Ab initio investigation of the stability of Si₃C₃ clusters and their structural and bonding features

Max Mühlhäuser[1], Georgios Froudakis[2], Aristides Zdetsis[2], Bernd Engels[1], Nikos Flytzanis[3], Sigrid D. Peyerimhoff[1]

[1] Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany
[2] Department of Physics, University of Patras, GR-26110 Patra, Greece
[3] Department of Physics, University of Iraklion, GR-71409 Iraklio, Crete, Greece

Abstract. Various structural possibilities for Si_3C_3 clusters are investigated by ab initio calculations employing basis sets of double- and triple-zeta quality augmented by d polarization functions. Correlation effects are included by a second-order Moeller Plesset perturbation treatment. For the two lowest-lying structures higher-order correlation corrections and multi-reference effects are also included. Bonding features are investigated by two different types of population analyses to obtain insight into the nature of chemical bonding. A total of 17 stationary points were investigated, 14 of which correspond to local minima and three being transition states. The energetically lowest-lying structures are: A "pyramid-like" structure with various multicenter bonds, followed by a C_s symmetric isomer closely related to the ground state Si_6 structure. Planar structures, favoured in small carbon clusters, lie higher in energy and are transition states. The lowest-lying triplet system is found to be the linear nonsymmetric $Si-C-C-C-Si-Si$ structure, which is calculated to lie about 38 kcal/mole above the singlet ground state. A building-up principle based on bonding criteria is suggested for the occurence of the various structural possibilities.

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1. Introduction

The study of clusters which constitute a link between molecules and the solid state has become an extremely active field of research in recent years. Among the elemental clusters carbon clusters are presently of greatest interest because of their significance in astrophysics, combustion processes and the design of new materials [1–8]. The review of Weltner and van Zee [8] summarizes the situation up to April 1989. Since then the growth of the carbon cluster literature is tremendous.

The isovalent silicon clusters have received less attention, but the structure, stability and reactivity of a con-siderable number of Si_n^+ compounds, in particular for $n \leq 60$, has been determined experimentally [9]. Several recent publications are focusing on the study of small elemental silicon clusters using ab initio methods [10–13].

Although the elemental silicon and carbon clusters have been studied quite extensively, both by experimental and theoretical methods, relatively little information seems to be available on the "mixed" silicon carbon clusters. The study of silicon-carbon clusters is very important not only because their properties could provide new insight into the physical and chemical behavior of the parent materials, but also on its own right. The three- and four-atom species Si_2C, SiC_2, Si_3C, SiC_3 and Si_2C_2 have been investigated both experimental [14] and theoretically [15–18], but less is known for the other species.

It is goal of the present work to study in detail the Si_3C_3 system which can be thought of as a link between Si_6 and C_6. Total energies, relative stabilities and bonding features of various competing structures will be discussed in order to get further insight in the relationship between structure and stability. As will be illustrated, the equilibrium geometry of the Si_3C_3 is "pyramid-like" and stabilized by the formation of multicenter bonds.

2. Technical details

The Hartree-Fock (HF) method was used as a starting point for determining the various stationary points on the Si_3C_3 hypersurface. Various initial structures were chosen and a complete geometry optimization within the given symmetry was then carried out until the structure corresponding to a stationary point was found. In order to check whether these points correspond to real local minima, the optimization procedure was continued without any symmetry constraints (C_1 symmetry). In addition the Hessian matrix was always checked for imaginary eigenvalues.

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For the optimization of the geometry of the various Si_3C_3 arrangements the AO basis set was of double-zeta quality augmented by d polarization functions with exponents $d(Si) = 0.4$, $d(C) = 0.8$; it will be referred to as DZP set [19]. From previous experience it is known that such bases in combination with HF treatments yield very realistic bond distances and bond angles [20]. In order to check to what extent electron correlation affects the computed structural geometrical parameters, geometry optimization was also undertaken for the lowest-energy structure employing the Moeller-Plesset (MP2) perturbation treatment in an AO basis of triple-zeta quality including polarization functions (TZ2P basis, $d(Si) = 0.23, 0.69$; $d(C) = 0.46, 1.39$). The change in bond lengths (relative to the SCF gradient procedure in the DZP basis) was about 1% (2-3 pm) while the difference in bond angles was around 3-5 degrees. These small changes were not considered important enough to justify the use of the more extensive MP2 (TZ2P) treatment for the optimization of the higher-energy structures.

For the determination of the energy difference between various isomers the effect of electron correlation must be considered in the theoretical treatment. For this reason single-point calculation were carried out for the optimized structures at the MP2 level of treatment using the DZP and a more flexible basis of triple-zeta plus polarization quality (TZP). Comparison of the DZP and TZP results give an indication of the AO basis set convergence. As mentioned above, in some cases a TZ2P basis [21,22] was also used. In cases in which the energy differences were needed with high accuracy single-point CASSCF calculations followed by second-order perturbation theory (CASPT2) were also undertaken in order to account for multi-reference effects; in these calculations a correlation-consistent basis suggested by Dunning and coworkers [23,24] was employed. The bulk of the computations was carried out with the TURBOMOLE program package [21,22]; the higher-order effects were determined with the MOLCAS program package [25,26].

Bonding features are investigated using the standard Mulliken population analysis [27]; in addition the method proposed by Roby-Davidson-Heinzmann-Ahlrichs (RDHA) [28-31] is also employed. In the latter the unassigned charge is minimized by the use of modified atomic orbitals MAOs leading to a better description of multicenter bonding effects. The s, p, and d orbital occupation numbers obtained from the Mulliken analysis also seem to be a reliable measure in the analysis of bonding properties.

3. Discussion of the results

A total of 17 structures has been examined; their equilibrium geometries are given in Figures 1 to 5. The starting points for the geometry optimization were pyramidal, linear, cyclic (planar and non-planar) and octaedral arrangements of the nuclei.

