Theoretical Study of SiC_3^+

Pilar Redondo, Ana Sagüillo, and Antonio Largo*

Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Received: July 24, 1997; In Final Form: January 5, 1998

A theoretical study of the SiC_3^+ isomers has been carried out, characterizing six different structures. Predictions for their geometries and vibrational frequencies have been made at both the MP2/6-31G* and B3LYP/cc-pVTZ levels. The nature of bonding in these isomers has been characterized by using Bader's topological analysis of the electronic charge density. According to our calculations, which range up to the CCSD(T)/cc-pVTZ level, the lowest-lying species is a rhombic structure, with the linear isomer and another rhomboidal isomer lying about 9.1 and 12.2 kcal/mol, respectively, higher in energy. Therefore, although SiC_3^+ is predicted to have a cyclic ground state, the linear isomer, and perhaps a second cyclic state, could be accessible to experimental detection. Both cyclic species are shown to be four-membered rings with only peripheral bonding, since there are no transannular Si−C or C−C bonds.

1. Introduction

Silicon−carbon binary compounds have been the subject of a growing interest in recent years. Much of this interest has been due to the detection of silicon carbide molecules in the interstellar medium and in the atmospheres of carbon stars. To date SiC,[1] SiC_2,[2] and SiC_4[3] have been observed in space. In addition binary silicon carbides are used in microelectronics.[4] Therefore, to the interest in small binary silicon−carbon clusters themselves, it must be added their importance as building blocks for more complex structures with technological applications. Furthermore, they could serve for the production of new compounds such as binary fullerenes.

Much effort has been devoted to the elucidation of the structure of small silicon−carbon clusters. Both theoretical and experimental studies have shown that the ground state of SiC_2 is cyclic,[5,6] whereas in the case of Si_2C it is strongly bent.[7,8] These results are in contrast with the well-known linear structure of C_3.[9−11]

In the series of tetraatomic carbon−silicon clusters there is also competition between cyclic and linear structures. The carbon cluster C_4 is difficult to isolate, and the interpretation of experimental data is somewhat ambiguous. Photoelectron spectra,[12] IR experiments,[13] and some ESR spectra[14,15] support a linear arrangement, whereas other ESR investigations[16] are indicative of a slightly bent form, and Coulomb explosion experiments[17] suggest a cyclic structure. From the theoretical side there is also a controversy about the ground state of C_4. Many ab initio calculations[18−20] point to a rhombic structure, with two tricoordinate carbons, as the lowest-lying C_4 isomer, although a recent coupled-cluster calculation[21] indicates that the rhomboidal and linear isomers are nearly isoenergetic. Furthermore, a multireference configuration interation study[22] finds the ground state to be linear.

On the other hand Si_4 and Si_3C are known to prefer strongly rhombic forms.[23,24] The rest of tetraatomic carbon−silicon clusters exhibit an intermediate behavior. In the case of Si_2C_2 a rhombic ground state is also found,[25−27] but the linear isomer lies quite close in energy (about 11 kcal/mol in most theoretical calculations). For SiC_3 a theoretical calculation[28] predicts the rhomboidal structure (with a transannular carbon−carbon bond) to lie about 4.1 kcal/mol lower in energy than the linear isomer (a second rhomboidal structure with a carbon−silicon transannular bond lies also 4.3 kcal/mol higher in energy than the ground state).

The structure of small silicon−carbon cluster ions is also of interest. Much of the interstellar chemistry is ionic, and therefore binary silicon−carbon cations may be present in space and could be precursors of the neutral species. Furthermore, laser vaporization of silicon−graphite mixtures produces SiC_n^+ ions in the laboratory, whose structure can be studied using injected ion drift tube techniques.[29] The reaction of SiC_n^+ ions with molecules such as O_2 has also been studied by using a radio-frequency ion trap.[30] As a result of this study, Negishi et al.[30] concluded that cyclic and linear structures coexist for SiC_3^+ and SiC_5^+. This result is in contrast with the conclusions of Parent[31] from another study of chemical reactivity of SiC_n^+ ions; they claimed that small SiC_n^+ cluster ions should have linear structures. Moreover, it is difficult to make predictions of the structure of SiC_n^+ ions based on the preferred arrangements of the neutral clusters. Despite the fact that C_3 clearly prefers a linear form, in the case of C_3^+ theoretical calculations[32−36] predict a bent ground state, a result that is supported by Coulomb explosion experiments.[37] Theoretical studies[38,39] suggest a cyclic ground state for SiC_2^+, although the linear isomer should lie very close in energy. Therefore in the case of SiC_2^+, contrary to C_3^+, the cyclic ground state of SiC_2 is retained for the cation.

In the case of SiC_3^+ we are only aware of a theoretical study by Pascoli and Comeau,[40] in which some of the possible geometrical arrangements of SiC_n^+ ($n = 1−5$) were considered. In their study geometry optimizations and predictions of vibrational frequencies were carried out at the Hartree−Fock level, whereas electronic energies were computed using second-order Møller−Plesset theory. They concluded that linear structures are energetically favored, except for $n = 2$ (in agreement with previous calculations[38,39]) and $n = 3$. Only two structures were found to be true minima on the HF potential surface for SiC_3^+, namely, the linear SiCCC isomer and a

---

* Author to whom correspondence should be addressed.

