Russian Chemical Bulletin, Vol. 46, No. 1, January, 1997

Simulation of the structure of some silicon carbide clusters by the MNDO method

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Simulations of the geometric and electronic structure of C_{44}, C_{45}, Si_{45}, $C_{40}Si_5$, and $C_{44}Si$ clusters were performed by the MNDO method. The geometries of the filled clusters, calculated by the MM2 method, were used as initial approximations. It was found that the filled clusters C_{45} and $C_{44}Si$ are transformed into endohedral clusters $X@C_{44}$ (X = C or Si, respectively) after energy optimization. The highest occupied energy level of the HOMO of the filled tetrahedral cluster Si_{45} of T symmetry is triply degenerate and is only occupied by four electrons. The structure of Si_{45}^{2-} dianion of T symmetry was calculated. Two filled structures for the $C_{40}Si_5$ cluster were found. The coordination numbers of the central Si atom in these structures are 4 and 3, respectively.

Key words: carbon, silicon, silicon carbide, clusters; quantum-chemical calculations, MNDO.

The results of investigations carried out recently point to the fact that stable carbon clusters containing several tens of atoms have the structure of a hollow polyhedron with an even number of vertices (see previously published reviews[1–3] and references therein). The configurations of the silicon clusters containing the same number of atoms has not been experimentally established. However, it was shown in a number of publications[4,5] that the clusters formed after evaporation of the crystalline silicon under the action of laser irradiation mainly contain an odd number of atoms, and the most intense peaks in the mass spectra correspond to Si_{45}^+, Si_{39}^+, and Si_{33}^+ cations.

The structure of silicon clusters containing various number of atoms was simulated by computational methods:[6–14] by the molecular mechanics method, in the MO LCAO approximation, and by the electron-density functional method. Along with the hollow polyhedral silicon clusters (fullerene structures, stacked, and some other forms),[11–13] so-called filled clusters consisting of sp^3- and sp^2-hybridized Si atoms (see Refs. 6–8, 14) were considered. Thus, the tetrahedral models of Si_{45} and Si_{33} filled clusters were designed using the method of atom-atom potentials and electron-density functional theory.[6,7] It was found, in particular, that the coordination number (CN) of the surface atoms in the Si_{45} cluster is 3. These atoms are bound to internal atoms, which have a coordination number of 4, and form six chains, in which π-bonding is partly realized.

The calculations of the geometric and electronic structure of Si_{45}, C_{44}, Si_{44}, and C_{45} clusters were carried out in the local electron density functional approximation.[8] The results, obtained by the molecular mechanics method,[7] were used as initial data for the Si_{45} calculations. In the case of C_{45}, the same cluster of the filled structure served as the initial approximation. The difference in the length of the C—C and Si—Si bonds was taken into account by the scaling method.

The central atoms of Si_{45} and C_{45} filled clusters were removed in the initial step of the calculations of Si_{44} and C_{44} clusters. After optimization of the energy over the geometric parameters, it was established that Si_{45} and C_{45} clusters have structures of filled polyhedra while Si_{44} and C_{44} clusters are transformed into fullerenes, *i.e.*, polyhedral hollow molecules. In addition, the Si_{45} cluster was shown to be more stable than Si_{44}.[8] On the contrary, in the case of C_{45} and C_{44} clusters, the C_{44} fullerene is more stable. We also note that on the basis of results of the calculations of Si_n clusters (n = 21, 29, 34, 44, and 45) by AM1 and *ab initio* methods, it was concluded[14] that the formation of fullerene structures is preferable in the case of an increase in the number of Si atoms.

Method of Calculations

The possible existence of filled clusters of both homoatomic and mixed compositions C_nSi_m (silicon carbides) was studied by the semiempirical MNDO method. Calculations using a DEC Alpha AXP 3000-400 workstation showed that this method allows qualitatively investigating atomic dynamics in the Born—Oppenheimer approximation depending on the starting approximation.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 54—56, January, 1997.

