

The Most Stable Structure of SiC₃ Studied by Multireference Perturbation Theory with General Multiconfiguration Self-Consistent Field Reference Functions[†]

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The most stable structure of the SiC₃ molecule has been investigated using second-order perturbation theory with general multiconfiguration self-consistent field reference functions (GMC-PT) and Dunning's augmented correlation-consistent polarized valence quadruple- ζ (aug-cc-pVQZ) basis set. The results showed that a closed-shell rhomboidal C_{2v} isomer with a C–C transannular bond (2s) was most stable. Another closed-shell rhomboidal C_{2v} isomer with a Si–C transannular bond (3s) and a linear triplet Si–C–C–C isomer (1t) was less stable by 5.3 and 6.7 kcal/mol, respectively, at the geometries optimized by the coupled cluster singles, doubles, and perturbative triples (CCSD(T)) method and the correlation-consistent polarized core-valence quadruple- ζ (cc-pCVQZ) basis set, and by 9.0 and 9.9 kcal/mol, respectively, at the geometries optimized by the fully optimized reaction space self-consistent field (FORS-SCF) method and the 6-31G(d) basis set.

1. Introduction

Silicon-containing carbon clusters, Si_mC_n, have recently received much attention from various fields, such as astrophysics and nanoscience. In particular, SiC_n (*n* = 1–4) molecules have been well studied, both experimentally and theoretically.^{1–11} However, among the theoretical studies, the most stable structure of SiC₃ is still in dispute.^{5–12}

The initial study on the global minimum of this molecule with high-level ab initio molecular orbital methods was performed by Alberts, Grev, and Schaefer.⁵ They examined three- and four-membered ring and linear isomers and predicted that the closed-shell rhomboidal isomer 2s (see Figure 1) was the most stable isomer. According to their results, which were obtained by the configuration interaction single and double excitations plus the quadruples correction (CISD + Q) method and a triple- ζ plus double-polarization function (TZ2P) basis set, the 2s isomer was 4.1 and 4.3 kcal/mol more stable than the linear triplet isomer 1t and another closed-shell rhomboidal isomer, 3s, respectively.

After experimental and astronomical detection of SiC₃,⁶ Stanton, Gauss, and Christiansen⁷ determined the structures of 2s and 3s isomers with the coupled-cluster singles and doubles with perturbative triples correction (CCSD(T)) method and the correlation-consistent polarized core-valence quadruple- ζ (cc-pCVQZ) basis set. Their geometrical parameters were in agreement with those by experimental estimation within 0.003 Å. Also in their results, the 2s isomer was lower in energy: the energy separation was 6.0 kcal/mol at the CCSD(T) level.

These studies were both performed with single-reference-based methods. Rintelman and Gordon⁸ have studied the structures and energetics of the SiC₃ molecule, as well as Si₂C₂, with a multireference-based method and have drawn a different conclusion on the relative stability of the isomers. In their extensive investigation, possible isomers in singlet and triplet states were searched for by using the fully optimized reaction field self-consistent field (FORS-SCF)¹³ method, and the

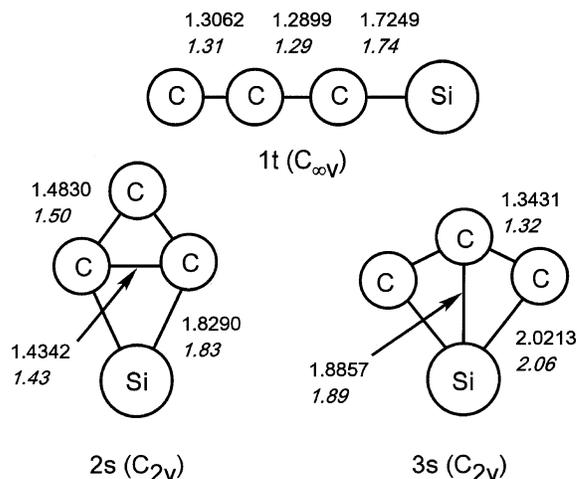


Figure 1. Three isomers of SiC₃: 1t, 2s, and 3s. The numbers in Roman and italic type represent the bond lengths in Å optimized by CCSD(T)/cc-pCVQZ (refs 7 and 10) and FORS-SCF/6-31G(d) (ref 8) methods, respectively. These two sets of geometries are used in the computations in the present article.

