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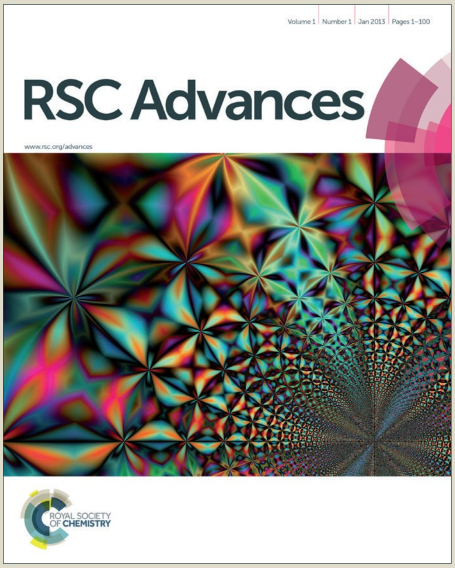

Smallest deltahedra silicon dicarbide: $C_2Si_3^{2-}$

Jing-jing Sui, Jing Xu, Yi-hong Ding*

Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China. E-mail: yhdd@jlu.edu.cn

Abstract

The composition and valence electrons of molecules usually have great impact on the eventual topology. With the high tendency to form *sp*/*sp*^{2}-hybridized multiple bonding of C_2, the main-group dicarbides (C_2X_n) usually adopt a non-closo (or open) topology. By contrast, naked Zintl anions (e.g., Si_5^{2-}) usually feature the deltahderal structures. In this paper, we report an unexpected example that the pentatomic carbon-silicon cluster $C_2Si_3^{2-}$ has the global minimum $C_2Si_3^{2-}$-**01** featuring a closo-structure with all deltahedras. The global minimum nature of $C_2Si_3^{2-}$-**01** was confirmed by various sophisticated methods including G3B3, G4, CBS-QB3 and W1BD as well as CCSD(T) extrapolated up to the complete basis set limit based on the CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z calculations. The AdNDP analysis revealed that $C_2Si_3^{2-}$-**01** possesses a lone pair of electrons on each of the three silicon atoms, four 2c-2e bonds and four 3c-2e bonds, among which the two 2c-2e bonds between the two carbons well indicates the existence of a multiply bonded C_2 (1.320 Å) that carries most negative charges. With a total of 22 valence electrons, $C_2Si_3^{2-}$-**01** formally resembles the known Wade-Mingos clusters with (n + 1) polyhedral skeletal electron pairs (PSEPs). Replacement of Si_2 by the highly electron-withdrawing C_2 does not break the deltahedral topology of the Zintl ion Si_5^{2-}. To our best knowledge, $C_2Si_3^{2-}$ represents the smallest deltahedral main-group dicarbide and also the first deltahedral main-group dicarbide with (n+1) PSEPs. To direct its organometallic applications, we designed the hetero-deckered sandwich compounds CpMg($C_2Si_3^{2-}$)MgCp, in which the $C_2Si_3^{2-}$-**01** unit can be nicely kept.

1. Introduction

In general, the topological structure of a chemical compound depends on its inherent elemental composition and electronic structure. Various conceptual rules have been developed to effectively connect the topology and electron number.[1] Among them is the famous Wade-Mingos rule, which usually apply to judge the structures of boranes and carboranes by the skeletal electron pairs, i.e., the n-vertex clusters with (n+1) polyhedral skeletal electron pairs (PSEPs) prefer to be arranged into closo-deltahedra.[1a,1b] On the other hand, the Zintl anions composed of heavier main-group or transition metal elements feature deltahderal structures, and their topology can in most cases be accounted for by the Wade-Mingos rule.[2]

The ligand-free dicarbides (C_2X_n) usually contain a multiply bonded C_2 unit. The simplest tri-atomic dicarbides, i.e., C_2X, have been the earlier focus of numerous studies.[3-6] They have played important roles in various fields. For example, the well-known C_2Ca can not only be used as the basic material to synthesize the organic compounds, but also be applied to the nonferrous metals and steel industry.[4] The actinide dicarbides as the appropriate fuels of nuclear reactors, have also received much attention.[6] Besides, some of them have been detected in space.[3]

Concerning the topological structures, the simplest C_2X usually take the chainlike or T-shaped ground states.[3,5,6] With more than one X-atom, the structure and bonding within the dicarbide are expected to be complicated since the C-C, C-X and X-X bonds may undergo interactive competition. It has now been found that some transition metals (e.g., X=Co,[7a] Fe[7b], Ni[7b]) can effectively allow the multiply bonded C_2 to be positioned as one edge of a closo-structure, forming the deltahderal topology. However, in spite of a large body of published research articles on the main-group dicarbides,[8-9] only the hexatomic cluster C_2Si_4 has been firmly shown to have a deltahedral structure.[8] The rather limited examples of the main-group dicarbides must be ascribed to the strong preference of the C_2-moiety to drive the whole or part of the molecule to be open in chainlike or planar forms.

