there is the possibility to use the four carbons to form a rectangular ring (with the silicons bridging the longer bonds) as seen in Fig. 2, even though there is the tendency to nonplanar distortion as discussed earlier (Fig. 4). Going from Si_2C_4 to Si_3C_3 the hexagonlike "ring structure" is even less stable relative to the Si_3C_3 ground state because only a CCC triangle is possible as stabilizing factor (Fig. 2) and the six SiC linkages (with an extremely small CSiC angle of 46°) cannot compensate for strong CC bonds; this structure is only a stationary point on the surface but no local minimum. Finally, in Si_4C_2 the SiSi bonds are not strong enough to support a hexagonal ring structure and, similarly, a Si_6 ring structure is not expected among low-energy isomers. From an earlier calculation⁸ the five-membered Si_5 ring is around 90 kcal/mol above the Si_5 ground state.

The second major trend in comparing the various silicon-carbon clusters is also seen in Fig. 6, namely bipyramidal structures become less stable relative to the ground state in going from Si_6 to the carbon-rich compounds. The lowest Si_6 structure⁸ (Si_6 -like structure in Fig. 4) can be

TABLE IX. Relative stabilities (in kcal/mol) and total energies (in a.u.) for the isomers VI and XII using various methods.

Isomer	SCF ^a	MP2 ^a	MP3 ^a	MP4 ^a	CASPT ^b
VI	-1231.234 89 0.0	-1231.847 65 0.0	-1231.846 86 0.0	-1231.915 53 0.0	-1232.044 79 0.0
XII	+20.0	+3.7	+13.7	+8.2	+0.6

^aPerformed with 6-31G* AO basis set.

^bPerformed with the ANO basis set {Si:(17*s*,12*p*,5*d*)→[6*s*,5*p*,2*d*]; C:(14*s*,9*p*,4*d*)→[5*s*,4*p*,2*d*]} as proposed by Widmark *et al.* (Ref. 38). The CASPT2 calculations were performed on top of a CAS calculation including twelve electrons in the active space. The nondiagonal zero-order Hamiltonian (Refs. 28 and 29) was used in all calculations. All valence electrons (24) were correlated.

viewed as an edge-capped trigonal bipyramid (the face-capped trigonal bipyramid is only about 1 kcal/mol higher⁸) or, alternatively, as a distorted octahedron. Since this is a three-dimensional entity its analog in the mixed clusters is somewhat more difficult to trace; in particular, if the clusters have low symmetry. In Si₄C₂, structure XII (Fig. 3) is most likely related to the Si₆ ground state. The observation that in Si₄C₂ clusters the trigonal structure is less apparent follows, of course, from the absence of a structural element forcing a definite triangle with strong bonding. The analogy of the Si₆ ground state to structure XI of Si₃C₃ (Fig. 2) is convincing, structure XI has also the main features of the trigonal bipyramid and an extra face-capped Si. Finally, in Si₂C₄ the trigonal bipyramid is also visible in structure X (Fig. 3). The evolution of the lowest-energy three-dimensional (3D) structures between Si₆ and C₆ is indicated in Fig. 4 and needs no further discussion.

Finally, the third major information extracted from Fig. 6, is the fact that in carbon-rich species (including C₆ itself), there are a number of low-energy local minima, while on the silicon-rich side of the figure, there is essentially only a single optimal structure while all other isomers are either very high in energy (>100 kcal/mol) or only stationary points (Si₆ and Si₄C₂ octahedron).

V. SUMMARY AND CONCLUSION

The calculations for the carbon-rich Si₂C₄ and silicon-rich Si₄C₂ clusters find a linear arrangement of nuclei for the absolute minimum in the Si₂C₄ hypersurface while for Si₄C₂, a Si₄ tetrahedron capped by a CC bridge is obtained as ground state. Comparison of the geometry and stability of

low-lying Si₂C₄ and Si₄C₂ clusters with their Si₃C₃, C₆, and Si₆ analogs fully supports the rules which seem to be important in the building-up principle of carbon-silicon clusters, e.g., strong CC bonds are favored over SiC bonds, and SiSi bindings are of smaller importance for the geometrical arrangement of the mixed clusters.