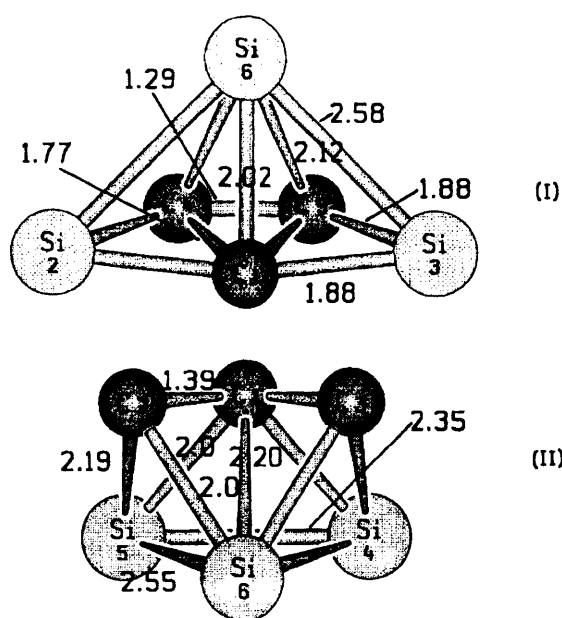Among the "pyramidal" structures we started with the four possible arrangements of the atoms: with silicon in

Fig. 1. Equilibrium geometries of the "pyramid-like" structures of Si_3C_3. Distances are in Å. Geometrical parameters which can be deduced easily from the C_s symmetry of the structures are not marked
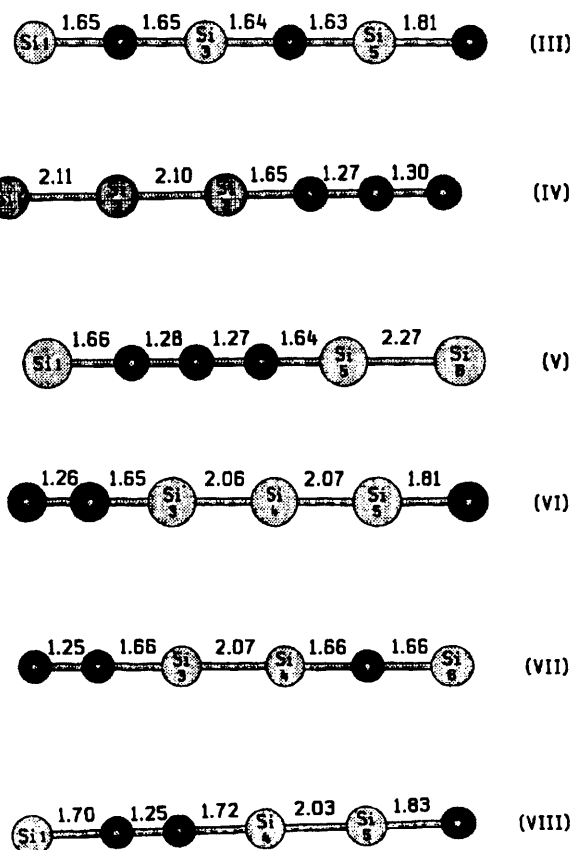

Fig. 2. Equilibrium geometries of the triplet linear structures. Distances are in Å
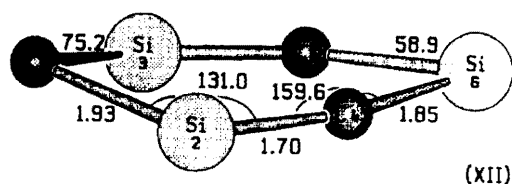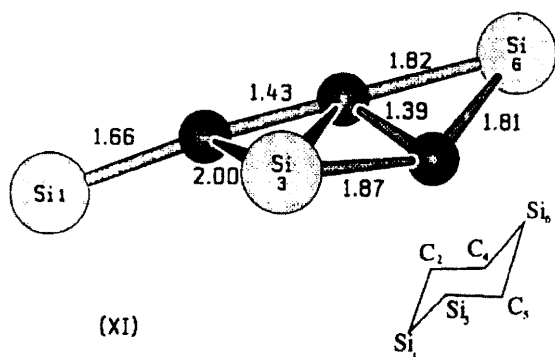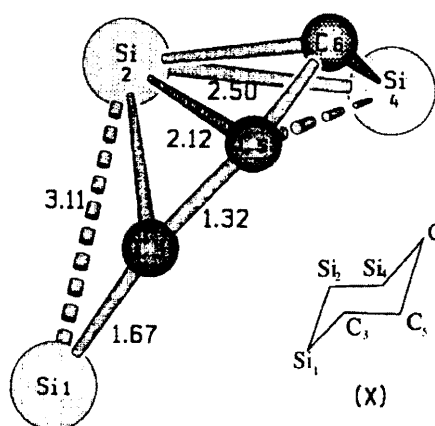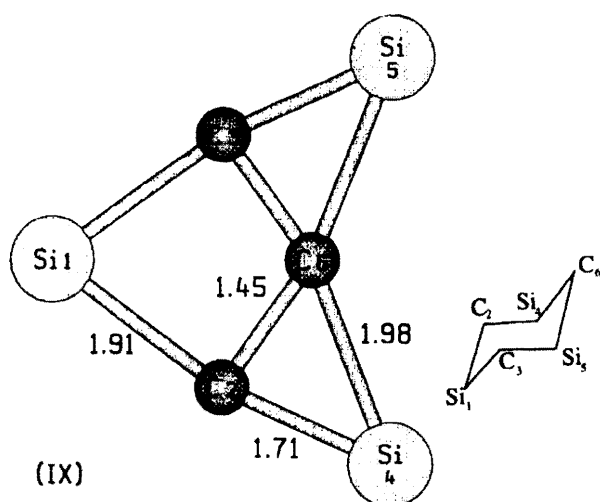
(IX)

(X)

(XI)

(XII)

Fig. 3. Equilibrium geometries of the "chair-like" structures IX to XI. Distances are in Å. The corresponding starting geometries are indicated. For these structures the equilibrium geometries are given in cartesian coordinates in Table 1. Structure XII is derived from the "boat" form

the apical position the arrangement of atoms in the 5-membered basal ring can be CCCSiSi or CCSiCSi; two analogous arrangements are possible with carbon in the apical position. However, optimization of different starting geometries (varying the CC distances) with carbon in the apical position leads to the same structures as obtained with apical silicon, so that only two "pyramidal" structures are minima on the hypersurface. They are displayed in Fig. 1.

Our second category involves linear nuclear chains in analogy to carbon clusters, which, as known from the literature [5-7], possess low-lying linear isomers. Several conformations (i.e. different arrangements of carbon and silicon nuclei) were considered; the optimum geometries obtained are displayed in Fig. 2. The linear structures in their singlet electronic configurations are found to be at least 100 kcal/mole above the corresponding triplet states, therefore only triplet species are presented in the figure. The triplet configuration $19\sigma^2 6\pi^2$ was found to be by far the lowest electronic state for all linear conformers.

Figure 3 shows three structures (IX, X, XI) which are derived from the "chair-like" geometries as indicated. The equilibrium geometries of these unsymmetric structures are given in cartesian coordinates in Table 1. A "boat" form (XII) was also investigated.

Structure XIII (C_s symmetry) is derived from the lowest Si_6 structure [13]. In Si_6 it represents an edge-capped trigonal bipyramid. All possible octahedral starting arrangements lead to the same distorted octahedron displayed as structure XIV in Fig. 4.