S1089-5639(97)02426-2 CCC: $15.00

rhombic structure. The latter is predicted to be the ground state, with the linear isomer lying about 32 kcal/mol higher in energy at the MP2 level. However, the relatively low level of theory employed in these calculations, as well as the possible spin contamination of the HF wave function for some of these structures, poses some doubts about the reliability of the study.

In this work the results of a theoretical study on $\mathrm{SiC_3^+}$ will be presented. We shall focus not only on the energies, geometries, and vibrational frequencies of the various conformations of $\mathrm{SiC_3^+}$ but also on the nature of bonding in these cluster ions. Although the main conclusion of our work coincides with that of Pascoli and Comeau[40] in that the ground state is the rhombic structure, there are new features that we think are important in the chemistry of $\mathrm{SiC_3^+}$.

2. Computational Methods

The geometries of the different $\mathrm{SiC_3^+}$ isomers have been obtained at several levels of theory. We will present only the results at the second-order Møller−Plesset (MP2) level with the 6-31G* basis set[41] including all electrons in the calculation, which is denoted MP2(full)/6-31G*, and those obtained using density functional theory (DFT). For the DFT calculations we selected the B3LYP exchange−correlation functional[42] and different basis sets. Only the results of the DFT calculations employing the cc-pVTZ (correlation-consistent polarized valence triple-zeta) basis set developed by Dunning[43,44] will be reported.

Harmonic vibrational frequencies have been computed on each optimized structure at its corresponding level of theory. This enables us to assess the nature of the stationary points, to verify that they correspond to true minima on the potential surface, and also to estimate the zero-point vibrational energy (ZPVE) correction.

On the MP2(full)/6-31G* geometries single-point calculations at the fourth-order Møller−Plesset (MP4) level[45,46] with the 6-311G* basis set[47] for carbon and the McLean and Chandler basis set[48] (supplemented with a set of d functions) for silicon were used. In these calculations we employed the frozen-core approximation (inner-shell orbitals were not included for computing electron correlation energies). For the three lowest-lying structures we carried out higher level calculations. On the MP2(full)/6-31G* and B3LYP geometries we used the QCISD(T) method,[49] which stands for a quadratic CI calculation with singles and doubles substitutions, followed by a perturbative treatment of triple sustitutions. In these QCISD(T) calculations the 6-311G* basis set was employed. In addition, we also carried out CCSD(T)[50] calculations (coupled-cluster single and double excitation model augmented with a noniterative triple excitation correction) on the B3LYP/cc-pVTZ geometries, employing the cc-pVTZ basis set. To assess the reliability of single-reference-based methods, configuration interaction calculations (CISD/6-31G*) were carried out for the more stable isomers. In all cases the leading configuration clearly dominates the expansion, and the coefficient for the second configuration lies in the range 0.039−0.061, strongly suggesting that these species can be treated by single-reference-based methods. Nevertheless we have also carried out limited CASSCF calculations (five electrons in six orbitals) with the 6-31G* basis set for the lower-lying isomers (structures **1**, **3**, and **4**; see below). The CASSCF optimized geometries were found to be quite similar to the HF ones. The HF (for all isomers) and CASSCF (for the more stable ones) geometries will not be reported for the sake of space, although they are available upon request. All calculations were carried out with the Gaussian-94 program package.[51]

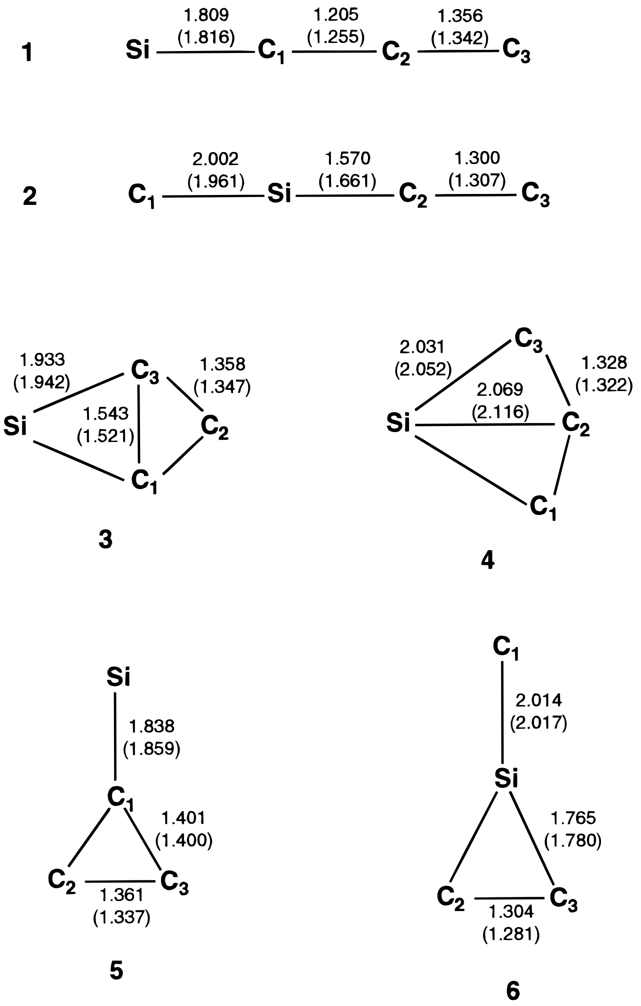


Figure 1. MP2/6-31G* and B3LYP/cc-pVTZ (in parentheses) optimized geometries for the different $\mathrm{SiC_3^+}$ isomers. Distances are given in angstroms and angles in degrees.