Can other ligand-free main-group dicarbides possess a deltahedral structure besides C_2Si_4? In this paper, based on a global isomeric search strategy and various sophisticated quantum chemical methods including G3B3, G4, CBS-QB3, W1BD and CCSD(T)/CBS, we report the smallest main-group dicarbide molecule $C_2Si_3^{2-}$ with all deltahedras. With 22 valence electrons, the pentatomic $C_2Si_3^{2-}$ formally has (n+1) PSEPs, differing from C_2Si_4 with (n) PSEPs. Using $C_2Si_3^{2-}$ as a decker, we designed novel hetero-deckered sandwich compounds.

2. Theoretical Methods

In order to explore the global structure of $C_2Si_3^{2-}$, we introduced a locally developed grid-based comprehensive isomeric search strategy for both the singlet and triplet systems.[10] For each system, a three-dimensional cubic boxes consisting of the uniformly distributed 125 candidate sites were constructed. The two C and three Si-atoms were placed into these candidate sites to get diversified structural forms. Eventually, a total of 138 effective grid-based structures were generated as the input for B3LYP[11]/6-31G(d)[12] optimizations followed by the harmonic vibrational calculations. All the B3LYP/6-31G(d) local minimum structures without imaginary frequencies were further subject to the B3LYP/aug-cc-pVTZ[13] re-optimization followed by the frequency calculations. The single-point energies were performed at the CCSD(T)[14]/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level with inclusion of the zero-point vibrational energy (ZPVE) correction from the B3LYP/aug-cc-pVTZ calculations. For the key isomers of $C_2Si_3^{2-}$, we applied the composite G3B3,[15] G4,[16] CBS-QB3[17] and W1BD[18] calculations that have been developed for reliable "model chemistry". In addition, the CCSD(T) calculations with extrapolation up to the complete basis set limit (denote as CCSD(T)/CBS[19]) were carried out based on the aug-cc-pVTZ, aug-cc-pVQZ[13] and aug-cc-pV5Z[13c,13d]-CCSD(T) single-point energies. The natural charge populations and Wiberg bond index were obtained at the B3LYP/aug-cc-pVTZ level using the natural bond orbital (NBO) analysis. Chemical bonding partition of global minimum structure was performed utilizing the Adaptive Natural Density Partitioning (AdNDP) method.[20] For the hetero-deckered sandwich compound, we used the PBE0[21]/cc-pVTZ//B3LYP/6-31G(d) to calculate the single-point energies. The calculation in tetrahydrofuran (THF) solution were carried out using the SMD solvent model of Gaussian 09.[22] All calculations were performed with the Gaussian03[23] and Gaussian09[24] program packages.

3. Results and discussions

By means of the grid isomeric search, a total of 20 for singlet and 36 for triplet $C_2Si_3^{2-}$ were obtained at the B3LYP/aug-cc-pVTZ level. For simplicity and for easier discussion, we only presented the selected singlet (in Figure 1) and triplet (in Figure 2) isomers within 30 kcal/mol. Note that the total energy of the closo isomer **01** was set to be 0.00 kcal/mol as the energy reference. In general, the singlet isomers are more stable than the triplet ones. The lowest-energy triplet isomer ^{3}**01** is higher than the lowest-energy singlet isomer by 15.04 kcal/mol, and is the seventh in the energy order of all the singlet and triplet isomers. So in the following context we only discuss the properties of singlet isomers. The information of all the isomers can be found in supporting information (SI).

3.1 Structural properties

At the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ+ZPVE level, the lowest-energy isomer **01** has a closo-structure, which is a result of the vertical attack of the C_2-moiety to the Si_3 ring, forming six deltahedras. Interestingly, the two carbon atoms occupy different sites, one is equatorial whereas the other is apex. In topology, **01** is quite analogous to the isoelectronic triagonal bipyramidal cluster Si_5^{2-}, which was synthesized in form of the $(Rb\text{-crypt})_2Si_5{\cdot}4NH_3$ crystal.[25] The equatorial Si-Si (2.503 Å) and axial Si-Si (2.393 Å) bond lengths of $C_2Si_3^{2-}$-**01** are in accordance with the experimental values 2.535 and 2.350 Å of Si_5^{2-},[25] respectively. Additionally, the C-C distance of **01**, i.e., 1.320 Å, lies around the experimental value of the conventional C=C double bond (1.34 Å)[26] and is supported by the large Wiberg bond index (WBI) of C-C (1.938). In Table 1, the natural charge population analysis indicates that the negative charge of $C_2Si_3^{2-}$ is mainly distributed on C_2 (-1.589e) with minor on Si_3 (-0.411e).

The species **02** and **03** in C_{2v} symmetry both exhibit a planar structure. The C_2 moiety connects terminally with the Si_3 ring in **02**, while it is inserted into the Si_3 ring in **03**. Alternatively, **03** can be viewed as a result of the SiC-terminal connection with the CSi_2 ring. The C-C bond length of **02** is very short (1.252 Å) with the WBI value 2.725, indicative of the triple bonding. In **03**, the internal C-C bond distance is 1.340 Å (WBI is 1.608), consistent with a double bond. The natural charge population analysis of **02** and **03** are similar to that of **01**, i.e., the negative charge is mostly localized on C_2. The almost doubly bonded C_2 unit in **03** carries more charge (-1.794e) than the triply bonded one in **02** (-1.290e).