energetics were examined using the multiconfigurational quasi-degenerate perturbation theory (MC-QDPT) with the FORS-SCF wave functions as reference. In contrast to the previous study by Alberts et al.,⁵ their results showed that the 1t isomer was the global minimum and the 2s isomer was 4.4 kcal/mol higher than the 1t isomer at the MC-QDPT/aug-cc-pVDZ level. They also concluded from the natural orbital occupation number (NOON) analysis that a multireference wave function was important for the SiC₃ and Si₂C₂ systems.

Because of this inconsistency in the 1t and 2s relative stabilities between the single-reference (CISD + Q) and multireference (MC-QDPT) based methods, Sattelmeyer, Schaefer, and Stanton¹⁰ performed CCSD(T) with the cc-pCVQZ basis set for the 1t isomer. Again, they obtained results showing that the 2s isomer was most stable: the 2s isomer was more stable than 1t and 3s by 7.5 and 6.2 kcal/mol, respectively. This was consistent with the results by Alberts et al. except for the order

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of 1t and 3s with a slight energy difference. There is still inconsistency on the most stable isomer between the single- and multireference-based methods.

The aim of the present article is to resolve this problem by using an enhanced multireference perturbation method with more active orbitals and larger basis sets than those of Rintelman and Gordon. Recently, we have proposed a quasidegenerate perturbation theory using general multiconfiguration self-consistent field reference functions (GMC-PT or GMC-QDPT),¹⁴ which is a generalization of MC-QDPT¹⁵ from FORS reference functions to general multiconfiguration (MC) reference functions. GMC-PT allows us to avoid the problem of the large dimension of active spaces by excluding unphysical multiple excitations appearing in FORS. As a result, we can take more active electrons and orbitals into account than is possible using FORS. In the present study, we took all 16 valence electrons and 16 valence orbitals into the reference MC-SCF functions in GMC-PT and accurately determined the relative energies of the isomers. We also considered the basis set and geometry effects on the order of the isomers and analyzed the first-order perturbed wave functions to confirm the reliability of the results.

2. Computational Methods

The energies of 1t, 2s, and 3s were computed using second-order GMC-PT. The geometries, basis sets, and MC-SCF active spaces used are given below.

Two sets of geometries of 1t, 2s, and 3s isomers were used (see Figure 1). One set was taken from refs 7 and 10 and was determined by CCSD(T) with the cc-pCVQZ basis set. The other set was taken from ref 8 and was determined by FORS-SCF (12 electrons were distributed in 10 orbitals for 2s and 3s, and 11 orbitals for 1t) with the 6-31G(d) basis set. Although determined with different methods and different qualities of basis sets, these two sets of geometries were close to each other. The largest difference in bond length was only 0.02 Å. However, the energy differences of the isomers are very small, and therefore the small difference of the structures can affect the energy order of the isomers. Both of the structure sets were used to check the geometry effect.

The basis sets used were Dunning's cc-pVXZ (X = D, T, Q)¹⁶ and augmented cc-pVXZ (X = D, T, Q) basis sets.¹⁷ Using these basis sets, we first carried out Hartree-Fock (HF) calculations (unrestricted HF calculations for 1t and restricted HF calculations for 2s and 3s). The active spaces in the reference MC-SCF calculations were constructed from the HF configuration plus single and double excitation configurations among valence orbitals, that is, valence configuration interaction singles and doubles (CISD) space. The 16 electrons in the 16 orbitals were correlated in MC-SCF calculations; hereafter, we refer to these spaces as MC(16,16) following the FORS(*n*, *m*) or CAS(*n*, *m*) notation. These reference spaces were not complete spaces as in the MC-QDPT calculations by Rintelman and Gordon.⁸ However, MC(16,16) includes all valence electrons and orbitals instead, which is probably preferable to FORS with a smaller number of electrons or orbitals. Note that the FORS-(16,16) computation is not possible even today because of its huge dimension.