Among planar six-membered ring structures three arrangements are possible: (a) The three silicon atoms build the upper part and the three carbons the lower part of the ring. Optimization leads to structure XVI in Fig. 5. (b) The silicon and carbon atoms are arranged alternating in the ring. Optimization leads to structures XV and XVII. In each of these structures the carbons build a CCC triangle; in the first the silicon is in a bridge-bonded position, in the second it is in an edged position relative to the carbon triangle. (c) The third possibility would be a
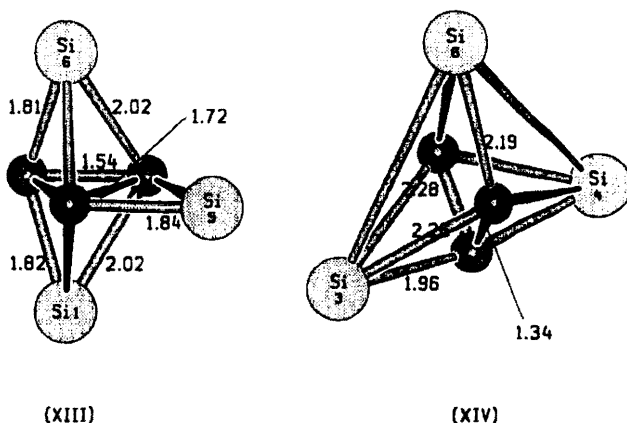

(XIII)

(XIV)

Fig. 4. Equilibrium geometries of the structures XIII (C_s) and XIV (C_s). Structure XIV is obtained from octahedral arrangements, whereas structure XIII is derived from a face-capped trigonal bipyramid. Distances are in Å
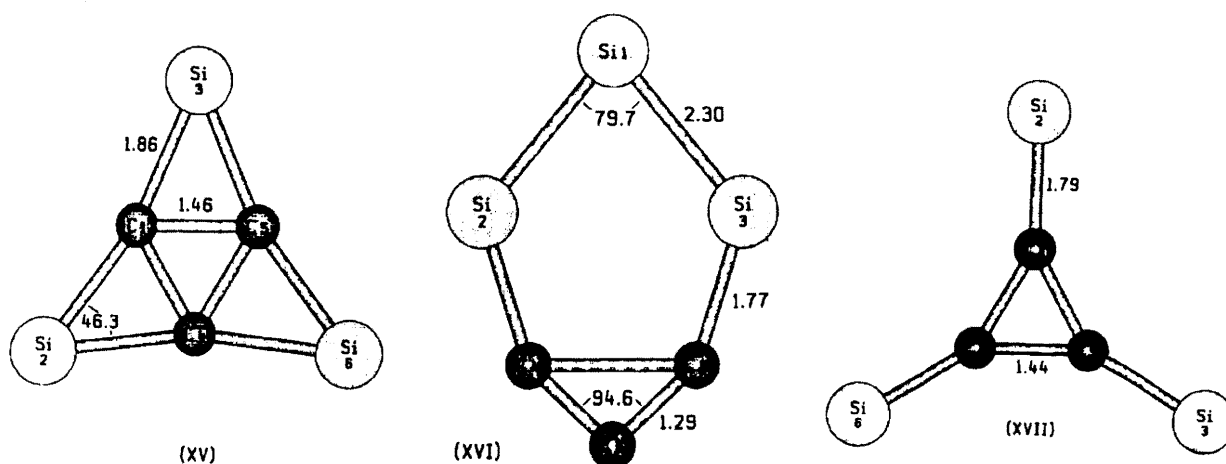
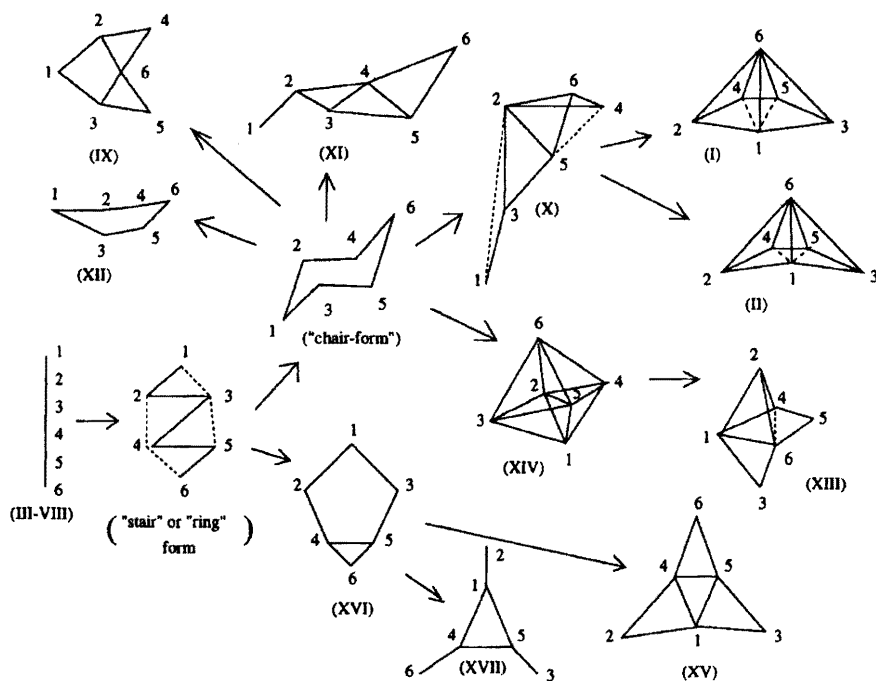**Fig. 5.** Optimal geometries of the planar structures. Distances are in Å. Angles are given in degrees

Fig. 6. Schematic representation of the generic relation between the various structural possibilities as discussed in the text. The *numbers* indicate either C or Si atoms as shown in Figs. 1 to 5. The *roman number in parentheses* refers to the particular silicon and carbon arrangement discussed earlier

Si-Si-C-C-Si-C six-membered planar ring; starting from such a structure the Si-Si bond breaks during geometrical optimization. It was therefore not possible to obtain even a planar transition state in spite of numerous attempts with different electronic configurations. One has to conclude therefore that such a system is fairly unstable. For all planar structures the vibrational analysis shows that one frequency is always imaginary; in other words all structures displayed in Fig. 5 represent transition states on the hypersurface.

The relationship of the various structures is best seen from Fig. 6. A folding of the linear arrangement of nuclei (III-VIII) leads to "stair" or "ring" forms. The stairlike structures do not represent a minimum on the hypersurface. The two-dimensional ring structures (XV-XVII) are

only stationary points on the surface; the actual structure depends on the arrangements of the silicon and carbon atoms. The "chair form" is the basic arrangement from which all three-dimensional structures can be deduced. Straight-forward ("down-hill") optimiztion starting from the different silicon-carbon ordering in the chair form (Fig. 4) leads to structures IX-XII. If atom number 6 in the chair-like form is moved to lie above the plane (2354) and atom 1 is moved correspondingly to lie below this plane, the octahedron-like form XIV is generated. Distortion leads to the lower-energy form XIII. The lowest-energy structure I and structure II (in which carbon and silicon atoms are exchanged relative to I) can be related to the chair-like structure via structure X.