3.2 Energetics

As shown in Figure 1, the relative energies of the former three isomers **01**, **02** and **03** are close within 2 kcal/mol, i.e., 0.00, 0.11 and 1.51 kcal/mol, respectively at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ+ZPVE level. **01** and **02** are almost isoenergetic. It's thus quite desirable to study their energetic competition at more sophisticated levels (see Table 2). First, we carried out the composite G3B3, G4, CBS-QB3 and W1BD calculations, which have been well defined for the purpose of accurately predicting the thermochemical properties of chemical systems. All the four composite methods showed the lowest-energy nature of **01**. Interestingly, the energetic competition between the two planar isomers **02** and **03** are not consistent at different levels. G3B3 and G4 place **03** to be more stable than **02**, whereas CBS-QB3 and W1BD show **02** to be more stable than **03**. Moreover, the relative energy of **02** with reference to **01** at the G3B3, G4 and CBS-QB3 levels are higher than that at W1BD by more than 2 kcal/mol. The W1BD method was designed to be computationally much more expensive and more accurate than the CBS-QB3 and G3 methods. It should be noted that the above four composite methods comprising a set of optimal parameters have been largely tested on diversified chemical systems. Alternatively, the CCSD(T) method extrapolated to the complete basis set (namely CCSD(T)/CBS) is also an easy-to-use and a powerful tool for predicting energetics of chemical systems especially in the case where the exotic structures that have not been included in the test of composite methods or the desired basis sets are not involved in the composite methods. Using the aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z-CCSD(T) calculations based on the B3LYP/aug-cc-pVTZ geometries, we derived the CCSD(T)/CBS relative energies of **02** and **03** as 0.49 and 2.95 kcal/mol, respectively above **01**. It's of interest to note that the CCSD(T)/CBS results are close to the W1BD values. We thus concluded that the global minimum of $C_2Si_3^{2-}$ is a closo-structure **01** with all deltahedras.

In consideration of the reliability of the B3LYP functional used in the electronically complex systems, we utilized the other two functionals (M06-2X and PBE0) to assess the computed structural parameters of the key isomers. The results indicated that the M06-2X and PBE0 functionals produce essentially the same structure for the former three low-lying isomers with only minor difference in bond lengths (see Table 3).

3.3 Bonding characteristics

To explore in detail the bonding situation within isomer $C_2Si_3^{2-}$-**01**, we applied the AdNDP analysis.[20] The deduced localized molecular orbitals of **01** were given in Figure 3. In **01**, there are three silicon lone pairs, four 2c-2e, bonds and four 3c-2e bonds. The occupation numbers (ON) of the silicon lone pairs in equator and apex are 1.96|e| and 1.95|e|, respectively. For the 2c-2e bonds, the ON (2.00|e| and 1.97|e|) of two C_1-C_2 bonds indicate that **01** retains the multiple bonding within C_2. The other two 2c-2e bonds are Si_3-Si_5 (ON=1.95|e|) and C_2-Si_4 (ON=1.94|e|). In addition, **01** possesses four 3c-2e bonds, i.e., C_1-C_2-Si_3, C_1-C_2-Si_5, C_2-Si_3-Si_4 and C_2-Si_4-Si_5. The former C_1-C_2-Si_3, C_1-C_2-Si_5 have higher occupancy (ON=1.98|e|) compared to the latter two identical 3c-2e bonds (ON=1.83|e|). The existence of four 3c-2e bonds within $C_2Si_3^{2-}$-**01** is reminiscent of the well-known boranes and carboranes that are electron deficient and typically characterized by the 3c-2e bonding.[1a-1c]

3.3 Sandwich compounds based on $C_2Si_3^{2-}$

The dianionic $C_2Si_3^{2-}$ belongs to the family of charged ligand-free clusters, which can play important roles in the organometallic or cluster-assembled chemistry.[27] They can effectively take part in the "sandwiching" interaction with metal ions together with the counter deckers, forming novel sandwich compounds. And vice versa, during the sandwiching, the charged ligand-free clusters can be stabilized electronically (by removal of the Coulomb repulsion) and sterically (by crowded substituents) by the metal ions and counter deckers.

In the sandwiching stabilization of $C_2Si_3^{2-}$, either $C_2Si_3^{2-}$ itself or other stable anionic clusters can be the counter decker, resulting in the "homo-deckered" or "hetero-deckered" sandwich compounds, respectively. To avoid the cluster fusion between nonstoichiometric deckers, the hetero-deckered sandwich strategy is a more favorable choice by introducing a stable decker such as cyclopentadienyl anion (Cp^-).[28] Nowadays, Cp^- is one of the versatile ligand in organometallic chemistry, and has been considered as the most commonly used reagent for the synthesis of many metallocenes that are important in a wide range of applications.[29]

As an example, we studied $CpM(C_2Si_3^{2-})MCp$ with M being the alkali-earth Mg. To reduce the computational cost, the PBE0 method was chosen for sandwich-like compounds since the relative energies of $C_2Si_3^{2-}$ at PBE0/cc-pVTZ//B3LYP/aug-cc-pVTZ+ZPVE are generally in accordance with the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ+ZPVE values as listed in Supporting Information (SI).