The second-order GMC-PT calculations using MC(16,16) were performed according to the scheme described in ref 14. The second-order perturbation calculation takes into account the contribution from singly and doubly (SD) excited configurations from the reference space MC(16,16). Thus, up to quadruple excitations from the main HF configuration were considered by GMC-PT calculations.

An exception from the scheme was the use of the spin-dependent orbital energies for the triplet state in the 1t isomer. A previous paper¹⁸ of ours indicated that the second-order multireference perturbation method using spin-averaged (SA) orbital energies

$$\epsilon_{p\alpha} = \epsilon_{p\beta} = h_{pp} + \sum_{rs} (D_{rs}^{\alpha} + D_{rs}^{\beta}) [(pp|rs) - (ps|rp)/2]$$

(D_{rs}^{α} and D_{rs}^{β} represent α and β one-particle density matrices, respectively) somewhat underestimates the energies of high spin states, and the use of spin-dependent (SD) orbital energies

$$\epsilon_{p\alpha} = h_{pp} + \sum_{rs} \{D_{rs}^{\alpha} [(pp|rs) - (ps|rp)] + D_{rs}^{\beta} (pp|rs)\}$$

$$\epsilon_{p\beta} = h_{pp} + \sum_{rs} \{D_{rs}^{\beta} [(pp|rs) - (ps|rp)] + D_{rs}^{\alpha} (pp|rs)\}$$

compensates for the underestimation. The consideration of this effect of the orbital energies is crucial for accurately determining the relative energies of isomers in different spin states.

All of the calculations were carried out with a modified version of GAMESS.¹⁹

3. Results and Discussion

The Hartree-Fock configurations were determined as

1t:

$$(\text{core})(7\sigma)^2(8\sigma')^2(9\sigma)^2(2\pi)^2(2\pi')^2(10\sigma)^2(11\sigma)^2(3\pi)^1(3\pi')^1$$

2s: (core)(6a₁)²(7a₁)²(3b₁)²(8a₁)²(2b₂)²(4b₁)²(9a₁)²(10a₁)²

3s: (core)(6a₁)²(3b₁)²(7a₁)²(8a₁)²(2b₂)²(4b₁)²(9a₁)²(5b₁)²

At the HF level, the order of the isomers was 1t < 2s < 3s in all the basis sets and both the CCSD(T) and FORS-SCF geometries.

The MC-SCF and GMC-PT calculations were based on these HF configurations plus singles and doubles within valence orbitals. The absolute energies and the relative energies measured from the 2s energy in each basis set and geometry set are shown in Tables 1 and 2, respectively. For the 1t isomer, the GMC-PT energies using spin-averaged orbital energies, as well as those with spin-dependent orbital energies, are also listed for comparison.

Table 1 shows that the geometry effect on the absolute energies is rather small, 4.1 millihartree at the maximum. However, the trend is different, depending on the isomers: for the 2s isomer the energies of FORS-SCF geometries were lower, while for the 3s isomer the energies of CCSD(T) geometries were lower. (The 1t energies of CCSD(T) and FORS-SCF geometries are very close to each other.) This trend affects the relative energy between the 2s and 3s isomers by 2–4 kcal/mol, as can be seen in Table 2.

Table 2 shows the relative stability of the 1t, 2s, and 3s isomers. The results indicate that the 2s isomer is most stable in all the basis sets and at both the CCSD(T) and FORS-SCF geometries except for some spin-averaged orbital energy numbers. The second most stable isomer is the 3s isomer, although the energy difference from the 1t isomer is quite small. The relative energy of the 3s isomer measured from the 2s isomer was 5.3 (9.0) kcal/mol in the calculations with the aug-cc-pVQZ basis and CCSD(T) (FORS-SCF) geometry, while the relative energy of the 1t isomer was 6.7 (9.9) kcal/mol. This