All important quantitative structural data, i.e. bond

Table 1. Cartesian coordinates for the unsymmetric structures derived from "chair-like" starting geometries. The values are given in a.u. The numbering is according to Fig. 3

Structure	Atom	x	y	z
IX	Si(4)	−2.171546	+0.013228	−3.166271
	Si(5)	−2.171546	+0.013228	+3.166271
	Si(1)	+3.940604	+0.022557	0.000000
	C(2)	+0.846738	−0.049947	−2.241874
	C(5)	+0.846738	−0.049947	+2.241874
	C(6)	−0.752329	−0.014717	0.000000
X	Si(2)	−1.086956	−2.207721	+0.556007
	Si(1)	+4.203357	−0.879889	−1.644038
	Si(4)	−3.797057	+0.723148	−1.997200
	C(6)	−2.391057	+1.606174	+1.048195
	C(3)	+2.208982	+0.642827	+0.286416
	C(5)	+0.014931	+1.636478	+0.976506
XI	Si(3)	−1.672800	−2.055332	+0.810489
	Si(6)	+4.493127	+0.361850	+1.086825
	Si(1)	−4.012635	+2.739407	−1.516386
	C(5)	+1.792627	−1.585294	+0.283518
	C(4)	+1.181651	+0.983381	+0.381797
	C(2)	−1.385001	+1.567281	−0.235867

lengths and bond angles obtained in the optimization, are listed in Figs. 1 to 5 and in Table 1. Before details will be discussed, however, we will focus on the relative stabilities of the various isomers in order to obtain information on their actual importance.

3.1. Relative stability of the various conformers

The calculated relaive energies of the various conformers obtained in the geometry optimization as minima (or

saddle points in case of the planar structures) on the Si_3C_3 potential energy surface are summarized in Table 2. The data include results on the SCF/DZP and SCF/TZP level. Furthermore the MP2/TZP results are also listed for ten energetically low-lying structures. As expected, only few of the structures are energetically important while all others are higher in energy (> 50 kcal/mole). The extension of the AO basis set from DZP to TZP quality does not change the qualitative picture, i.e. the relative energies between the various conformers remain essentially the same. On the other hand, consideration of electron correlation (MP2) plays a significant role and changes the energetical ordering of the various structures. In particular structures I, II, XIII, XV and XVI become lower in energy relative to structure XI, which is the absolute minimum on the SCF/DZP level of treatment.

The TZP/MP2 results indicate that structure I is the absolute minimum of all Si_3C_3 conformers treated. It lies about 9 kcal/mole below structure XIII. All other structures are found to be higher in energy (about 30 kcal/mole above the absolute minimum) and are therefore less important from an energetical point of view.

Because consideration of electron correlation strongly influences the relative ordering of the various minima, in addition more sophisticated methods (MP3, MP4, CASPT2) are employed for the low-energy isomers I and XIII. This approach seemed to be necessary since the MP2 treatment lowered the energy of structure XIII more than that for structure I. For other isomers a more extensive correlation treatment is less important because either they are much higher in energy than structures I and XIII or MP2 calculations showed already that correlation effects are smaller than in structure I. Calcula-

Table 2. Relative stabilities ΔE (in kcal/mole) of the different Si_3C_3 isomeres obtained from different treatments. The symmetry and configuration of the different species is also given

No.[a]	Sy[b]	Conf.[b]	SCF/DZP	SCF/TZP	MP2/TZP[e]
I	C_s	$19a'^2 11a''^2$	+ 1.4	− 1.7	−27.7
II	C_s	$19a'^2 11a''^2$	+ 75.5	+ 72.1	+28.8
III	C_v	$19\sigma^2 6\pi^2$	+113.6	+ 91.6	−
IV	C_v	$19\sigma^2 6\pi^2$	+105.4	+ 97.2	−
V	C_v	$19\sigma^2 6\pi^2$	+ 12.9	+ 10.6	−
VI	C_v	$19\sigma^2 6\pi^2$	+164.9	+160.4	−
VII	C_v	$19\sigma^2 6\pi^2$	+ 82.7	+ 77.8	−
VIII	C_v	$19\sigma^2 6\pi^2$	+134.1	+130.8	−
IX	C_s	$18a'^2 12a''^2$	+ 12.9	+ 8.0	+ 9.9
X	C_1	$30a^2$	+ 20.6	+ 17.6	+ 8.2
XI	C_1	$30a^2$	0.0[c]	0.0[d]	0.0[f]
XII	C_s	$19a'^2 11a''^2$	+145.5	+142.7	−
XIII	C_s	$23a'^2 7a''^2$	+ 17.8	+ 15.0	−18.7
XIV	C_{2v}	$14a_1^2 2a_2^2 6b_1^2 8b_2^2$	+ 58.1	+ 50.5	−
XV	D_{3h}	$7a_1^2 8e'^4 2e''^4$	+ 81.7	+ 82.3	+36.8
XVI	C_{2v}	$15a_1^2 2a_2^2 9b_1^2$	+ 86.6	+ 84.0	+58.3
XVII	D_{3h}	$7a_1^2 2a_2^2 8e'^4 2e''^4$	+ 34.6	+ 36.2	+39.8

[a] The numbering of the different structures is according to Figs. 1–5
[b] Symmetry and configuration of the different species
[c] Absolute SCF energy in the DZP basis is −980.10095 hartree
[d] Absolute SCF energy in the TZP basis is −980.20350 hartree
[e] Values obtained with a second order Moeller Plesset perturbation treatment. The valence electrons are included in the perturbation treatment, whereas the core orbitals are kept doubly occupied
[f] Absolute MP2 energy in the TZP basis is −980.83784 hartree

Table 3. Relative stabilities and total energies for the isomers I, XIII, and V using various methods. The energies of structure XIII and V are given with respect to isomer I

Isomer	SCF[a]	MP2[a]	MP3[a]	MP4[a]	CASPT2[b]
I	−980.1273	−980.7745	−980.7704	−980.8390	−980.8397
XIII	16.5	9.8	14.7	11.8	4.3
V	13.0	−	−	−	38.0

[a] Performed with 6-31 G* AO basis set
[b] Performed with correlation consistent AO basis set (ccpvtz) as proposed by Dunning and coworkers [23, 24]

tions on the CASPT2 level were also performed for the lowest triplet state (structure V) in order to check whether multi-reference effects push the triplets below the singlet structures. All values are summarized in Table 3. Table 3 shows that the use of higher-sophisticated methods does not change the energetic ordering of isomers I and XIII. The actual energy difference depends on the treatment employed, however. The results indicate that both structures are relatively close in energy. The finding that correlation effects increase the energy difference between the singlet (structure I) and triplet (structure V) is in accordance with prior experience on carbon C_6 clusters [4, 7].