The nature of bonding for the different $\mathrm{SiC_3^+}$ species was characterized by using Bader's topological analysis.[52] Extrema or critical points in the one-electron density $\rho(r)$ were identified, through its gradient vector field $\nabla\rho(r)$, and classified according to rank and curvature. A (3,−1) critical point has a minimum value of $\rho(r)$ along the line linking nuclei and a maximum along the interatomic surfaces and represents a "bond critical point" (three nonzero eigenvalues, λ_i, of the Hessian of $\rho(r)$, two of them being negative and the other one positive). "Ring critical points" correspond to (3,+1) points ($\rho(r)$ is a minimum in two directions and a maximum in one direction). In addition, the Laplacian of $\rho(r)$ provides information where the electronic charge is concentrated ($\nabla^2\rho(r) < 0$) or depleted ($\nabla^2\rho(r) > 0$). The ellipticity is defined as $\epsilon = \lambda_1/(\lambda_2 - 1)$, where λ_1 and λ_2 are the two negative curvatures of a bond critical point, λ_2 being the softest mode. The total energy density, $H(r)$, is the sum of the potential and kinetic energy density at a critical point and characterizes a bond as covalent ($H(r) < 0$) or ionic ($H(r) > 0$).[53]

These calculations were performed with the AIMPAC series of programs,[54] using the MP2/6-311G* wave fuctions.

3. Results and Discussion

We have searched for different isomers on the $\mathrm{SiC_3^+}$ potential surface. Their optimized geometries at the MP2(full)/6-31G* and B3LYP/cc-pVTZ levels are shown in Figure 1. It is worth

TABLE 1: MP2/6-31G* and B3LYP/cc-pVTZ (in Parentheses) Vibrational Frequencies, in cm^{-1}, for the Different SiC_3^+ Isomers. Dipole Moments (in Debyes) Have Been Computed at the HF/6-311G* Level Taking the Center of Mass as the Origin

	1	2	3	4	5	6
$\nu_1(a_1,\sigma)$	2265 (2056)	2213 (1813)	1643 (1621)	1326 (1258)	1699 (1581)	1655 (1706)
$\nu_2(a_1,\sigma)$	1141 (1203)	1127 (751)	847 (848)	721 (590)	1232 (1293)	964 (895)
$\nu_3(a_1,\sigma)$	597 (553)	637 (489)	574 (570)	555 (507)	563 (512)	499 (476)
$\nu_4(b_2,\pi)$	412 (282)	161 (35)	1383 (1289)	1714 (1627)	2804 (823i)	600 (467)
	428 (360)	220 (44)				
$\nu_5(b_1,\pi)$	155 (112)	14 (129i)	384 (290)	278 (141)	235 (213)	131 (115)
	168 (132)	803 (95)				
$\nu_6(b_2)$			493 (415)	427 (308)	108 (43)	145 (135)
μ	5.251	4.288	1.573	1.993	5.741	3.348

mentioning that we have carried out geometry optimizations for all isomers at the B3LYP level with different basis sets (namely, 6-31G*, 6-311G*, and cc-pVTZ), but we did not find many changes in the geometrical parameters. In addition we also made optimizations for selected structures at the MP2/6-311G* level, but the results were nearly coincident with those obtained with the smaller 6-31G* basis set. For the sake of space we will present results only for the lowest-lying electronic state for each isomer, although explorations were also made for other states.

The numbering of isomers in Figure 1 parallels the notation employed by Alberts et al.[28] in their study of neutral SiC_3. In Table 1 we also report the dipole moments and vibrational frequencies, at the MP2(full)/6-31G* and B3LYP/cc-pVTZ levels, for the different SiC_3^+ isomers. The corresponding IR intensities are not shown but are available upon request.

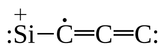
In general there are not severe discrepancies between the MP2 and B3LYP geometrical parameters, except in the case of the linear isomers **1** and **2**. For isomer **1** the C_1-C_2 bond distance is lengthened 0.05 Å when passing from MP2 to B3LYP, whereas for **2** even a larger difference is observed for the $Si-C_2$ bond distance at both levels of theory (about 0.09 Å), and the $Si-C_1$ bond length is 0.04 Å shorter at the B3LYP level. The discrepancies can be mainly attributed to the high spin contamination of the HF reference wave function for the linear isomers employed in the MP2 calculations, a problem that is not so important in the DFT calculations. The S^2 expectation values are as follows (B3LYP values in parentheses): **1**, 1.020(0.763); **2**, 1.030(0.796); **3**, 0.775(0.756); **4**, 0.890(0.771); **5**, 0.775(0.756); **6**, 0.757(0.753). For this reason in the case of linear isomers the B3LYP geometries should be in principle more reliable.