TABLE 1: Total Energy (plus 402 hartree) of the 1t, 2s, and 3s Isomers Calculated with GMC-PT (in hartree)

structure	cc-pVXZ sets			aug-cc-pVXZ sets		
	X = D	X = T	X = Q	X = D	X = T	X = Q
	CCSD(T) geometry					
1t (SD) ^a	-0.744867	-0.863768	-0.903740	-0.762337	-0.872068	-0.907437
1t (SA) ^a	-0.752028	-0.872534	-0.912698	-0.770804	-0.881304	-0.916723
2s	-0.750235	-0.871854	-0.913848	-0.768269	-0.880661	-0.918187
3s	-0.743583	-0.864030	-0.905472	-0.762792	-0.872974	-0.909701
	FORS-SCF geometry					
1t (SD) ^a	-0.745647	-0.864093	-0.903939	-0.762107	-0.872034	-0.906580
1t (SA) ^a	-0.752752	-0.872759	-0.913100	-0.770535	-0.881267	-0.916024
2s	-0.752950	-0.875651	-0.917938	-0.770941	-0.884669	-0.922311
3s	-0.741307	-0.862181	-0.903593	-0.760450	-0.872477	-0.907936

^a SD and SA indicate that the numbers were computed with spin-dependent and spin-averaged orbital energies, respectively.

TABLE 2: Relative Energy of the 1t and 3s Isomers Measured from the Energy of the 2s Isomer (in kcal/mol)

structure	cc-pVXZ sets			aug-cc-pVXZ sets			CCSD(T) ^a (cc-pCVQZ)	MC-QDPT ^b (aug-cc-pVDZ)
	X = D	X = T	X = Q	X = D	X = T	X = Q		
	CCSD(T) geometry							
1t (SD)	3.4	5.1	6.3	3.7	5.4	6.7 (7.2) ^c	7.5 (8.0) ^c	
1t (SA)	-1.1	-0.4	0.7	-1.6	-0.4	0.9 (1.4) ^c		
2s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
3s	4.2	4.9	5.3	3.4	4.8	5.3 (5.1) ^c	6.2 (6.0) ^c	
	FORS-SCF geometry							
1t (SD)	4.6	7.3	8.8	5.5	7.9	9.9 (9.9) ^d		
1t (SA)	0.1	1.8	3.0	0.3	2.1	3.9 (4.0) ^d		-4.4 (-4.3) ^d
2s	0.0	0.0	0.0	0.0	0.0	0.0		0.0
3s	7.3	8.5	9.0	6.6	7.7	9.0 (8.7) ^d		3.4 (3.1) ^d

^a References 7 and 10. ^b Reference 8. ^c The numbers in the parentheses are zero point corrected energies. The zero point vibrational energies are taken from ref 10. ^d The numbers in the parentheses are zero point corrected energies. The zero point vibrational energies are taken from ref 8.

TABLE 3: Reference and SD Configuration Weights in the First-Order GMC-PT Wave function (in %)^a

