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The Structure and Stability of Si_{60} and Ge_{60} Cages: A Computational Study

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Abstract: Structural studies of fullerene-like Si_{60} and Ge_{60} cages using *ab initio* methods were augmented by density functional tight-binding molecular dynamics (DFTB-MD) simulations of finite temperature effects. Neither the perfect I_h symmetry nor the distorted T_h structures are true minima. The energies of both are high relative to distorted, lower symmetry minima, C_i and T, respectively, which still preserve C_{60}-type connectivity. Both Si_{60} and Ge_{60} favor C_i symmetry cages in which Si and Ge vertexes exhibit either near-trigonal or pyramidal geometries. These structural variations imply significant reactivity differences between different positions. The small magnetic shielding effects (NICS) indicate that aromaticity is not important in these systems. The inorganic fullerene cages have lower stabilities compared with their carbon analogs. Si_{60} is stable towards spontaneous disintegration up to 700 K according to DFTB-MD simulations, and thus has potential for experimental observation. In contrast, Ge_{60} preserves its cage structure only up to 200 K.

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Key words: inorganic fullerenes; Si_{60}; Ge_{60}; DFT; DFTB

Introduction

Soon after the discovery of fullerene, the structures of its silicon and germanium analogs were proposed and investigated at various level of theory. However, the literature does not agree, and the lowest energy geometries were not established. Most of the studies simply assumed Si_{60} and Ge_{60} to preserve the perfect I_h symmetry cage structure of C_{60} as the ground state.[1] Such intuitive geometries also were employed to model endohedral complexes[2] and double-layered heterofullerenes $C_{60}@Si_{60}$.[1,3] Even after taking other structures into account, Nagase et al.[4] found the hollow spherical cage still to be preferred energetically. However, several authors pointed out that icosahedral Si_{60} is not stable and relaxes into a distorted structure.[5] Tight-binding molecular dynamics simulations gave a puckered ball-like geometry (Khan and Broughton[5a]) and lower symmetry C_{2h} structure (Menon and

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Table 1. Calculated Relative Energies (kcal/mol), HOMO-LUMO Gap Energies (eV), the Number of Imaginary Frequencies (NImag), and Lowest Vibrational (Real or Imaginary) Frequencies (ω_1; cm^{-1}) for Si_{60}.

Symmetry	I_h	T_h	T	C_i
E_{rel}[a]	76.5	72.5	3.6	0.0
NImag[a]	16	10	0	0[c]
ω_1[a]	−211.3	−164.7	67.5	62.9[c]
E_{gap}[a]	4.41	4.14	4.54	4.68
E_{rel}[b]	91.3	56.2	4.7	0.0
E_{gap}[b]	1.31	1.06	1.31	1.40
E_{rel}[d]	132.8	66.4	4.2	0.0

[a]At HF/3-21G.
[b]At B3LYP/6-31G*.
[c]At HF/STO-3G.
[d]At DF-TB.

Subbaswamy).[5b] According to full-potential LMTO molecular dynamics (FP-LMTO-MD),[5c,5d] the icosahedral Si_{60} and Ge_{60} cages distort to T_h symmetry. First-principle quantum-molecular-dynamics calculations predict the fullerene-like structure to be metastable, but still relatively low in energy, while the compact network (high coordination) structure is the equilibrium configuration.[5e] Based on tight-binding molecular dynamic calculations using the bulk diamond lattice fragments as the initial structure, Yu et al. proposed that the most stable Si_{60} form is composed of cage subunits like Si_6, Si_7, Si_{10} and Si_{12}.[5f]

A similarly confusing picture exists experimentally. The fullerene structure was implied by a saturation study of Si_{60} positive ions, which revealed that ammonia only binds to a small number of cluster sites[6] (as for C_{60}).[7] A stacked naphthalene-like layer structure was suggested by the fragmentation analysis of Si_{60} positive ions.[8]

Less attention has been paid to germanium than to silicon fullerenes. The perfect I_h symmetry Ge_{60} cage structure has been proposed by Nagase[1d] and by Leszczynski.[1k] However, Slanina found the Ge_{60} cage to be distorted while retaining the fullerenic connectivity; in contrast, he claimed Si_{60} still to exhibit the exact I_h symmetry.[1g] Menon declared that among the group IV elements, perfect icosahedral symmetry is unique to carbon.[5b] Ge_{60} has been found to favor a distorted cage structure with T_h symmetry by full-potential molecular dynamic studies.[5c]

To clarify the bewildering discrepancies in the literature and to gain further insight into the electronic properties of Si_{60} and Ge_{60} cages, we have now optimized structures with different symmetries and performed vibrational frequency analyses at *ab initio* and DFT levels. Density functional tight-binding molecular dynamics (DFTB-MD) simulations revealed the finite temperature effects on the stabilities.