3.2. Equilibrium structures and bonding properties

The lowest Si_3C_3 structure (I) can be viewed either as a pyramid with Si(6) on top of the distorted five-membered ring C(1)Si(3)C(5)C(4)Si(2) or alternatively as being derived from a slightly distorted Si(6)C(1)C(4)C(5) tetrahedron which is edge-capped by the two silicon atoms Si(2) and Si(3). Both, Si(2) and Si(3) are located below the C(1)C(4)C(5) plane. The bond lengths Si(6)C(4) and Si(6)C(5) are equal (2.21 Å) while the third Si(6)C(1) bond is somewhat shorter (2.02 Å); in an earlier paper [32] this shortening has been traced to a higher charge in the Si(6)C(1) bonding region. The bonds connecting Si(6) to the silicons Si(2) and Si(3) are 2.58 Å; this value is perfectly in line with the bond lengths (2.3–2.5 Å) predicted by Raghavachari [10] for several elemental silicon clusters. The basal carbon ring of the tetrahedron shows a very short C(4)C(5) bond of 1.29 Å and two longer bonds of 1.77 Å. The short bond matches the CC equilibrium separation of 1.28 Å in the linear Si-C-C-Si molecule [16]. The carbon-silicon bonds between Si(2) or Si(3) and the carbon triangle are 1.88 Å, which is a standard value for such bonds [16].

The second low-lying structure XIII has been obtained as the result of optimizing a structure derived from the Si_6 ground state isomer [10]. Comparison with structure I is best undertaken if the carbon triangle C(2)C(3)C(4) is taken as the central part. Within this triangle there are two bonds of 1.54 Å (similar to a standard carbon-carbon single bond) and one long C(3)C(4) bond of 1.72 Å. The latter is comparable to the long CC bonds of structure I, and as in structure I it is bridged by a silicon. The bonding distances of this silicon to the carbons C(3) and C(4) (1.84 Å) are similar to those found in the bridged silicon-carbon bonds in structure I. A bridging of the shorter CC bonds by silicon atoms lying within the carbon triangle plane is not favoured so that the two remaining

silicons Si(1) and Si(6) are located above and below the CCCSi plane forming a bipyramidal-like structure.

Structure II can be considered as if the carbon and silicons are exchanged relative to structure I. The tetrahedron consists of the carbon atom (C1) and the Si(4)Si(5)Si(6) basal triangle. In analogy to the carbon triangle in structure I the silicon triangle possesses one short and two longer bonds; but in contrast to structure I the long silicon-silicon bonds are not bridged by carbons lying in the basal triangle plane. Obviously it is energetically much more favorable to build carbon-carbon bonds, i.e. the bond distances C(1)C(2), C(1)C(3) of 1.39 Å point almost to a dobule bond. In spite of this rearrangement of the bonding situation occurring during the optimization procedure this structure is still much higher in energy (74 kcal/SCF and 57 kcal/MP2) than structure I. This analysis underscores the importance of carbon-carbon bonds in comparison to silicon-silicon or silicon-carbon bonding. This rule can also be seen to some extent in all the other structures investigated.

The equilibrium geometries of the linear arrangements in their triplet states are given in Fig. 2. Short CC bonds (1.26 Å – 1.30 Å) are dominant. The lengths of the SiC bonds vary between 1.63 Å and 1.83 Å; the longer SiC bond appears at the end of the chains. Considering that a typical SiC double bond is 1.71 Å [5], the strengths of the SiC bonds located inside the chains are between that of a standard double and triple bond. Schaefer et al. [33] obtained a value of 1.75 Å in the triplet state of linear Si_2C. The lengths of the SiSi bonds are found between 2.06 Å and 2.27 Å, whereby the longer of these appear again in the terminal position of the chains.

Comparison of the relative energetical positions of these linear isomers demonstrates that in addition to the strong CC bonds strong SiC bonds are also important. For example, structure V which possesses two strong CC bonds as well as two strong silicon-carbon bonds is much lower in energy than all other linear isomers. Considerably higher in energy is structure IV, which has also two CC bonds but only one SiC bond because the carbon centers lie at the end of the chain. Structure VII is favoured over structure IV even though it possesses only one CC bond; this shortcoming is overcompensated by the presence of three strong SiC bonds. The fact that structure VIII is found to be much higher in energy can be traced to the much weaker SiC bonds [Si(5)C(6) and Si(4)C(3)]. Altogether only structure V seems to be of real importance; it is found to lie 12 kcal above structure I (TZP/SCF); if electron correlation effects are considered (CASPT2) the energy difference to structure I increases (38 kcal/mole).

Figure 3 gives the optimized geometries when starting from a "chair-like" structure; the starting geometries are indicated. The equilibrium structures of IX, X and XI are very unsymmetric. The most stable structure derived from a "chair-like" geometry is structure XI. It is rather obvious, however, that this equilibrium geometry can no longer be viewed as a chair. The Si(1) atom is edge-linked and the Si(6) is bridge-bonded to a distorted Si(3)C(5)C(4)C(2) quadrangle. The SiC bond distances in this quadrangle indicate single bonds (1.87 Å). A value of 1.39 Å for the C(4)C(5) bond indicates a double bond; the C(2)C(4) distance of 1.43 Å is between typical single and double bond lengths. Obviously the edged Si(1)C(2) bond is much shorter than the two bridged SiC bonds.

Structure IX with alternating SiC bonds also results in a geometrical arrangement that is totally different from the starting geometry. During the optimization the Si(1) and C(6) atoms move towards the Si(4)Si(5)C(2)C(3) plane and form a cluster of planar equilibrium geometry. The movement of C(6) into the square is favoured because two strong CC bonds can be formed in this manner. Three different types of SiC bonds can be distinguished in this structure according to their bond lengths: Si(4)C(6) and Si(5)C(6) as well as Si(1)C(2) and Si(1)C(3) resemble single bonds while Si(4)C(2) and Si(5)C(3) are stronger.

Contrary to what was expected, structure X with a "chair-like" starting geometry in which three silicon atoms and three carbon atoms are linked together ends up in a totally different equilibrium geometry. During the optimization the C(6) atom moves towards the Si(2)Si(4)C(3)C(5) plane forming a strong C(5)C(6) bond in analogy to structure IX. However, this time the Si(1) atom moves more closely to the C(3) center. Therefore the Si(1)C(3) bond becomes very strong (1.67 Å). The starting and the optimized geometry for the "boat" form XII is very similar. Three different SiC bond lengths indicate a Si(2)C(4) double bond (1.70 Å), whereas the bond lengths of Si(6)C(4) (1.85 Å) and Si(2)C(1) (1.93 Å) indicate bond strengths between single and double bonds. The geometrical trends observed in the optimization of these structures originating from a chair-like arrangement of nuclei underline the importance of strong CC and CSi bonds in the formation of the silicon-carbon clusters.