structure	cc-pVXZ sets						aug-cc-pVXZ sets					
	X = D		X = T		X = Q		X = D		X = T		X = Q	
	Ref.	SD	Ref.	SD	Ref.	SD	Ref.	SD	Ref.	SD	Ref.	SD
	CCSD(T) geometry											
1t (SD)	90.9 (80.8+10.1)	9.1 (0.9+8.2)	89.1 (79.3+9.8)	10.9 (0.9+10.0)	88.6 (78.9+9.8)	11.4 (0.9+10.5)	89.9 (80.0+10.0)	10.1 (0.9+9.2)	88.8 (79.0+9.8)	11.2 (0.9+10.4)	88.5 (78.8+9.8)	11.5 (0.9+10.6)
1t (SA)	90.2 (80.2+10.0)	9.8 (1.1+8.7)	88.2 (78.5+9.7)	11.8 (1.0+10.8)	87.7 (78.0+9.7)	12.3 (1.0+11.3)	88.9 (79.1+9.9)	11.1 (1.0+10.0)	87.8 (78.1+9.7)	12.2 (1.0+11.2)	87.5 (77.9+9.6)	12.5 (1.0+11.5)
2s	91.1 (81.3+9.9)	8.9 (0.7+8.2)	89.6 (79.8+9.8)	10.4 (0.7+9.7)	89.2 (79.5+9.7)	10.8 (0.7+10.1)	90.5 (80.7+9.8)	9.5 (0.7+8.8)	89.4 (79.6+9.7)	10.6 (0.7+9.9)	89.1 (79.4+9.7)	10.9 (0.7+10.2)
3s	90.8 (80.7+10.1)	9.2 (0.8+8.4)	89.3 (79.6+9.8)	10.7 (0.7+10.0)	88.9 (79.2+9.7)	11.1 (0.7+10.4)	90.1 (80.1+10.0)	9.9 (0.7+9.1)	89.1 (79.4+9.7)	10.9 (0.7+10.2)	88.9 (79.1+9.7)	11.1 (0.7+10.5)
	FORS-SCF geometry											
1t (SD)	90.9 (80.7+10.2)	9.1 (0.9+8.2)	89.1 (79.2+9.9)	10.9 (0.9+10.1)	88.6 (78.7+9.8)	11.4 (0.9+10.5)	89.9 (79.9+10.0)	10.1 (0.9+9.2)	88.8 (79.0+9.8)	11.2 (0.9+10.4)	88.5 (78.7+9.8)	11.5 (0.8+10.7)
1t (SA)	90.2 (80.1+10.1)	9.8 (1.1+8.8)	88.2 (78.4+9.8)	11.8 (1.1+10.8)	87.6 (77.9+9.7)	12.4 (1.0+11.4)	88.9 (79.0+9.9)	11.1 (1.0+10.0)	87.8 (78.1+9.7)	12.2 (1.0+11.2)	87.4 (77.7+9.7)	12.6 (1.0+11.6)
2s	91.2 (81.4+9.8)	8.8 (0.7+8.1)	89.7 (80.0+9.7)	10.3 (0.7+9.6)	89.3 (79.6+9.6)	10.7 (0.7+10.1)	90.7 (80.9+9.7)	9.3 (0.7+8.7)	89.4 (79.8+9.7)	10.5 (0.7+9.9)	89.2 (79.5+9.6)	10.8 (0.7+10.1)
3s	90.8 (80.8+10.0)	9.2 (0.7+8.4)	89.4 (79.8+9.6)	10.6 (0.7+9.9)	89.0 (79.4+9.6)	11.0 (0.7+9.9)	90.2 (80.2+9.9)	9.8 (0.7+9.1)	89.2 (79.4+9.7)	10.8 (0.7+10.2)	88.9 (79.3+9.6)	11.1 (0.7+10.4)

^a The numbers in parentheses in reference weight indicate HF and excited configuration weights, and those in parentheses in the SD space weight indicate internal and external excitation weights (see the text for more details).

order of the isomers is unchanged even though the zero-point vibrational energy (ZPVE) correction is included. The ZPVEs for the 1t, 2s, and 3s isomers are very close to one another: 7.41, 7.37, and 7.07 kcal/mol, respectively, at the FORS-SCF level.⁸ [The differences of ZPVEs at the CCSD level are $E_{ZPV}(1t) - E_{ZPV}(2s) = 0.5$ kcal/mol and $E_{ZPV}(3s) - E_{ZPV}(2s) = -0.2$ kcal/mol at the CCSD level.¹⁰ ZPVEs themselves were not reported in ref 10]. The zero-point corrected energies are also listed in Table 2. On the whole, the results were in good agreement with the CCSD(T) results of Stanton et al.⁷ and Sattelmeyer et al.¹⁰