Figure 4 shows the representative isomers obtained at the PBE0/cc-pVTZ//B3LYP/6-31G(d)+ZPVE level. Others isomers can be found in Supporting Information (SI). The hetero-deckered sandwich compound of **Mg-1** (closo-$C_2Si_3^{2-}$) is more stable than the second low-lying isomer **Mg-2** (open-$C_2Si_3^{2-}$) by 16.70 kcal/mol. From the structural parameters listed in Table 4, we can see that the six bond distances of the closo-$C_2Si_3^{2-}$ vary little before and after the hetero-deckered sandwiching. Thus, the dianionic closo-**01** can be nicely retained within the sandwich compounds.

To investigate whether the designed sandwich compound **Mg-1** is stable or not against fragmentation, we studied various dissociation pathways as follows:

$CpMg(C_2Si_3)^{2-}MgCp \rightarrow CpMgCCMgCp + Si_3$ (1)

$CpMg(C_2Si_3)^{2-}MgCp \rightarrow CpMgMgCp + C_2Si_3$ (2)

$CpMg(C_2Si_3)^{2-}MgCp \rightarrow CpMgCp + C_2Si_3Mg$ (3)

The easiest pathway is (3) with the dissociation energy of 57.25 kcal/mol. The pathways (1) and (2) need to absorb much more energy. The corresponding endothermicities are 80.41 and 88.23 kcal/mol. Clearly, due to the very high dissociation energies, the hetero-deckered sandwich compounds $CpMg(C_2Si_3^{2-})MgCp$ are quite stable against fragmentation.

Due to the exposure of the highly electron-withdrawing C_2 moiety within $CpMg(C_2Si_3^{2-})MgCp$, the solvent effect might have an influence on the isomeric stability. The tetrahydrofuran (THF) solution was chosen for our study. The relative energies of **Mg-1**, **Mg-2**, **Mg-3** and **Mg-4** in gas phase are 0.00, 16.70, 17.46 and 21.43 kcal/mol, respectively. Their corresponding energies in the THF solution are 0.00, 20.36, 24.54 and 16.20 kcal/mol. Although the relative energy order of the latter three isomers in solution is different from that in gas phase, the global minimum structure of CpMg($C_2Si_3^{2-}$)MgCp in both phases remains to be **Mg-1** with closo $C_2Si_3^{2-}$.

3.4 Implications

Besides the easy accessibility for spectroscopic study, small-sized clusters are relevant to the growth or assembly into larger systems. The p-block first-row elements (e.g., B,C,N) are prone to form strongly π-bonded structure. Thus, when incorporated into the heavier main-group clusters, they have strong trend to destabilize the formation of a closo or deltahedral structure, especially in small clusters.[30] Understandably, the structure of C_2X_n is usually fully or partially open instead of being closo, resulting in the formation of the multiply bonded C_2. Thus, our computational finding at various sophisticated levels that the global structure of the small $C_2Si_3^{2-}$ features a closo polyhedra is quite unexpected.

In sharp contrast, the deltahedra is known to be the characteristics of the Zintl anions. Deltahderal Zintl anions composed of the group 14 elements have been known for more than 100 years.[31] Many such compounds have been prepared including the smallest E_5^{2-} (E=Si,Ge,Sn,Pb).[32] The bonding of these ligand-free clusters cannot be accounted for by classical octet rule, i.e., 2c-2e bond. Instead, they feature the delocalized 3c-2e bonds and their topologies can usually be explained in terms of the Wade-Mingos rule as for boranes and carboranes. Clearly, replacement of Si_2 moiety within Si_5^{2-} by the highly electron-withdrawing C_2 does not break the closo topology. To our best knowledge, $C_2Si_3^{2-}$ is the smallest main-group dicarbide. The carried two additional electrons render $C_2Si_3^{2-}$ to be applicable in organometallic chemistry, e.g., to form sandwich compounds. Also, with the multiply bonded C_2, the $C_2Si_3^{2-}$

compounds are expected to have particular applications such as in catalysis and cycloaddition reactions.

4. Conclusions

In this paper, we reported the smallest silicon dicarbide with all deltahedras, which is also the first main-group dicarbide with (n + 1) polyhedral skeletal electron pairs (PSEPs). In addition, to counteract the coulomb repulsion within the dianion $C_2Si_3^{2-}$, we introduced the Cp^- to design the hetero-deckered sandwich compounds, in which the closo unit **01** can be nicely kept. Due to the strong preference of the C_2-moiety in making the whole or partial molecule be open, the main-group dicarbides with no ligands usually adopt a non-closo topology. The presently disclosed closo-$C_2Si_3^{2-}$ really represents an exception, and its sandwich-like compounds warmly welcome future laboratory studies.

Acknowledgements

This work was funded by the National Natural Science Foundation of China (Nos. 21273093, 21473069, 21073074). The authors are very thankful for the reviewers' helpful comments and suggestions.