1066-5285/97/4601-0049 $18.00

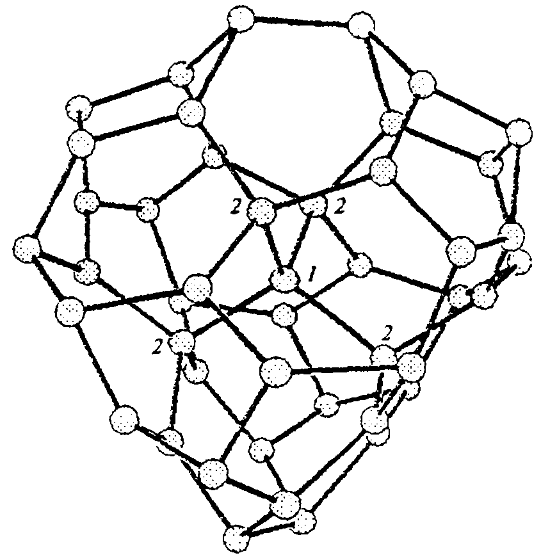

Fig. 1. Structure of the Si_{45}^{2-} (**1**) filled cluster (MNDO): *1*, central atom (tetrahedral); *2*, one of the four nearest neighbors (tetrahedral); non-designated atoms (*3*) are located at the cluster surface and have sp^2-hybridization. Bond lengths (Å): 2.17 (*1—2*), 2.10 (*2—3*), and 2.07 (*3—3'*).

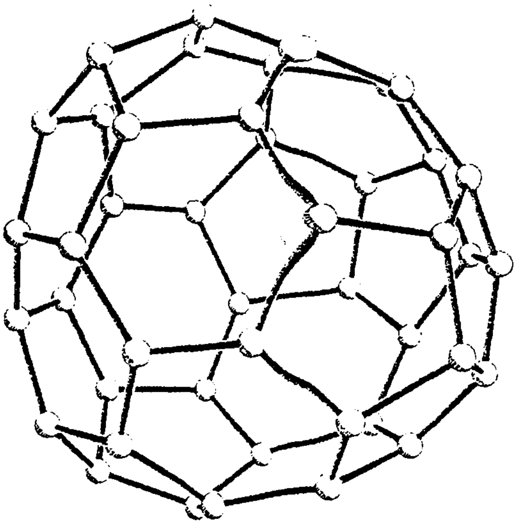

Fig. 2. Structure of the C_{44} (**2**) polyhedral cluster (MNDO). The C—C bond lengths vary from 1.39 to 1.52 Å.

Results and Discussion

The geometry obtained in the molecular mechanics approximation[7] for the Si_{45} cluster with tetrahedral *T* symmetry was used as the starting geometry for the Si_{45} calculations. However, according to the MNDO calculations, the highest occupied energy level of the HOMO in the Si_{45} cluster with *T* symmetry is triply degenerate and only occupied by four electrons. Therefore, either a cluster with lower symmetry or a dianion with a fully occupied degenerate energy level can have a closed electron shell.

We failed to find the structure of the neutral Si_{45} cluster with a closed electron shell, therefore, we performed calculations for Si_{45}^{2-} dianion (**1**) whose geometry was optimized by the MNDO method taking into account its *T* symmetry. A local minimum was found on the corresponding potential energy surface. The lengths of the bonds of the central Si atom to the four nearest neighboring atoms in the optimized structure of dianion **1** are 2.165 Å (Fig. 1).

Full optimization of the geometry was performed in simulating the structure of C_{44}, $C_{44}Si$, $C_{40}Si_5$, $C_{40}Si_5^{2-}$, and C_{45} clusters. In this case, it was assumed that the central atom in compounds $C_{44}Si$ and $C_{40}Si_5$ is the Si atom. The central atom is only bound to Si atoms in the $C_{40}Si_5$ cluster. The geometric parameters obtained after optimization of the above systems by the molecular mechanics method were taken as the starting geometric parameters. It should be noted that in this approximation, the C_{45}, $C_{44}Si$, and $C_{40}Si_5$ clusters have the structures of filled polyhedra in which the central atom (the Si atom in the last two systems) forms four covalent bonds. Using the MNDO method, in the case of the C_{45} and $C_{44}Si$ clusters structures were obtained in which the central atoms (C and Si, respectively) are located inside the fullerene C_{44} (structure **2** in Fig. 2) and are not chemically bound to other atoms. (It is conventional to denote similar clusters as $C@C_{44}$ and $Si@C_{44}$).