Both linear isomers correspond to $^2\Pi$ electronic states with the following electronic configuration:

$$\{\text{core}\}\ 7\sigma^2\ 8\sigma^2\ 9\sigma^2\ 2\pi^4\ 10\sigma^2\ 11\sigma^2\ 3\pi^1 \tag{1}$$

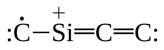
and the most contributing valence bond structures are, respectively,

1



$:\overset{+}{Si}-\dot{C}=C=C:$

2



$:\dot{C}-\overset{+}{Si}=C=C:$

The B3LYP geometrical parameters of **1** are close to the HF results of Pascoli and Comeau[40] ($d(Si-C_1) = 1.775$ Å; $d(C_1-C_2) = 1.266$ Å; $d(C_2-C_3) = 1.360$ Å), with the only exception of the Si−C bond distance, which is noticeably increased at the B3LYP level. These authors did not report results for isomer **2**. Nevertheless, comparing with the SCF results for the neutral analogue of **2** reported by Alberts et al.,[28] a weakening of the C_1-Si bond is observed, resulting in a lengthening of nearly 0.2 Å for this bond distance (our results at the HF level for structure **2** of SiC_3^+, which are not shown in Figure 1, give a C_1-Si bond distance of 2.025 Å, compared with the value of 1.807 Å for neutral SiC_3[28]).

As can be seen in Table 1, structure **1** is a true minimun in the SiC_3^+ potential surface at both levels of theory, since all its frequencies are real. The largest discrepancy in the vibrational frequencies is found for ν_1 (C−C stretching). However the most important difference between MP2 and B3LYP results concerns the IR intensities, since at the MP2 level ν_3 (Si−C stretching) is predicted to be the most intense line, whereas the B3LYP level predicts that the IR spectrum should be dominated by ν_2 (C−C stretching), with an intensity of 278.74 km/mol. It is also worth mentioning that the B3LYP/cc-pVTZ ν_1 frequency for this species differs considerably from the HF/6-31G* result[40] (1737 cm^{-1}). In the case of structure **2** even more severe discrepancies are observed in the vibrational analysis. At the MP2 level **2** is a true minimum, whereas this structure is shown to be in fact a transition state at the B3LYP level. The HF/6-31G* results (which are not given in Table 1) also suggest that **2** is a true minimum, since all frequencies are real at that level of theory. Nevertheless one of the π bending modes has a very small component (only 14 cm^{-1} at the MP2 level and 35 cm^{-1} at the HF level), indicating that distortion from linearity is not energetically expensive. In the case of the neutral analogue Alberts et al.[28] also found a very small value for the bending frequency (96 cm^{-1} at the SCF level). According to both MP2 and HF results the most intense line in the IR spectrum of **2** should be ν_1 (C−C stretching).

The lowest-lying electronic state of the cyclic isomer **3** is $^2A_1$, corresponding to the following electronic configuration:

$$\{\text{core}\}\ 6a_1^{\ 2}\ 7a_1^{\ 2}\ 3b_2^{\ 2}\ 8a_1^{\ 2}\ 2b_1^{\ 2}\ 4b_2^{\ 2}\ 9a_1^{\ 2}\ 10a_1^{\ 1} \tag{2}$$

The unpaired electron is essentially localized at the unique carbon atom. The geometrical parameters of structure **3** are much closer to those of the triplet state of its neutral counterpart than to the singlet ones.[28] In particular it is worth pointing out that the C_1-C_3 distance is much longer than for the neutral singlet state (1.469 at the CISD level), suggesting that possibly the transannular C_1-C_3 bond is lost in the cation. Pascoli and Comeau[40] have reported a HF geometry for this isomer that is close to our MP2 and B3LYP geometries.

For the other four-membered ring, structure **4**, we have also found very similar geometries at the MP2 and B3LYP levels. This isomer has a $^2B_2$ electronic state with an electronic configuration similar to (2) but with the unpaired electron occupying a $5b_2$ orbital instead of the $10a_1$ molecular orbital. However the geometrical parameters of **4** are very different from those of **3**. Structure **4** is best described as a Si^+ cation bonded to a quasi-linear C_3 unit (the C−C−C angle is 154.7° and 153.1°, respectively, at the MP2 and B3LYP levels). The main difference with the neutral counterpart of **4** is the longer Si−

C_2 distance found for the cation (1.880 Å at the CISD level for the neutral singlet state). In their HF study Pascoli and Comeau[40] did not considered this structure.

Both cyclic structures, **3** and **4**, are shown to be true minima at both MP2 and B3LYP levels, as can be seen in Table 1, where their vibrational frequencies are reported. For these two isomers there are no large discrepancies between the frequencies at both levels of theory, perhaps with the exception of ν_2 for structure **4**. Furthermore, both MP2 and B3LYP levels predict the same relative IR intensities for these isomers. In the case of **3** the IR spectra should be dominated by ν_3 (106.47 km/mol at the B3LYP level), followed by ν_2, ν_1, and ν_6 (63.36, 45.62, and 33.05 km/mol, respectively). On the other hand in the case of **4** the most intense lines should be ν_4 and ν_3 (84.36 and 51.34 km/mol, respectively). On the other hand there are noticeable discrepancies between the B3LYP frequencies and the HF ones[40] for structure **3**, particularly in the case of ν_1, ν_2, and ν_6.