Figure 4 shows the equilibrium geometry of the distorted octahedral system. All possible octahedral structures lead to the same equilibrium structure XIV. This octahedral system shows short CC bonds and is therefore distorted in such a way that C(2) and C(5) are located close to C(1) (1.34 Å). The values of the bond lengths point out that all SiC bonds are of single bond character, whereas the SiSi bonds are slightly stronger.

Figure 5 gives the equilibrium geometries of the planar (ring) structures considered in this work. The optimization was carried out under the constraint of a planar arrangement of nuclei. The analysis shows, however, that these structures are not local minima but only stationary points on the energy hypersurface. Structure XV is obtained when starting from a normal six-membered ring with alternating Si and C centers. During the optimization the carbon atoms move towards the center of the ring so that the optimized geometry shows a CCC triangle

with bridge-bonded silicon atoms. A second planar arrangement containing a CCC triangle is also possible (structure XVII) in which the silicons are linked at edged positions. In the six-membered ring (structure XVI) the bond lengths of the SiSi bonds are between normal single and double bonds, whereas the SiC bonds show double bond character. The C-C bonds are very strong indicating double to triple bond character. The starting geometry of a CCSiSiCSi ring did not lead to a Si_3C_3 molecular structure because the SiSi linkage opened up during the geometry optimization leading to two fragments.

3.3. Population analysis

In the previous section it was seen that the formation of strong CC bonds is very important in the building up principle of mixed carbon silicon clusters while SiSi bonds contribute much less to the cluster stability. In order to analyze the bonding properties somewhat further, in particular multicenter effects and charge transfer, a population analysis for all structures investigated is performed (Table 4). The values are obtained by employing population analyses according to Mulliken [27] and to Roby-Davidson-Heinzmann-Ahlrichs (RDHA) [28–31]. In the Mulliken analysis the s-, p-, and d-orbital occupation numbers are also given. They have to be compared to the values of the corresponding atomic ground states. In the RDHA analysis of the wavefunction the shared electron number SEN is the value of interest. It is a criterion for the strength of a chemical bond between two or more atoms. All the values displayed in Table 4 were obtained using the TZP basis set at the DZP equilibrium structure. In general the carbon centers are found to be negatively charged which is in agreement with the fact that silicon is less electronegative than carbon.

It is seen from Table 4 that the large stability of structure I results not only from the formation of a strong CC bond but also from multicenter effects. The SEN values indicate several multicenter bonds; in particular in the carbon triangle and in all triangles formed by silicon-bridged CC bonds. If multicenter-effects are taken into account, very little charge transfer between the silicons and carbons is noted, based on the values $q(A)$ for the atomic charges in the RDHA analysis. Looking at the charge density as expressed by the orbital occupation numbers in the Mulliken analysis one finds that the s and p occupation numbers of the carbons are increased while at silicon the electron density of p character is decreased. The small population numbers for the d orbitals show that one should not give too much emphasize on dp_π-bonding in such pyramidal-like structures.

The observation that the second low-energy structure XIII does not possess one strong CC bond but two CC bonds of intermediate strength (Fig. 4) as discussed before, is also supported by the two-center SEN values in Table 4. One of the most important results of Table 4 is that multicenter bonding effects play an important role not only in the description of structure I, but also in structure XIII, which is closely related to the ground state of Si_6. While the CCC three-center SEN of 0.39 is similar to that of structure I, the multi-center effects for the var-

Table 4. Calculated atomic (partial) charges $q(A)$ obtained according to the Mulliken and Roby-Davidson-Heinzmann-Ahlrichs method of population analysis for the silicon and Carbon atoms in the Si_3C_3 cluster structures. In the Mulliken analysis 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 occurence of either three-center- or four-center SEN values