Table 2 also tells us a clear trend of the basis set effect, with a larger basis set giving larger 2s-3s and 2s-1t energy

separations. This implies that the most stable isomer will not change if we use larger basis sets than those used. To check the basis set effect on the order of the isomers, we calculated the complete basis set limits. The complete basis set extrapolation of the CCSD energy is given by the Gaussian dependence²⁰ on basis set sizes, i.e.,

$$E(n) = E(\infty) + E_0 \exp[-(n-1)] + E_1 \exp[-(n-1)^2]$$

where n is the cardinal number of the basis set (2, 3, 4 for DZ, TZ, QZ, respectively), $E(\infty)$ is the complete basis set limit, and E_0 and E_1 are constants. By assuming the basis set dependence of GMC-PT is the same, apart from a multiplicative factor,

we extrapolated the energy in the complete basis set. The relative energies at the complete basis set limit, computed through the above extrapolation, were 7.6 (11.1) and 5.6 (9.9) kcal/mol for the 1t and 3s isomer, respectively, in the CCSD(T) (FORS–SCF) geometry. The relative order of the 1t and 3s isomers was unchanged, which supports our conclusion that the 2s isomer is most stable.

To obtain more information on the relative stability of the isomers, we further analyzed the wave functions. Table 3 shows the weights of the reference MC–SCF functions occupied in the first-order perturbed wave function,

$$W_{\text{ref}} = \langle \Psi_{\text{ref}} | \Psi_{\text{ref}} \rangle / \langle \Psi_{\text{ref}} + \Psi^{(1)} | \Psi_{\text{ref}} + \Psi^{(1)} \rangle = [1 + \langle \Psi^{(1)} | \Psi^{(1)} \rangle]^{-1}$$

which is a measure of the quality of the perturbed wave function. The relative weight calculated in different structures gives a measure of the balance of the calculation. We can further decompose the reference weight into the weights of the main HF configuration and others using CI coefficients of the MC–SCF wave functions. The nonreference weight can also be decomposed into internal and external weights, where the internal weight means the contribution from the active- to active-orbital excitations that are not included in MC(16,16), and the external weight means the contribution from the excitation involving the virtual orbitals. These numbers are also listed in parentheses in Table 3. From Table 3 we can see that the reference weights are fairly large, about 90% (88.5–91.2% with the 1t(SA) values excluded), and moreover the differences between the isomers in the same basis and geometry sets are very small ($\Delta W_{\text{ref}}^{\text{max}} = 0.7\%$ with the 1t(SA) values excluded). This means that the quality of the wave functions is almost identical, namely well-balanced, among the isomers, which supports our relative energy data. One more feature we can see from the table is that the main HF configuration determined a large part of the wave function, and that the internal contribution was very small. About 80% of the wave function was contributed by the HF configurations. This fact justifies the construction scheme of MC(16,16), namely, taking an HF configuration and adding SD configurations to it.

Finally, let us consider the reason that the order differs between Rintelman and Gordon⁸ and us. Table 2 tells us that the use of spin-averaged orbital energies and a relatively small basis set of aug-cc-pVDZ underestimates the 1t relative energies by about 5–6 kcal/mol (from 1t(SD)) and 3–5 kcal/mol (from aug-cc-pVQZ), respectively. This accounts for about two-thirds of the difference (14.3 (= 9.9 + 4.4) kcal/mol) in relative energy. The remainder should be due to the difference in active space in the MC–SCF and following perturbation method. A possible cause would be the treatment of the C(2s) and Si(3s) electrons, part of which were missing in the FORS–SCF wave functions of Rintelman and Gordon.

4. Conclusions

We have investigated the relative stability of SiC₃ isomers using GMC–PT with full valence electrons and orbitals for the reference and obtained the order 2s < 3s < 1t. The GMC–PT with aug-cc-pVQZ gave energy separations of 5.3 (5.1) kcal/

mol for 2s–3s and 6.7 (7.2) kcal/mol for 2s–1t at the CCSD(T)/cc-pCVQZ geometry, and 9.0 (8.7) and 9.9 (9.9) kcal/mol, respectively, at the FORS–SCF/6-31G(d) geometry, where the numbers in the parentheses are zero-point corrected energies. The wave function analysis for the first-order perturbed wave function showed that the quality of the wave functions was almost uniform among the isomers, supporting our results. The trends of the relative energies for the basis set and geometry tell us that the difference from the results of MC–QDPT by Rintelman and Gordon were partly due to their use of the relatively small basis set and the spin-averaged orbital energies. We hope that the problem of inconsistency between the previous studies is now resolved.

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