Structures **5** and **6** are three-membered rings. Both correspond to $^2B_2$ electronic states, although in the case of **6** the $^2B_1$ state is nearly isoenergetic with the $^2B_2$ one. Stucture **5** can be viewed as the result of the interaction of a Si^+ cation with cyclic C_3 through an apex. Its geometrical parameters are quite close to those of the neutral triplet state.[28] As can be seen in Table 1, this isomer has all its frequencies real at the MP2 level, whereas it has an imaginary b_2 frequency (823i) at the B3LYP level and therefore should be considered a transition state at this level of theory. This b_2 mode corresponds to C_3 asymetric stretching, and it is also found to be unphysically large (2804 cm^{-1}) at the MP2 level, suggesting the possibility of symmetry breaking at this level of theory.

On the other hand, structure **6** with an exocyclic carbon atom is shown to be a true minimum on the potential surface at both the MP2 and B3LYP levels. This species has not been considered in the work of Pascoli and Comeau,[40] but our HF results also suggest that this structure is a true minimum at this level of theory. No signs of symmetry breaking are detected at any level of calculation. The main difference between its geometrical parameters and those of the neutral counterpart resides in the much longer C_1-Si bond distance (1.785 and 1.794 Å, respectively, for the singlet and triplet states of SiC_3[28]).

To gain more insight into the nature of bonding in SiC_3^+ species, we have carried out a topological analysis of the electronic charge density at the MP2/6-311G* level, whose results are shown in Table 2.

It is readily seen in Table 2 that all bond critical points have negative values for the total energy density, and therefore they have a certain degree of covalent bond character. However, most of the silicon−carbon bonds in SiC_3^+ isomers have positive values of $\nabla^2\rho(r)$, a sign of a closed-shell interaction, and therefore should be classified as intermediate interactions. The exceptions are the C_1-Si bonds in **2** and **6**, which are characterized by negative values of $\nabla^2\rho(r)$, truly characteristic of a shared interaction. Nevertheless, in both cases $\nabla^2\rho(r)$ is rather small in magnitude, and consequently they should also be classified as intermediate cases.

The highest value of $\rho(r)$ for carbon−carbon bonds is found for the C_1-C_2 bond critical point of **1**, whereas for silicon−carbon bonds the highest value of $\rho(r)$ is observed for the other linear isomer **2**. These values correspond to the shortest C−C and Si−C bonds, respectively.

The most interesting cases from the electronic density point of view are the cyclic species. Both **3** and **4** are shown to be four-membered rings. In particular, contrary to what has been observed by Sudhakar and Lammertsma for the neutral singlet counterpart[55] (with a C_1-C_3 bond distance of 1.513 Å), isomer **3** has no carbon−carbon transannular bond. Nevertheless, our study of the SiC_3 triplet state shows also a four-membered ring with no C_1-C_3 bending (the topological analysis for the singlet and triplet states of SiC_3 are not shown for the sake of space, but are available upon request). In the case of the isomer **4** Sudhakar and Lammertsma[55] found that silicon was bonded to the central carbon atom, but no bond critical points were found between silicon and C_1 and C_3 and therefore is best described as a T-shape structure. Our results for the cation (which are similar to those of triplet SiC_3) show only peripheral Si−C bonding, whereas no $Si-C_2$ bond is observed.

TABLE 2: Critical Point Data for SiC_3^+ Species

structure	type	R[a] (Å)	R[b] (Å)	$\rho(r)$ (au)	$\nabla^2\rho(r)$ (au)	ϵ	$H(r)$ (au)
1	$Si-C_1$ bond	1.809	1.809	0.1212	0.4039	0.3310	−0.1687
	C_1-C_2 bond	1.205	1.205	0.4119	−1.3379	0.1154	−0.2829
	C_2-C_3 bond	1.356	1.356	0.3410	−1.1738	0.1975	−0.1102
2	C_1-Si bond	2.002	2.002	0.1212	−0.0950	0.2858	−0.0716
	$Si-C_2$ bond	1.570	1.570	0.1692	0.8144	0.0343	−0.3087
	C_2-C_3 bond	1.300	1.300	0.3631	−1.1856	0.0908	−0.1638
3	$Si-C_1$ bond	1.933	1.939	0.0919	0.2415	1.1999	−0.1098
	C_1-C_2 bond	1.358	1.359	0.3140	−0.7113	0.4751	−0.1797
	$SiC_1C_2C_3$ ring			0.0885	0.2435		−0.1069
4	$Si-C_1$ bond	2.032	2.039	0.0833	0.0746	1.0168	−0.0695
	C_1-C_2 bond	1.328	1.330	0.3341	−0.9723	0.1841	−0.1674
	$SiC_1C_2C_3$ ring			0.0077	0.1422		−0.0763
5	$Si-C_1$ bond	1.838	1.838	0.1244	0.3062	0.0816	−0.1548
	C_1-C_2 bond	1.401	1.442	0.2752	−0.3017	1.8891	−0.2046
	C_2-C_3 bond	1.361	1.365	0.3359	−0.8816	0.3541	−0.1718
	$C_2C_3C_4$ ring			0.2666	0.0836		−0.2363
6	C_1-Si bond	2.013	2.013	0.1116	−0.0891	0.0860	−0.0626
	$Si-X$[c] bond	1.640		0.1271	0.5510	4.2773	−0.2077
	C_2-C_3 bond	1.303	1.304	0.3779	−1.1539	0.0650	−0.1996

[a] Bond length. [b] Bond path length. [c] X being the middle point between the two symmetric carbon atoms.