Computational Details

The geometries were fully optimized and vibrational frequencies were computed at the Hartree–Fock (HF) level with the 3-21G basis set for silicon and the Lanl2DZ pseudopential for germanium (except for C_i symmetry Si_{60} where the STO-3G basis set was used for frequency analysis). I_h and T_h symmetry structures were computed initially; following the displacements of the first of the imaginary frequencies which resulted then led to the C_i and T symmetry cages. Further full optimizations were performed using the B3LYP hybrid density functional method[9] with 6-31G* and Lanl2DZ basis sets for silicon and germanium, respectively. Moreover, single-point energy computations were carried out for Ge_{60} using the Lan2DZp basis set (with one additional set of d polarization functions at Ge).[10] Nucleus-independent chemical shifts (NICS),[11] calculated at the centers of the cages and of the individual rings, evaluated the aromaticity. All these calculations employed the GAUSSIAN 98 suite of programs.[12] The relative total energies at both HF and DFT levels, the number of imaginary frequencies (NImag), and the lowest-magnitude (imaginary) vibrational frequencies at the HF level are summarized in Tables 1 and 2. To investigate the finite temperature effects, molecular dynamics (MD) simulations were performed using the Density-Functional Tight-Binding (DFTB) method;[13] a time step of 0.24 fs was chosen in the total simulation time of 12 ps.

Results and Discussion

Although silicon and carbon are isovalent group IV elements, it is well known that they have different chemical bonding properties.[14] Due to the versatile bonding behavior and the ability to form single, double, and triple bonds, carbon can form many diverse structures such as graphite, diamond, fullerenes, carbon nanotubes, amorphous carbon, porous carbon, and graphite intercalation compounds. Carbon clusters can utilize strong π-bonds to produce chains, rings, cages, and tubes. In contrast, silicon does not form energetically favorable double and triple bonds, also in cages. This is indicated by various distorted[5d,15] silicon clusters that also may

Table 2. Calculated Relative Energies (kcal/mol), HOMO-LUMO Gap Energies (eV), the Number of Imaginary Frequencies (NImag), and Lowest Vibrational (Real or Imaginary) Frequencies (ω_1; cm^{-1}) for Ge_{60}.

Symmetry	I_h	T_h	T	C_i
E_{rel}[a]	163.7	123.7	3.5	0.0
NImag[a]	19	13	0	0
ω_1[a]	−145.9	−60.6	33.6	35.2
E_{gap}[a]	4.45	3.90	4.46	4.55
E_{rel}[b]	206.4	86.8	4.8	0.0
E_{gap}[b]	0.99	1.02	1.28	1.40
E_{rel}[c]	212.8	91.2	6.4	0.0
E_{rel}[d]	275.3	80.3	15.2	0.0

[a]At HF/LANL2DZ.
[b]At B3LYP/LANL2DZ.
[c]At B3LYP/LANL2DZp//B3LYP/LANL2DZ.
[d]At DF-TB. The validity of DFTB for describing germanium containing systems has been shown in Hajnal, Z.; Vogg, G.; Meyer, L. J. P.; Szuecs, B.; Brandt, M. S.; Frauenheim, T. Phys Rev B 2001, 64, 33311.