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Smallest deltahedra silicon dicarbide: $C_2Si_3^{2-}$

Jing-jing Sui, Jing Xu, Yi-hong Ding*

Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Repusblic of China. E-mail: yhdd@jlu.edu.cn;

Figure 1. Representative singlet isomers (ΔE<30 kcal/mol) of $C_2Si_3^{2-}$ with their symmetry and relative energies (kcal/mol) at CCSD(T)/aug-cc-pVTZ//B3LYP/ aug-cc-pVTZ+ZPVE level. The gray and gray blue balls are used for carbon and silicon atoms, respectively.

Figure 2. Representative triplet isomers (ΔE<30 kcal/mol) of $C_2Si_3^{2-}$ with their symmetry and relative energies (kcal/mol) at CCSD(T)/aug-cc-pVTZ//B3LYP/ aug-cc-pVTZ+ZPVE level. The total energy of the singlet isomer **01** was set to be 0.00 kcal/mol as the energy reference. The left superscript number "3" denotes the triplet state. The gray and blue balls are used for carbon and silicon atoms, respectively.

Figure 3. The localized molecular orbitals of $C_2Si_3^{2}$-**01** obtained by AdNDP analyses. The ON denotes the occupation numbers on the localized orbital

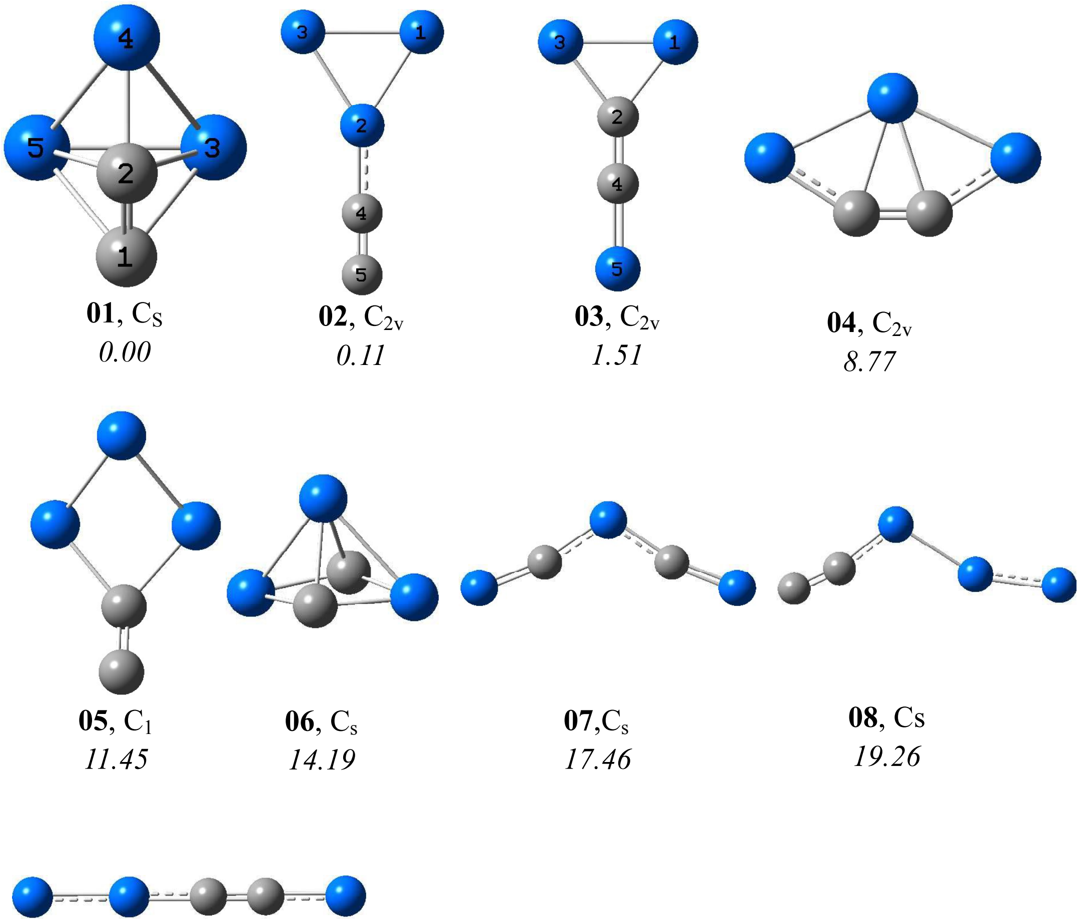
Figure 4. Representative isomers of CpMg($C_2Si_3^{2-}$)MgCp with their relative energies (kcal/mol) at the PBE0/cc-pVTZ//B3LYP/6-31G(d)+ZPVE level. The gray, blue, white and yellow balls are used for carbon, silicon, hydrogen and magnesium, respectively.

Table 1. The natural charge (e) of the three lowest-energy isomers of $C_2Si_3^{2-}$ at the B3LYP/ aug-cc-pVTZ level

Table 2. Relative energies (kcal/mol) of the three lowest-energy isomers of $C_2Si_3^{2-}$ at different levels.