From the values of bond path lengths for isomers **3** and **4**, it can be seen that the Si−C bonds are only slightly curved. In the case of structure **5** the C_1-C_2 and C_1-C_3 bonds are somewhat more curved, as evidenced by their bond path lengths, and are the weakest of all carbon−carbon bonds according to their very small value of $\rho(r)$. In addition these carbon−carbon bonds show some characteristics of topological instability, since the ellipticity is somewhat high and the value of $\rho(r)$ is certainly close to that of the ring critical point.

The topological analysis of the electronic charge density for isomer **6** reveals quite a different structure. There is no individual $Si-C_2$ and $Si-C_3$ bonding, since only one bond critical point is found connecting silicon and the middle point of the C_2 unit. Therefore the molecular topology suggests a T-shape structure rather than a truly three-membered ring. Nevertheless it must be emphasized that this structure also exhibits characteristics of topological instability, since the ellipticity of the Si−X bond critical point is very high, which suggests a near-bifurcation catastrophe. This means that this bond is at the verge of splitting into two silicon−carbon bonds.

Sudhakar and Lammertsma[55] in their work on SiC_3 only studied the topology of isomers **3** and **4** in their singlet states. Our results for isomers **5** and **6** of the neutral species SiC_3 lead to conclusions very similar to those obtained for the cation. In both singlet and triplet states **5** is described as a three-membered ring, whereas **6** has a T-shape structure.

Finally we shall comment on the relative stability of SiC_3^+ species. Their relative energies at different levels of theory are shown in Table 3. At the MP2(full)/6-31G* geometries we have

TABLE 3: Relative Energies (kcal/mol) for the SiC_3^+ Isomers at Different Levels of Theory

	1	2	3	4	5	6
MP2/6-31G* Geometry[a]						
HF/6-311G*	−1.4	104.4	0.0	15.5	28.1	97.3
MP2/6-311G*	30.3	137.1	0.0	24.3	34.7	107.9
MP4/6-311G*	21.4	124.9	0.0	17.1	32.1	101.4
PMP4/6-311G*	16.1	121.4	0.0	13.8	32.1	102.0
QCISD(T)/6-311G*	11.5		0.0	14.0		
B3LYP/cc-pVTZ Geometry[b]						
B3LYP/cc-pVTZ	1.7	109.6	0.0	11.9	22.2	102.5
HF/cc-pVTZ	−1.4		0.0	14.0		
MP2/cc-pVTZ	33.8		0.0	22.2		
CCSD/cc-pVTZ	7.8		0.0	14.3		
CCSD(T)/cc-pVTZ	9.1		0.0	12.2		
QCISD(T)/6-311G*	7.0		0.0	13.3		
QCISD(T)/6-311+G*	6.4		0.0	13.2		

[a] Including ΔZPVE at the MP2/6-31G* level. [b] Including ΔZPVE at the B3LYP/cc-pVTZ.

carried out MP4 and QCISD(T) calculations with the 6-311G* basis set, whereas on the B3LYP geometries electronic energies were calculated at the CCSD(T) level with the cc-pVTZ basis set. In addition, QCISD(T) calculations with the 6-311G* basis set were also carried out on the B3LYP geometries.

In their previous study on SiC_3^+ Pascoli and Comeau[40] carried out MP2 single-point calculations at the HF/6-31G(d) geometries and found isomer **3** to be the ground state, with the linear isomer **1** and the three-membered ring **5** lying about 32.9 and 47.7 kcal/mol, respectively, higher in energy. They did not consider isomers **2**, **4**, and **6**.

According to our results given in Table 3, the linear structure **1** is shown to be the lowest-lying isomer at the HF level. However, inclusion of correlation effects favors the cyclic isomer **3**. At the MP2 level we obtain energy differences close to that found by Pascoli and Comeau[40] (about 30 kcal/mol) between isomers **1** and **3**. This energy difference is reduced to 21.4 kcal/mol at the MP4 level. However, we have previously pointed out that the HF wave function for **1** is highly spin-contaminated, and therefore the MP results could be questioned, given the poor convergence of the MP series for spin-contaminated wave functions. In fact at the projected MP4 (PMP4) level the energy difference is further reduced to 16.1 kcal/mol. The QCISD(T) level of theory, which should be affected to a lesser extent by spin contamination, predicts an energy difference of just 11.5 kcal/mol between structures **1** and **3**.

The same level of theory, QCISD(T)/6-311G*, but at B3LYP geometries (which should be more reliable for **1**) reduces the energy gap to only 7 kcal/mol. Perhaps the most reliable level of calculation used in this work is CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ, which predicts that isomer **1** should lie about **9** kcal/mol above **3**. This result differs only by 2 kcal/mol from that provided by the less expensive QCISD(T)/6-311G* level.