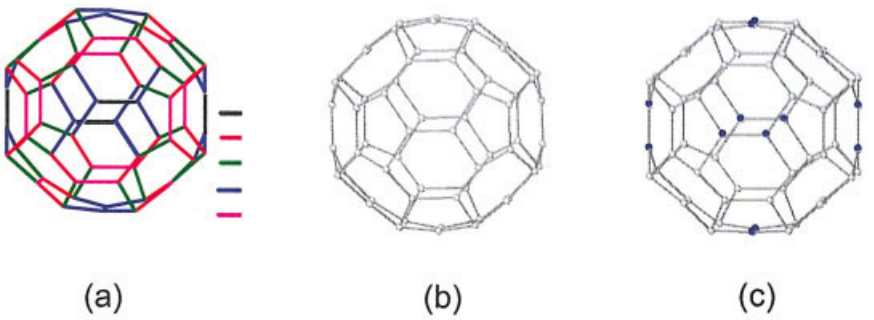

Figure 1. DFT optimized T_h symmetry clusters (a) five types of bonds (given in Table 3); (b) Si_{60}. (c) Ge_{60}; the germainum atoms with π conjugation are distinugished by blue coloring.

utilize hypercoordinate bonding.[16] Similarities between germanium and silicon clusters have been reported,[5c,17] and are supported experimentally by photofragmentation and reactivity results.[18]

Data in Tables 1 and 2 confirm that I_h symmetry Si_{60} and Ge_{60} clusters are far from being true minima. Frequency analyses at the HF level of theory reveal 16 and 19 imaginary frequencies, respectively! The vectors of the first imaginary frequencies lead to C_i symmetry clusters that are true minima both for Si_{60} and Ge_{60}.

Employing full-potential LMTO molecular dynamics (FP-LMTO-MD) method,[5c,5d] Li et al. found that Si_{60} and Ge_{60} distort to T_h symmetry. However, our frequency analyses indicate that T_h symmetry structures are also higher order saddle points with 10 and 13 imaginary frequencies, respectively (Tables 1 and 2). Instead, lower energy T symmetry minima were obtained following the first imaginary vibration in T_h structures for both Si_{60} and Ge_{60}.

In I_h symmetrical clusters, all atoms have near trigonal geometries. The bond lengths for 6-6 and 6-5 bonds are 2.236 and 2.284 Å in Si_{60} and 2.363 and 2.426 Å in Ge_{60}, respectively. The previously proposed T_h symmetry clusters have five types of bonds (shown in Fig. 1; bond lengths are given in Table 3). These structures resemble puckered balls with some pyramidally distorted vertexes.

At our DFT level, the C_i minima are preferred over the T minima by 4.7 and 4.8 kcal/mol for Si_{60} and Ge_{60}, respectively (adding polarization functions does not change the Ge_{60} isomer energy order, Table 2). The optimized T symmetry geometries are shown in Figure 2 their bond lengths are summarized in Table 4.

Table 3. Optimized Bond Lengths (Å) of Si_{60} (T_h) and Ge_{60} (T_h).[a,b]

Bond	Si_{60}	Ge_{60}
a	2.226	2.367
b	2.274	2.469
c	2.302	2.501
d	2.320	2.514
e	2.287	2.460

[a]See Figure 1.
[b]B3LYP/6-31G* for Si_{60}, B3LYP/LANL2DZ for Ge_{60}.

Eight sets of bonds exist in T symmetry clusters; the ranges are 2.224–2.337 Å in Si_{60} and 2.375–2.551 Å in Ge_{60}. Figure 3 shows the optimized structures of the most stable C_i clusters, the bond length ranges are 2.234–2.344 Å in Si_{60} and 2.393–2.561 Å in Ge_{60}. Some atoms have three nearly coplanar neighbors (24 in T and 30 in C_i), while others favor tetrahedral-like geometries, with atoms popped outside the plane of their neighbors. These atoms should be more reactive than their trigonal counterparts. The DFT binding energies of the most stable Si_{60} and Ge_{60} clusters are only 3.36 and 2.69 eV/atom, about or less than half of the binding energy of C_{60} (6.98 eV/atom), which indicates their relative low stability compared to their carbon analog. To assist future experiments, the vertical ionization potentials (IP, 6.234 and 6.166 eV) and electron affinities (EA, 3.141 and 3.360 eV) of the most stable C_i symmetrical Si_{60} and Ge_{60} cages, respectively, also were computed.