Table 3. The bond lengths(Å) of the **01**, **02** and **03** at the B3LYP/aug-cc-pVTZ, M06-2X/aug-cc-pVTZ and PBE0/aug-cc-pVTZ

Table 4. The bond lengths(Å) of the closo-$C_2Si_3^{2-}$ in the **01**, **Mg-1**



01, C_S
0.00

02, C_{2v}
0.11

03, C_{2v}
1.51

04, C_{2v}
8.77

05, C_1
11.45

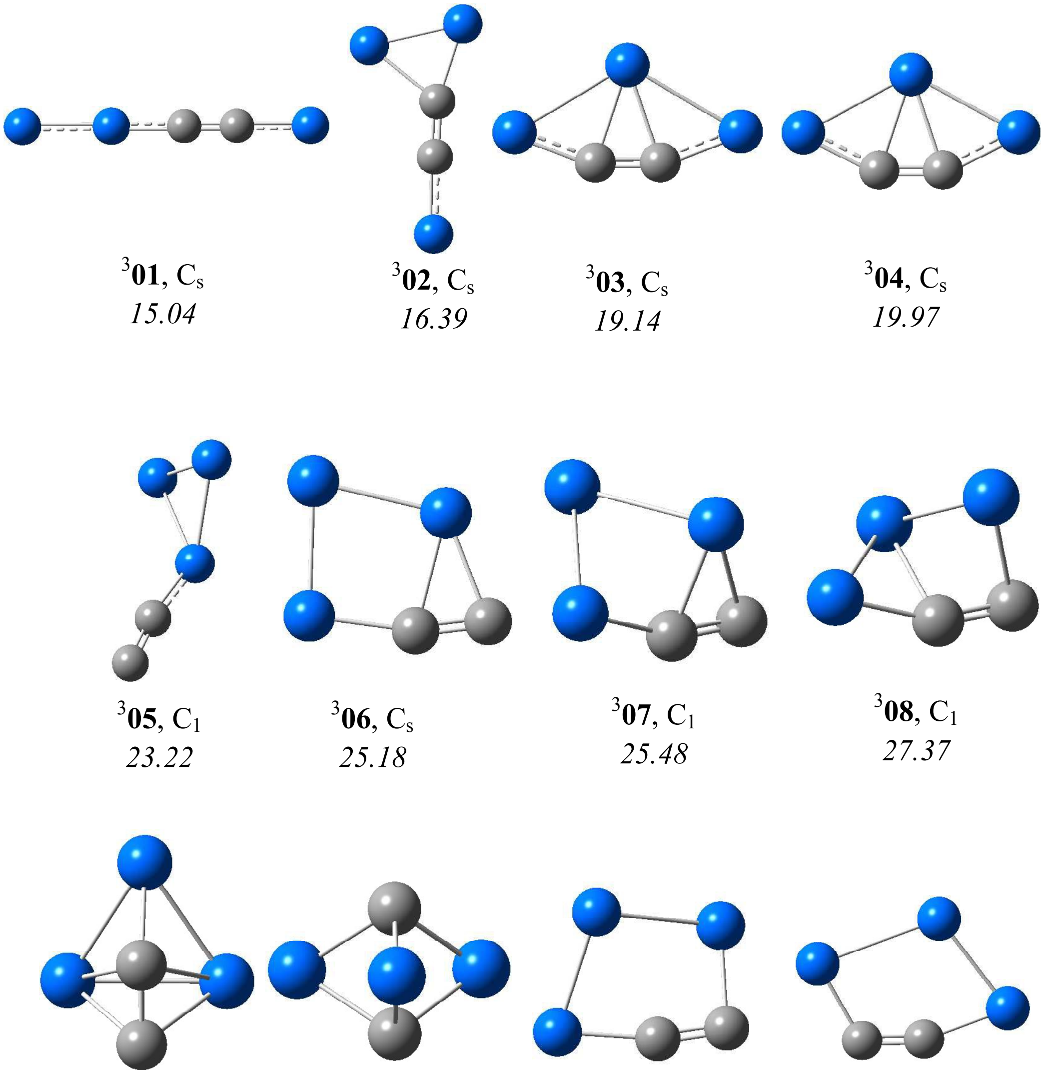
06, C_s
14.19

07,C_s
17.46

08, Cs
19.26

09, Cs
25.32

Figure 1. Representative singlet isomers ($\Delta E<30$ kcal/mol) of $C_2Si_3^{2-}$ with their symmetry and relative energies (kcal/mol) at CCSD(T)/aug-cc-pVTZ//B3LYP/ aug-cc-pVTZ+ZPVE level. The gray and gray blue balls are used for carbon and silicon atoms, respectively.