At the MP2, MP4, and PMP4 levels of theory the other four-membered-ring structure **4** is shown to lie even below the linear structure. However, higher levels of theory favor the latter, and at both the QCISD(T) and CCSD(T) levels isomer **1** lies below isomer **4**, although by only 6.3 and 3.1 kcal/mol, respectively.

The three-membered-ring isomer **5** is shown to lie 34.7 kcal/mol above **3** at the MP2/6-311G* level (47.7 kcal/mol in the study of Pascoli and Comeau[40]), an energy difference that is further reduced to 32.1 kcal/mol at the MP4 level of theory. The rest of the isomers, **2** and **6**, with silicon in central positions are high-lying isomers with energy differences from the ground state of 121.4 and 102.0 kcal/mol, respectively, at the PMP4 level of theory.

To check the effect of employing diffuse functions, we have also carried out QCISD(T) calculations with the 6-311+G* basis set for the more stable structures **1**, **3**, and **4**. As can be seen in Table 3, the relative energy of **1** is just 0.6 kcal/mol smaller than the value without diffuse functions, whereas in the case of **4** a nearly coincident relative energy is obtained. Therefore we may conclude that neglecting diffuse functions does not have an important effect for these species.

It is worth pointing out that the stability order of SiC_3^+ isomers parallels that found for the neutral parent molecule. In the case of SiC_3 Alberts et al.[28] found that **3** is the lowest-lying isomer, with the triplet linear isomer **1** lying 4.1 kcal/mol higher in energy, whereas for singlet **4** an energy difference of 4.3 kcal/mol is predicted. On the other hand, the phosphorus analogue has a rather different behavior. We have previously found that C_3P^+ has a linear ground state,[56] with the four-membered ring **3** lying 9.8 kcal/mol higher in energy at the PMP4 level. The other cyclic isomer, **4**, was shown to lie about 19.2 kcal/mol above the ground state. Therefore, as in the case of C_2X^+ species, silicon seems to prefer a cyclic arrangement rather than a linear one, contrary to what is obseved for other second-row atoms such as phosphorus.[57]

4. Conclusions

A theoretical study of the SiC_3^+ isomers has been carried out. Predictions for their geometries and vibrational frequencies have been made at both the MP2/6-31G* and B3LYP/cc-pVTZ levels. Since the latter method provides rather accurate results, and in any case should be expected to be more reliable than those computed at the HF/6-31G*,[40] it is hoped that these predictions could help in the possible experimental detection of these species. The major qualitative discrepancies between MP2 and B3LYP results is that at the MP2 level the six isomers studied in this work are shown to be true minima, whereas the B3LYP method characterizes two of them (a linear isomer, **2**, with an internal silicon atom and a three-membered-ring isomer, **5**, with an exocyclic silicon atom) as transition states. In the case of linear isomers **1** and **2**, which have a HF wave fuction with high spin contamination, the DFT predictions should be in principle more reliable.

The nature of bonding in these isomers has been characterized by using Bader's topological analysis of the electronic charge density. The main conclusion of this study concerns the cyclic species. **3** and **4** are shown to be four-membered rings with only peripheral bonding, since there are no transannular Si−C or C−C bonds. **5** is found to be a truly three-membered ring, although it shows signs of topological instability. On the other hand **6**, with an exocyclic carbon atom, is best described as a T-shape structure since there is no ring critical point for this species.

According to our calculations, which range up to the CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ level, the lowest-lying species is the rhombic structure **3**, with the linear isomer **1** and the other four-membered ring **4** lying about 9.1 and 12.2 kcal/mol, respectively, higher in energy. Therefore, although SiC_3^+ is predicted to have a cyclic ground state, the linear isomer, and perhaps a second cyclic state, could be accessible to experimental detection. In addition our calculations show that caution must be exercised when applying MP2 theory to compute relative energies in this type of systems since they could be overestimated, particularly when spin contamination is important. This is particularly evident when one compares our computed energy difference between the ground state, structure **3**, and the next lowest-lying isomer, structure **1**, with the same energy difference computed at the MP2/6-31G*//HF/6-31G* level[40] (30 kcal/mol). From our calculations it is also observed that QCISD(T) seems a reasonable, less expensive alternative to CCSD(T) for these systems, leading to very close energy differences.

Acknowledgment. This research has been supported by the Ministerio de Educación y Cultura of Spain (DGICYT, Grant PB94-1314-C03-02).

References and Notes

(1) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J. Lett.* **1989**, *341*, L25.

(2) Thaddeus, P.; Cummins, S. E.; Linke, R. A. *Astrophys. J. Lett.* **1984**, *283*, L25.

(3) Ohishi, M.; Kaifu, N.; Kawaguchi, K.; Murakami, A.; Saito, S.; Yamamoto, S.; Ishikawa, S.; Fujita, Y.; Shiratori, Y.; Irvine, W. M. *Astrophys. J. Lett.* **1989**, *345*, L83.

(4) Parsons, J. D.; Bunshah, R. F.; Stafsudd, O. M. *Solid State Technol.* **1985**, *28*, 133.

(5) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1984**, *80*, 3552.