Further insight into the bonding nature of silicon and germanium fullerenes was provided by NBO (Natural Bonding Orbital) analyses[19] at the B3LYP level. Regardless of different symmetries ranging from I_h to C_i, there are 120 BD (two-center bond) NBOs in Si_{60}, 90 corresponding to σ bonds and 30 to π bonds, with nearly pure p character at the silicon atoms. Hence, there are 30 double bonds at the hexagon-hexagon junctions of Si_{60}, which resembles C_{60} in I_h symmetry. However, unlike the nonpolarized bonds in C_{60}, the π bonds in the most stable C_i symmetry Si_{60} cage are heavily polarized with ca. 66% towards the pyramidal Si atoms, whereas the σ bonds are only slightly polarized. The π conjugation around the whole silicon cage shortens the silicon–silicon bond lengths significantly; the double bond range is 2.234–2.301 Å, somewhat shorter than the Si–Si bond length in bulk silicon (2.35 Å).

However, Ge_{60} is different. The unrealistic Ge_{60} (I_h) has bonding similar to C_{60}, with 30 nonpolarized single bonds and 30 nonpolarized double bonds. But the distorted Ge_{60} cages only have six π bonds located at the hexagon-hexagon junctions (Figs. 1–3) and 90 σ bonds, instead of the other 24 π bonds, there are 24 lone pair NBOs. The π bonds still have >90% p character and while the π bonds are nonpolarized in T_h and T symmetrical cages, some polarization towards the trigonal atoms (ca. 56%) exists in Ge_{60} (C_i). The double bond lengths are nearly the same, 2.367 , 2.375, and 2.393 Å in the T_h, T, and C_i symmetry cages, respectively,

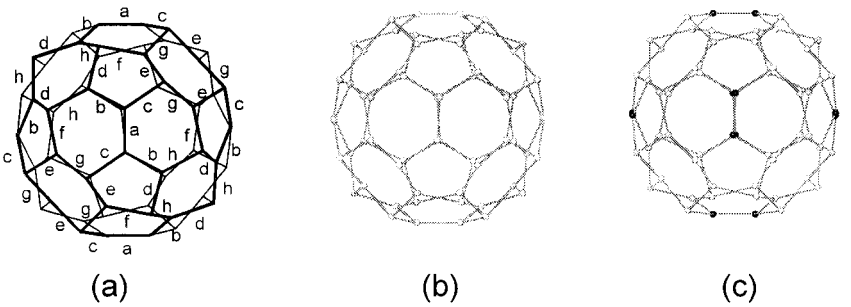

Figure 2. DFT optimized *T* symmetrical clusters (a) eight types of bonds (given in Table 4); (b) Si_{60}; (c) Ge_{60}; the germainum atoms with π conjugation are distinguished by dark coloring.

shorter than the single bond in bulk germanium (2.45 Å). The 24 lone pairs in the distorted Ge_{60} cages are located at the pyramidal atoms at other hexagon–hexagon junctions without π conjugation. Except for the six double bonds mentioned above, all the other 84 bonds, at both hexagon–hexagon and hexagon–pentagon junctions are single bonds in the distorted cages, even longer than the single bond in the bulk. Figure 4 shows the π bonds in Si_{60} (C_i) and the lone pair electrons in Ge_{60} (C_i) to illustrate the difference of the bonding properties in the most stable distorted cages.

As in the inorganic Si_{60} and Ge_{60} fullerenes, the inorganic benzene homologs, Si_6H_6 and Ge_6H_6, also do not have planar energy minima. The most stable Si_6H_6 and Ge_6H_6 geometries have D_{3d} symmetry; the D_{6h} form has NImag = 1 for Si_6H_6 and NImag = 3 for Ge_6H_6. The D_{3d} structures of Si_6H_6 and Ge_6H_6 are more stable than the D_{6h} forms by 2.3 and 14.5 kcal/mol at the B3LYP/6-311+G** level. However, this distortion does not affect the aromaticity significantly, as indicated by their NICS(1) values of −12.8 (D_{6h}) and −11.4 (D_{3d}) ppm for Si_6H_6, as well as −14.5 (D_{6h}) and −9.9 (D_{3d}) ppm for Ge_6H_6; these are comparable to the benzene NICS(1) of −10.7 ppm.[20]