The C_{44} cluster contains 12 pentagons, 12 hexagons, and 66 C—C bonds. In the topological approximation, this molecule has a pseudoclosed electron shell (the highest bonding orbital is vacant); the width of the forbidden zone separating the energies of the occupied and filled orbitals is $0.44|\beta|$ (β is the resonance integral). One can design a model of the C_{44} cluster having tetrahedral symmetry; in this case, the pentagons are located in triplets at each of the tetrahedron vertices. However, optimization of the geometry of this cluster by the MNDO method results in a fullerene of distorted tetrahedral structure (see Fig. 2).

Two structures, **3a** (Fig. 3) and **3b**, in which the coordination numbers of the central Si atom are 4 and 3, respectively, were found after geometric optimization of the $C_{40}Si_5$ molecule. Structure **3b** is energetically more favorable than **3a** by 14.5 kcal mol^{-1}.

The enthalpies of formation, HOMO and LUMO energies, and the distances between the central atom and the nearest neighboring atoms in C_{44}, C_{45}, Si_{45}^{2-}, $C_{40}Si_5$, and $C_{44}Si$ clusters calculated by the MNDO method are listed in Table 1.

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It follows from the results of our calculations that the formation of filled structures is preferential for Si_{45} and

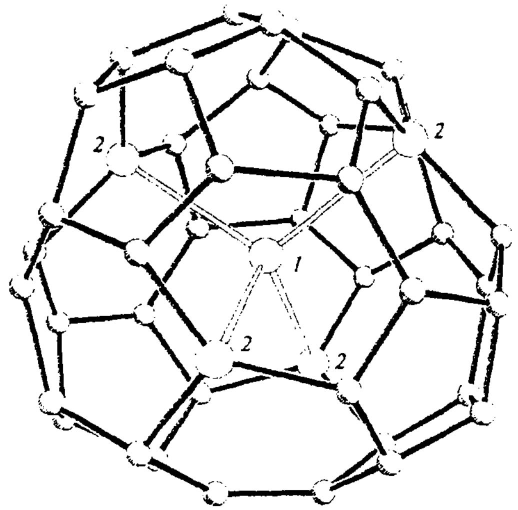

Fig. 3. Structure of the $C_{40}Si_5$ (**3a**) filled cluster (MNDO): *1*, central Si atom (tetrahedral); *2*, one of the four Si atoms nearest to *1* (tetrahedral); non-designated atoms (*3*) are located on the cluster surface and have sp^2-hybridization. Bond lengths (Å): 2.20 (*1—2*), 1.74 (*2—3*) and 1.48 (*3—3'*).

Table 1. Enthalpies of formation ($\Delta_f H$/kcal mol^{-1}), HOMO and LUMO energies (E/eV), $\Delta E = E_{LUMO} - E_{HOMO}$, and distances ($R$/Å) between the central atom and nearest neighboring atoms, calculated by the MNDO method

Cluster	Symmetry	$\Delta_f H$	$-E_{HOMO}$	E_{LUMO}	ΔE	R
C_{44}	C_1	993.0	8.80	−3.21	5.59	—
$C@C_{44}$	C_1	1259.7	8.51	−3.50	5.01	2.86
$Si@C_{44}$	C_1	1171.9	8.56	−3.56	5.00	2.10
$C_{40}Si_5$ (**3a**)	C_1	1181.6	8.64	−2.23	6.41	2.40—2.45
$C_{40}Si_5$ (**3b**)	C_1	1167.1	8.35	−2.97	5.38	2.20
$Si_{45}{}^{2-}$	T	1207.0	2.14	0.20	2.34	2.16

$C_{40}Si_5$ clusters whereas the endohedral fullerene structures are characteristic of C_{45} and $C_{44}Si$ clusters. An analogous conclusion on the instability of filled carbon clusters was also drawn in Ref. 15; it was shown (using the electron-density functional method) that the C_{100} system, whose inner part has a diamond-like structure, is transformed into the $C_{20}@C_{80}$ endohedral cluster without a barrier. These results point to the fact that the geometry of silicon compounds and carbon compounds containing several tens of atoms must differ fundamentally. In the case of silicon carbide clusters, the existence of both filled and fullerene structures is possible.

The authors express their gratitude to M. Schmidt for submitting the GAMESS program[16] adapted for the DEC Alpha AXP 3000-400 workstation.

This work was supported in part by the Intellectual Cooperation Foundation within the framework of the program "Physics of continuous media" (the investigation line "Fullerenes and atomic clusters", Project No. 94-013), as well as by the International Scientific-Technical Center (Project No. 079).

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Received July 24, 1996