No.[a]	Atom[a]	Mulliken				Roby-Davidson-Heinzmann-Ahlrichs				
		$q(A)$	s^m	p^n	$d^{r\,b}$	$q(A)$	$SEN_{two-center}$		$SEN_{multi-center}$	
I	Si(6)	+0.16	5.85	7.84	0.14	+0.12	C(4)C(5)	2.43	C(1)C(4)C(5)	0.45
	C(4)	−0.22	3.52	2.64	0.05	−0.07	C(1)C(5)	0.96	Si(6)C(4)C(5)	0.44
	Si(2)	+0.36	5.82	7.65	0.17	+0.08	Si(2)C(1)	1.66	C(1)C(4)Si(2)	0.39
	C(1)	−0.44	3.56	2.83	0.04	−0.15	C(4)Si(2)	1.47	Si(6)C(4)Si(2)	0.30
							Si(6)C(1)	1.20	C(1)Si(2)Si(6)	0.36
							Si(6)C(4)	0.96	C(1)Si(2)Si(3)	0.36
							Si(6)Si(2)	0.92		
II	Si(6)	+0.18	5.86	7.75	0.17	+0.21	C(1)C(2)	1.94	C(2)C(1)C(3)	0.27
	Si(5)	+0.21	5.85	7.80	0.14	+0.12	C(2)C(3)	0.45	Si(5)C(2)C(1)	0.42
	C(2)	−0.19	3.78	2.30	0.04	−0.22	Si(6)C(2)	1.28	Si(6)C(2)C(1)	0.38
	C(1)	−0.25	3.38	2.78	0.07	−0.01	Si(5)C(1)	1.20	Si(5)Si(4)C(1)	0.46
							Si(5)C(2)	0.89	Si(6)Si(5)C(2)	0.32
							Si(6)C(1)	0.74	Si(6)Si(5)C(1)	0.25
							Si(5)Si(4)	1.53	Si(6)Si(5)Si(4)	0.38
							Si(6)Si(5)	0.99		
III	Si(1)	+0.47	5.80	7.61	0.11	+0.28	Si(1)C(2)	2.69		
	C(2)	−0.93	3.32	3.59	0.01	−0.68	C(2)Si(3)	2.21		
	Si(3)	+1.01	5.02	7.71	0.24	+0.89	Si(3)C(4)	2.17		
	C(4)	−0.98	3.28	3.68	0.01	−0.85	C(4)Si(5)	2.42		
	Si(5)	+0.81	5.19	7.78	0.21	+0.82	Si(5)C(6)	1.52		
	C(6)	−0.39	3.84	2.53	0.02	−0.47				
IV	Si(1)	+0.32	5.85	7.76	0.07	+0.18	Si(1)Si(2)	2.40		
	Si(2)	−0.45	5.33	9.08	0.03	−0.40	Si(2)Si(3)	2.00		
	Si(3)	+0.65	5.21	7.96	0.15	+0.62	Si(3)C(4)	2.16		
	C(4)	−0.39	3.22	3.14	0.02	−0.39	C(4)C(5)	2.53		
	C(5)	−0.11	3.26	2.80	0.05	+0.24	C(5)C(6)	2.12		
	C(6)	−0.02	3.70	2.29	0.04	−0.24				
V	Si(1)	+0.41	5.85	7.62	0.11	+0.23	C(2)C(3)	2.35		
	C(2)	−0.62	3.34	3.25	0.02	−0.44	C(3)C(4)	2.32		
	C(3)	+0.35	3.27	2.31	0.06	+0.40	Si(1)C(2)	2.53		
	C(4)	−0.57	3.25	3.29	0.02	−0.50	C(4)Si(5)	2.29		
	Si(5)	+0.44	5.33	8.07	0.15	+0.47	Si(5)Si(6)	1.51		
	Si(6)	−0.01	5.90	8.05	0.04	−0.17				
VI	C(1)	+0.11	3.66	2.19	0.04	−0.06	C(1)C(2)	2.64		
	C(2)	−0.67	3.21	3.44	0.02	−0.43	C(2)Si(3)	2.01		
	Si(3)	+0.73	5.19	7.90	0.17	+0.73	Si(5)C(6)	1.61		
	Si(4)	−0.39	5.19	9.17	0.03	−0.55	Si(3)Si(4)	2.17		
	Si(5)	+0.54	5.39	7.91	0.14	+0.70	Si(4)Si(5)	2.02		
	C(6)	−0.31	3.86	2.44	0.02	−0.37				
VII	C(1)	+0.08	3.62	2.25	0.04	−0.12	C(1)C(2)	2.71		
	C(2)	−0.67	3.21	3.44	0.01	−0.46	C(5)C(6)	2.63		
	Si(3)	+0.45	5.12	8.25	0.18	+0.43	C(2)Si(3)	1.93		
	Si(4)	+0.52	5.08	8.20	0.19	+0.48	Si(4)C(5)	2.18		
	C(5)	−0.86	3.35	3.51	0.00	−0.62	Si(3)Si(4)	1.96		
	Si(6)	+0.48	5.81	7.58	0.11	+0.28				
VIII	Si(1)	+0.54	5.87	7.48	0.11	+0.38	C(2)C(3)	2.74		
	C(2)	−0.47	3.37	3.07	0.02	−0.27	Si(1)C(2)	2.26		
	C(3)	+0.05	3.35	2.55	0.03	+0.18	Si(5)C(6)	1.53		
	Si(4)	−0.17	5.14	8.95	0.08	−0.33	C(3)Si(4)	1.09		
	Si(5)	+0.42	5.32	8.10	0.14	+0.51	Si(4)Si(5)	2.38		
	C(6)	−0.38	3.85	2.51	0.01	−0.47				
IX	Si(1)	+0.55	5.70	7.50	0.16	+0.49	C(2)C(6)	1.80	Si(4)C(2)C(6)	0.55
	C(3)	−0.66	3.54	3.08	0.03	−0.44	Si(4)C(2)	2.22	Si(1)C(2)C(6)	0.13
	Si(5)	+0.44	5.81	7.60	0.15	+0.21	Si(1)C(2)	1.24		
	C(6)	−0.11	3.32	2.72	0.05	−0.04	Si(5)C(6)	1.15		

Table 4. (continued)

No.[a]	Atom[a]	Mulliken				Roby-Davidson-Heinzmann-Ahlrichs				
		$q(A)$	s^m	p^n	$d^{r\,[b]}$	$q(A)$	$SEN_{two\text{-}center}$		$SEN_{multi\text{-}center}$	
X	Si(2)	+0.96	5.92	7.86	0.12	+0.11	C(5)C(6)	2.72	Si(2)C(6)C(5)	0.47
	Si(1)	+0.43	5.83	7.62	0.12	+0.28	C(3)C(5)	2.33	Si(2)C(3)C(5)	0.32
	C(6)	−0.37	3.50	2.83	0.04	−0.17	Si(1)C(3)	2.51	Si(4)C(6)C(5)	0.30
	C(3)	−0.57	3.37	3.18	0.03	−0.26	Si(4)C(6)	1.42	Si(1)C(3)C(5)	0.28
	C(5)	+0.12	3.24	2.57	0.06	−0.33	Si(2)C(6)	0.92	Si(2)Si(1)C(3)	0.29
	Si(4)	+0.30	5.85	7.74	0.16	+0.38	Si(2)C(5)	0.85	Si(2)Si(4)C(6)	0.26
							Si(2)C(3)	0.79		
							Si(1)C(5)	0.35		
							Si(4)C(5)	0.28		
							Si(2)Si(4)	1.10		
							Si(1)Si(2)	0.41		
XI	Si(3)	+0.47	5.80	7.56	0.16	+0.57	C(5)C(4)	1.98	Si(3)C(5)C(4)	0.14
	Si(6)	+0.43	5.79	7.62	0.16	+0.18	C(4)C(2)	1.65	Si(3)C(4)C(2)	0.15
	Si(1)	+0.38	5.84	7.66	0.18	+0.18	Si(1)C(2)	2.56	Si(6)C(5)C(4)	0.51
	C(5)	−0.52	3.53	2.59	0.04	−0.41	Si(6)C(5)	1.78	Si(3)Si(1)C(2)	0.22
	C(4)	−0.04	3.36	2.62	0.06	−0.02	Si(6)C(4)	1.62		
	C(2)	−0.72	3.43	3.26	0.02	−0.51	Si(3)C(5)	1.28		
							Si(3)C(2)	1.09		
							Si(3)C(4)	0.28		
							Si(3)Si(1)	0.22		
XII	Si(6)	+0.49	5.33	7.98	0.20	+0.44	C(4)C(5)	1.02		
	C(5)	−0.57	3.46	3.09	0.02	−0.34	C(5)Si(3)	2.09		
	Si(3)	+0.54	5.76	7.54	0.16	+0.25	Si(6)C(5)	1.68		
	C(1)	−0.38	3.80	2.56	0.02	−0.45	Si(3)C(1)	1.43		
							Si(3)C(4)	0.24		
							Si(3)Si(2)	0.83		
XIII	C(3)	−0.51	3.60	2.86	0.05	−0.27	C(2)C(3)	1.44	C(2)C(3)C(4)	0.39
	C(2)	−0.28	3.56	2.66	0.06	−0.09	C(3)C(4)	1.05	C(3)C(4)Si(5)	0.51
	Si(6)	+0.38	5.81	7.62	0.18	+0.16	C(3)Si(5)	1.67	C(2)C(3)Si(1)	0.41
	Si(5)	+0.54	5.78	7.50	0.17	+0.31	C(2)Si(1)	1.63	C(2)C(3)Si(6)	0.40
							C(2)Si(6)	1.63	C(3)C(4)Si(6)	0.23
							C(3)Si(1)	1.14	C(3)C(4)Si(1)	0.23
							C(3)Si(6)	1.14	C(3)Si(5)Si(6)	0.26
							Si(5)Si(6)	0.44	C(2)C(3)C(4)Si(1)	0.22
									C(2)C(3)C(4)Si(1)	0.22
									C(3)C(4)Si(1)Si(5)	0.17
									C(3)C(4)Si(5)Si(6)	0.17
XIV	Si(6)	+0.39	5.86	7.60	0.15	+0.27	C(1)C(5)	2.41	Si(6)C(1)C(5)	0.43
	C(1)	−0.27	3.36	2.83	0.08	−0.67	Si(6)C(1)	1.13	Si(4)Si(6)C(1)	0.31
	Si(4)	+0.12	5.73	7.99	0.15	+0.26	Si(4)C(5)	0.97	Si(4)Si(6)C(5)	0.27
	C(5)	−0.32	3.77	2.50	0.05	−0.04	C(1)Si(4)	0.85	Si(6)Si(2)C(5)C(1)	0.20
							Si(6)C(5)	0.85		
							Si(4)Si(6)	1.41		
XV	Si(2)	+0.32	5.86	7.68	0.14	+0.39	C(1)C(4)	1.56	C(1)C(4)C(5)	0.60
	C(1)	−0.32	3.48	2.78	0.06	−0.39	Si(2)C(1)	1.09	Si(2)C(1)C(4)	0.43
XVI	C(6)	+0.14	3.28	2.53	0.06	+0.01	C(5)C(6)	2.40	C(4)C(5)C(6)	0.46
	C(5)	−0.27	3.39	2.84	0.03	−0.02	C(4)C(5)	0.54	Si(1)Si(2)Si(3)	0.49
	Si(3)	+0.16	5.56	8.15	0.12	+0.04	C(5)Si(3)	1.75		
	Si(1)	+0.08	5.85	7.98	0.09	−0.05	Si(1)Si(3)	1.58		
							Si(2)Si(3)	0.70		
XVII	C(1)	−0.29	3.36	2.89	0.04	−0.23	C(1)C(4)	1.65	C(1)C(4)C(5)	0.48
	Si(2)	+0.29	5.89	7.72	0.09	+0.23	C(1)Si(2)	1.97		