^{3}**01**, C_s
15.04

^{3}**02**, C_s
16.39

^{3}**03**, C_s
19.14

^{3}**04**, C_s
19.97

^{3}**05**, C_1
23.22

^{3}**06**, C_s
25.18

^{3}**07**, C_1
25.48

^{3}**08**, C_1
27.37

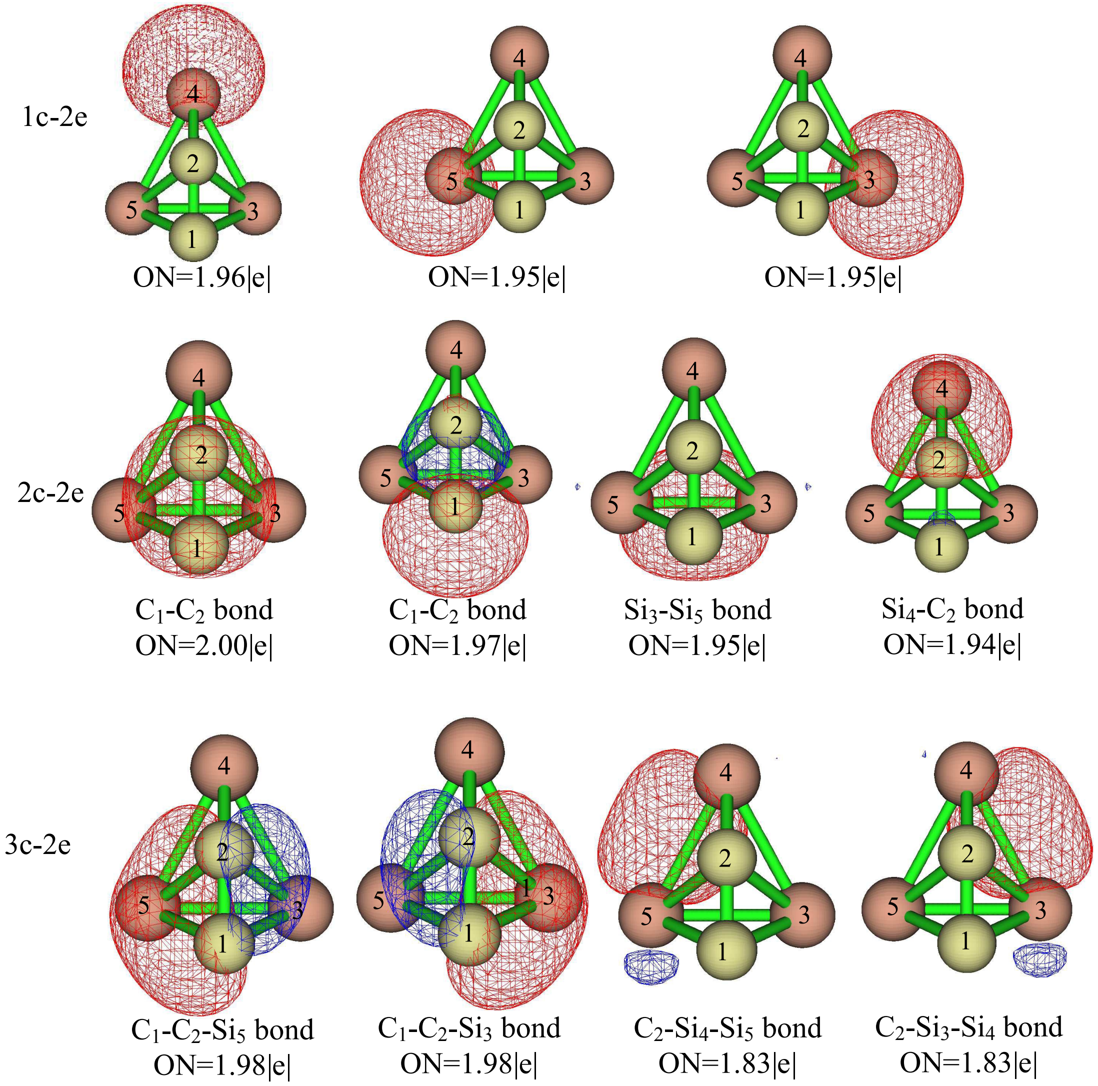
^{3}**09**, C_1
28.70

^{3}**10**, D_{3h}
28.80

^{3}**06**, C_1
29.31

^{3}**07**, C_s
29.88

Figure 2. Representative triplet isomers ($\Delta E<30$ kcal/mol) of $C_2Si_3^{2-}$ with their symmetry and relative energies (kcal/mol) at CCSD(T)/aug-cc-pVTZ//B3LYP/ aug-cc-pVTZ+ZPVE level. The total energy of the singlet isomer **01** was set to be 0.00 kcal/mol as the energy reference. The left superscript number “3” denotes the triplet state. The gray and blue balls are used for carbon and silicon atoms, respectively.



ON=1.96|e|

ON=1.95|e|

ON=1.95|e|

C_1-C_2 bond
ON=2.00|e|

C_1-C_2 bond
ON=1.97|e|

Si_3-Si_5 bond
ON=1.95|e|

Si_4-C_2 bond
ON=1.94|e|

C_1-C_2-Si_5 bond
ON=1.98|e|

C_1-C_2-Si_3 bond
ON=1.98|e|

C_2-Si_4-Si_5 bond
ON=1.83|e|

C_2-Si_3-Si_4 bond
ON=1.83|e|

Figure 3. The localized molecular orbitals of $C_2Si_3^{2}$-**01** obtained by AdNDP analyses. The ON denotes the occupation numbers on the localized orbitals.