(6) Michalopoulos, D. L.; Geusic, M. E.; Langridge-Smith, P. R. R.; Smalley, R. E. *J. Chem. Phys.* **1984**, *80*, 3556.

(7) Kafafi, Z. H.; Hauge, R. H.; Fredin, L.; Margrave, J. L. *J. Phys. Chem.* **1983**, *87*, 797.

(8) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *82*, 4126.

(9) Gausset, L.; Herzberg, G.; Lagerqvist, A.; Rosen, A. *Astrophys. J.* **1965**, *142*, 45.

(10) Liskow, D. H.; Bender, C. F.; Schaefer, H. F. *J. Chem. Phys.* **1973**, *56*, 5075.

(11) Whiteside, R. A.; Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P.v.R. *Chem. Phys. Lett.* **1981**, *80*, 547.

(12) Yang, S.; Taylor, K. J.; Craycroft, M. J.; Conceicao, J.; Pettiette, C. L.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1988**, *144*, 431.

(13) Shen, L. N.; Graham,W. R. M. *J. Chem. Phys.* **1989**, *91*, 5115.

(14) Graham, W. R. M.; Dismuke, K. I.; Weltner, W. *Astrophys. J.* **1976**, *204*, 301.

(15) Van Zee, R. J.; Ferrante, R. F.; Zeringue, K. J.; Weltner, W. *J. Chem. Phys.* **1987**, *88*, 3465.

(16) Cheung, H. M.; Graham, W. R. M. *J. Chem. Phys.* **1989**, *91*, 6664.

(17) Algranati, M.; Feldman, H.; Kella, D.; Malkin, E.; Miklazky, E.; Naaman, R.; Vager, Z.; Zajfman, J. *J. Chem. Phys.* **1989**, *90*, 4617.

(18) Whiteside, R. A.; Krishnan, R.; DeFrees, D. J.; Pople, J. A.; Schleyer, P.v.R. *Chem. Phys. Lett.* **1981**, *78*, 538.

(19) Michalska, D.; Chognacki, H.; Hess, B. A.; Schaad, L. J. *Chem. Phys. Lett.* **1987**, *141*, 376.

(20) Raghawachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191.

(21) Watts, J. D.; Gauss, J.; Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 8372.

(22) Parasuk, V.; Almlof, J. *J. Chem. Phys.* **1991**, *94*, 8172.

(23) Raghavachari, K. *J. Chem. Phys.* **1986**, *84*, 5672.

(24) Rittby, C. M. L. *J. Chem. Phys.* **1992**, *96*, 6768.

(25) Trucks, G. W.; Bartlett, R. J. *J. Mol. Struct. (THEOCHEM)* **1986**, *135*, 423.

(26) Lammertsma, K.; Guner, O. *J. Am. Chem. Soc.* **1988**, *110*, 5239.

(27) Presilla-Márquez, J. D.; Gay, S. C.; Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys.* **1995**, *102*, 6354.

(28) Alberts, I. L.; Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1990**, *93*, 5046.

(29) Fye, J. L.; Jarrold, M. F. *J. Phys. Chem.* **1997**, *101*, 1836.

(30) Negishi, Y.; Kimura, A.; Kobayashi, N.; Shiromaru, H.; Achiba, Y.; Watanabe, N. *J. Chem. Phys.* **1995**, *103*, 9963.

(31) Parent, D. C. *Int. J. Mass. Spectrom. Ion Processes* **1992**, *116*, 275.

(32) Grev, R. S.; Alberts, I. L.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 3379.

(33) Raghavachari, K. *Chem. Phys. Lett.* **1990**, *171*, 249.

(34) Martin, J. M. L.; François, J. P.; Gijbels, R. *J. Chem. Phys.* **1990**, *93*, 5037.

(35) Watts, J. D.; Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *94*, 4320.

(36) Taylor, P. R.; Martin, J. M. L.; François, J. P.; Gijbels, R. *J. Phys. Chem.* **1991**, *95*, 6530.

(37) Faibis, A.; Kanter, E. P.; Tack, L. M.; Bakke, E.; Zabransky, B. J. *J. Chem. Phys.* **1987**, *91*, 6445.

(38) Flores, J. R.; Largo-Cabrerizo, A.; Largo-Cabrerizo, J. *Chem. Phys. Lett.* **1987**, *140*, 26.

(39) Flores, J. R.; Largo, A. *Chem. Phys.* **1990**, *140*, 19.

(40) Pascoli, G.; Comeau, M. *Astrophys. Space Sci.* **1995**, *226*, 147.

(41) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(42) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(43) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(44) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(45) Pople, J. A.; Krishnan, R. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(46) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(47) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(48) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(49) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(50) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. J.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(52) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

(53) Cremer, D.; Kraka, E. *Croat. Chim. Acta* **1984**, *57*, 1259.

(54) Biegler-Koing, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1980**, *27*, 1924.

(55) Sudhakar, P. V.; Lammertsma, K. *J. Phys. Chem.* **1992**, *96*, 4830.

(56) Rio, E.; Barrientos, C.; Largo, A. *J. Phys. Chem.* **1996**, *100*, 585.

(57) Largo, A.; Barrientos, C.; López, X.; Ugalde, J. M. *J. Phys. Chem.* **1994**, *98*, 3985.