The underlying reason for these rules is the basic competition between the relative strengths of σ and π bonds already apparent in diatomic C₂ and Si₂: in the first the π bond is relatively strong and therefore leads to the $\sigma_g^0\pi_u^4$ occupation for the ${}^1\Sigma_g^+$ ground state of C₂, in Si₂ it is the σ bond which is favoured relative to π and, therefore, the $\sigma_g^2\pi_u^2$ configuration is preferred, resulting in the ${}^3\Sigma_g^-$ ground state. In the ${}^3\Pi_u$ states with the $\sigma_g^1\pi_u^3$ occupation there is a competition between the two types of bonds and this state is indeed very close to the ground state in both isovalent systems.⁴⁰ This tendency is fully carried over to the larger systems: In C₆ the linear and planar structures are preferred, favored by multiple bonding, while in Si₆ the three-dimensional structures with silicon in the higher coordination number are favored over planar and linear arrangements. The carbon-rich mixed silicon-carbon clusters can be derived from their C₆ analog, the silicon-rich clusters show the 3D tendency known for Si₆.

The aforementioned "rules" seem to be the major element in the building-up principle and they explain, to a large extent, the geometries and relative energetics found for the various Si₂C₄, Si₃C₃ and Si₄C₂ structures. Multicenter effects involving carbon and silicon are also of importance and tend to stabilize the structures, in particular if carbon bonds are bridged by a silicon atom. The possibility to form not only

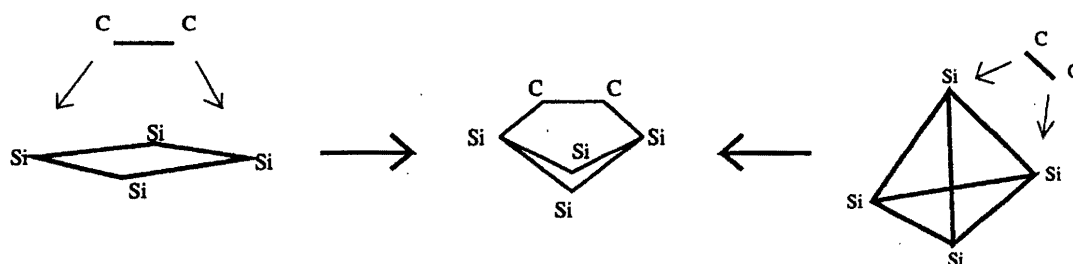


FIG. 5. Schematic illustration of the two possibilities to bridge a Si₄ cluster with a C₂ fragment to obtain the Si₄C₂ ground state.

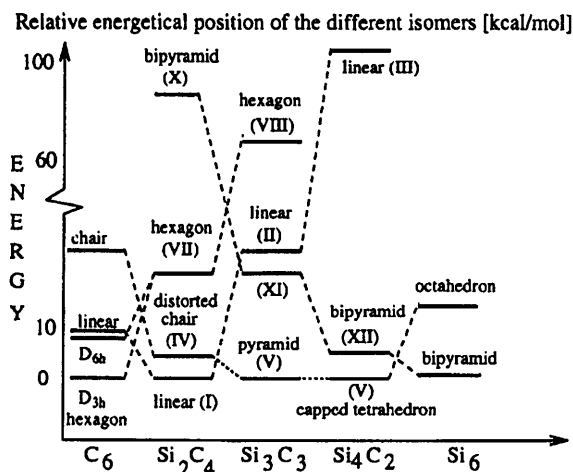


FIG. 6. Schematic representation of the relative stabilities of the six atomic Si_nC_m species considering them as a bridge between the corresponding elemental Si₆ and C₆ clusters. The relative energy is given with respect to the linear structure of C₆, structure IV of Si₂C₄, structure V of Si₃C₃, structure VI of Si₄C₂, and the bipyramidlike ground state of Si₆. The number of the structures contained in Figs. 1–3 are also given.

single but also multiple bonds favor several local minima for carbon-rich clusters while the more simple bonding pattern of silicon-rich three-dimensional compounds leads essentially to a single energy minimum, while higher-lying structures are more likely to constitute transition states.

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