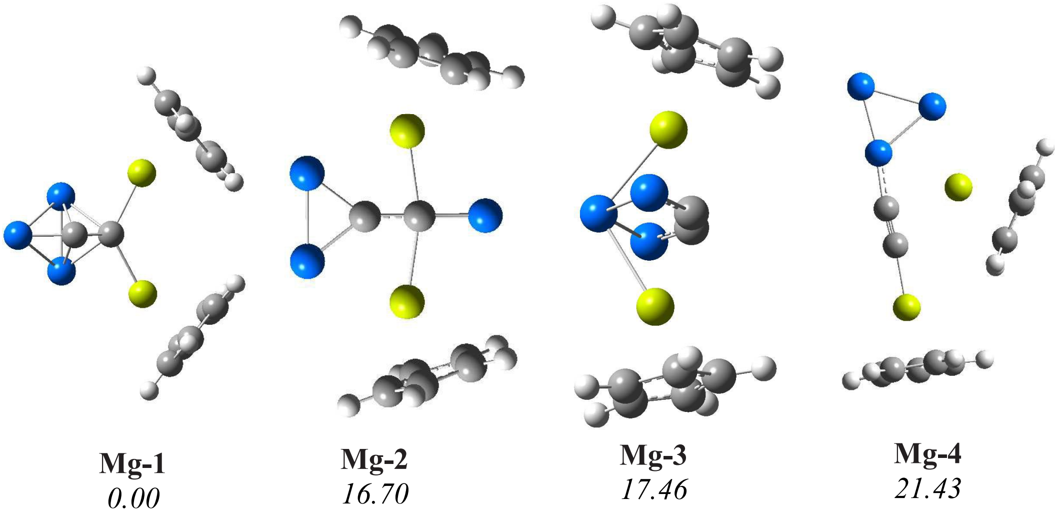


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Table 1. The natural charge (e) of the three lowest-energy isomers of $C_2Si_3^{2-}$ at the B3LYP/ aug-cc-pVTZ level

	1	2	3	4	5
01	-0.639	-0.950	-0.127	-0.156	-0.127
02	-0.527	0.345	-0.527	-0.974	-0.316
03	-0.073	-0.991	-0.073	-0.803	-0.060

Table 2. Relative energies (kcal/mol) of the three lowest-energy isomers of $C_2Si_3^{2-}$ at different levels.

	01	**02**	**03**
G3B3	0.00	2.77	1.02
G4	0.00	3.73	1.78
CBS-QB3	0.00	3.64	4.14
W1BD	0.00	0.69	2.17
CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ+ZPVE	0.00	0.11	1.51
CCSD(T)/aug-cc-pVQZ//B3LYP/aug-cc-pVTZ+ZPVE	0.00	0.26	1.96
CCSD(T)/aug-cc-pV5Z//B3LYP/aug-cc-pVTZ+ZPVE	0.00	0.38	2.44
CCSD(T)_CBS	0.00	0.49	2.95

Table 3. The bond lengths(Å) of the **01**, **02** and **03** at the B3LYP/aug-cc-pVTZ, M06-2X/aug-cc-pVTZ and PBE0/aug-cc-pVTZ

01	C_1-C_2	C_1-Si_3	C_1-Si_5	C_2-Si_3	C_2-Si_4	C_2-Si_5	Si_3-Si_4	Si_3-Si_5	Si_4-Si_5
B3LYP	1.320	2.176	2.176	2.143	1.842	2.143	2.503	2.393	2.503
M06-2X	1.318	2.117	2.117	2.165	1.843	2.165	2.467	2.368	2.467
PBE0	1.331	2.127	2.127	2.113	1.834	2.113	2.471	2.370	2.471

02	Si_1-Si_2	Si_1-C_3	Si_2-C_3	C_3-C_4	C_4-Si_5
B3LYP	2.286	1.876	1.876	1.340	1.703
M06-2X	2.275	1.859	1.859	1.351	1.689
PBE0	2.272	1.866	1.866	1.344	1.696

03	Si_1-Si_2	Si_1-Si_3	Si_2-Si_3	Si_3-C_4	C_4-C_5
B3LYP	2.405	2.251	2.251	1.792	1.252
M06-2X	2.376	2.234	2.234	1.796	1.248
PBE0	2.385	2.242	2.242	1.789	1.252

Table 4. The bond lengths(Å) of the closo-$C_2Si_3^{2-}$ in the **01** and **Mg-1**

	C_1-C_2	C_1-Si_3	C_1-Si_5	C_2-Si_3	C_2-Si_4	C_2-Si_5	Si_3-Si_4	Si_3-Si_5	Si_4-Si_5
01	1.320	2.176	2.176	2.143	1.842	2.143	2.503	2.393	2.503
Mg-1	1.355	2.200	2.200	2.150	1.771	2.150	2.577	2.316	2.577

Smallest deltahedra silicon dicarbide: $C_2Si_3^{2-}$

Jing-jing Sui, Jing Xu, Yi-hong Ding*

Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China. E-mail: yhdd@jlu.edu.cn

In this paper, we reported the smallest main-group dicarbide with all deltahedras, which is also the first main-group dicarbide with (n + 1) polyhedral skeletal electron pairs (PSEPs).