[a] The numbering of the structures and atomic centers is according to Figs. 1–5

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

ious CCSi combinations are larger than those found in structure I. The charge transfer from the silicons to the carbons seems to be enhanced relative to the lowest-energy structure.

The SEN values show that in structure II two strong CC bonds exist even though the starting geometry possessed three SiSi bonds. The different geometrical arrangement of the carbon centers leads to a smaller CCC SEN of 0.27, which is only half of the the value found for structure I (SEN = 0.45). This finding is in line with the smaller stability of this compound.

In the linear structures III to VIII a considerable charge transfer between the various centers is apparent from the results in Table 4; alternating charges are preferred. In the most stable triplet structure V the carbon C(3) becomes positive ($q = 0.4$), whereas the C(2) and C(4) atomic centers show negative partial charge. This is indicated also by p orbital occupation numbers of 3.25 and 3.29, respectively. The SEN values indicate strong double bonds except for the edged Si(5)Si(6) bond, which is somewhat weaker. The various bonding features discussed in the previous section on the basis of bond lengths are supported numerically by the various data of the population analysis.

For the three-dimensional Si_3C_3 structures (IX, X, XI) resulting from chair-like starting geometries the multicenter bonding effects are of similar importance as in the pyramidal-like structures I, II and XIII. In contrast to the latter no CCC bond is formed, however. The charge transfer between the various silicons and carbons is generally larger. Similar as in structures I, II and XIII the d population is small. Because the bonding situation is very similar it is not surprising that structures IX–XI are quite close in energy.

Considering the planar structures XV, XVI and XVII large CCC multicenter bonding effects are found as expected from the geometrical arrangement. Three center SEN (CCC) values of 0.60 (structure XV) and 0.48 (structure XVII) emphasize the stability of the CCC triangles in these isomers. The charge transfer found in structure XV and XVII is considerable while it is negligible for structure XVI. It is surprising that on the SCF level structure XV is higher in energy (47 kcal/mole) than structure XVII although a reversed ordering would be expected from the bonding features. The reason may lie in the very small CSiC angle found in structure XV. If correlation effects are included both structures are similar in energy.

of these two structures persists if more sophisticated correlation energy treatments (MP4, CASPT2) are employed; the difference between the two structures is reduced from approximately 10 kcal/mole (MP2) to about 4 kcal/mole (CASPT2). For all structures except the linear arrangements singlet states are energetically preferred over the triplet states.

Most structures, especially all linear and planar isomers are much higher in energy than the ground state. While the linear isomers repesent still local minima, all planar nuclear arrangements change into three dimensional structures if the geometry optimization is performed without any symmetry constraints (C_1 symmetry), e.g. they are only saddle points of the hypersurface.

This situation is in contrast to the findings for the isovalent C_6 whose lowest-lying isomers are the triplet cumulene and a distorted planar benzene ring. The comparison shows that there is a definite tendency in Si_3C_3 towards 3-dimensional structures.

The relation between the various structures, i.e. the manner in which one can be generated from the others are summarized in Fig. 6.

From the optimized structures obtained in this work and the analysis of the respective bonding properties and charge distributions the following rules for the stability of mixed silicon-carbon clusters can be extracted:

(1) CC bonds are energetically favoured over SiC bonds; Si-Si binding is less important.

(2) Multi-center bonding effects play a significant role in Si_3C_3 clusters.

(3) Generally all carbon centers are negative, all silicon centers positive in accordance with the difference in electronegativity. In linear structures alternating charges ($\delta^+, \delta^-, \delta^+, \delta^-$ ...) are preferred.

Electron correlation effects are of different magnitude for the various structures; its consideration seems to be particularly important for strained structures.

4. Summary and conclusion

In the present work various nuclear arrangements of the mixed silicon-carbon cluster Si_3C_3 were studied. In total 17 stationary points were located, 14 of which represent local minima on the hypersurface while 3 are identified to be saddle points.

If correlation effects are taken into account via the MP2 method a pyramid-like structure (structure I in Fig. 1) is found to be the ground state. Isomer XIII (Fig. 4) which was derived from the Si_6 ground state lies only somewhat higher in energy. The energetic ordering

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