The modest aromaticity of C_{60},[21] is evidenced by the experimentally measured endohedral helium chemical shift (−6.3 ppm),[22] which is close to the −8.0 ppm computed NICS(0) value at the cage center (at GIAO-HF/3-21G//B3LYP/6-31G*),[23] and the modest NICS(sum) = −34.3 ppm of all the ring centers. How aromatic are the heavier C_{60} analogs, Si_{60} and Ge_{60}? Table 5 summarizes computed NICS(0) and NICS(sum) values together with the relative energies of the four isomers. NICS(0) of the high energy I_h symmetry Si_{60} and Ge_{60} forms are both quite small (ca −1.5 ppm), suggesting essentially nonaromatic character. Although the distorted but more stable isomers have somewhat more negative NICS(0) in the −6.0 to −8.6 ppm range, there is no apparent relationship with the relative energies. Strain and other effects are more important than aromatic stabilization energies. The NICS(sum) values are larger, but the variations do not correlate with the relative energies. In short, "aromaticity" is not the main effect responsible for the enhanced stability of the distorted Si_{60} and Ge_{60} cages.

The relative energy order given by DFT is reproduced well at the DFTB level by conjugate gradient relaxation calculations (see Tables 1 and 2). The latter method was also used to perform constant temperature molecular dynamics simulations to elucidate the stability of C_i symmetrical structures. During a simulation time of 12 ps (50,000 steps), heating Si_{60} (C_i) to 700 K did not lead to structural breakdown and Si_{60} retained essentially the same structure, while the highest temperature of Ge_{60} to preserve its C_i symmetrical cage structure is only 200 K. Si_{60} and Ge_{60} collapse at 750 K and 250 K, respectively, in MD simulations of 12 ps. For comparison, C_{60} is stable against thermal disintegration up to 4500 K.[24] These MD simulations indicate that Si_{60} and Ge_{60} cages are less stable than their C_{60} analog, but Si_{60} should be viable, in contrast to Ge_{60}.

Table 4. Optimized Bond lengths (Å) of Si_{60} (*T*) and Ge_{60} (*T*).[a,b]

Bond	Si_{60}	Ge_{60}
a	2.224	2.375
b	2.290	2.457
c	2.334	2.535
d	2.311	2.519
e	2.325	2.529
f	2.337	2.551
g	2.299	2.502
h	2.293	2.494

[a]See Figure 2.
[b]B3LYP/6-31G* for Si_{60}, B3LYP/LANL2DZ for Ge_{60}.

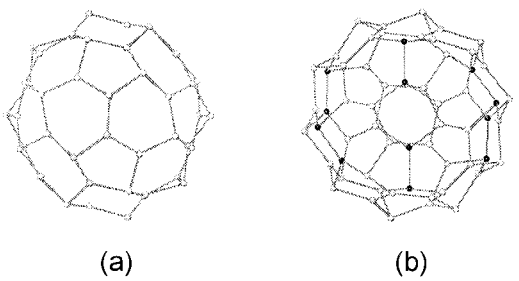

Figure 3. DFT optimized C_i symmetry clusters (a) Si_{60} (b) Ge_{60}; the germanium atoms with π conjugation are distinguished by dark coloring.

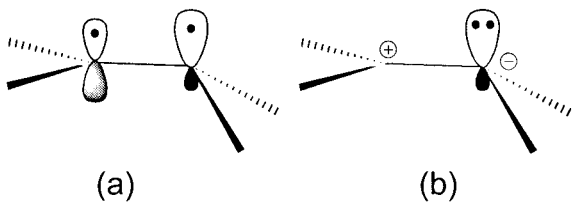

Figure 4. The π bonds in Si_{60} (C_i) and lone pair electrons in Ge_{60} (C_i).

Conclusion

The lowest energy structures of Si_{60} and Ge_{60} cages, computed by *ab initio* and DFT methods, do not possess the perfect I_h symmetry of C_{60} nor the recently proposed distorted T_h structures. Both I_h and T_h forms are multiorder saddle points with unfavorable energies. Instead, the distorted C_i and T symmetrical cages (derived from I_h and T_h structures) are true minima, and preserve the C_{60} connectivity. The C_i symmetries are preferred energetically. Both near-trigonal and pyramidal vertexes are found in these C_i and T structures; this implies a significant reactivity difference between these two kinds of atoms. The geometries of Ge_{60} are rather similar to Si_{60}; however, the nature of the bonding is quite different according to NBO analysis. Neither cage exhibits more than weak aromaticity, judging from the NICS values. The inorganic fullerene cages have lower thermal stabilities than their carbon analogue, but Si_{60} may be a viable preparative target.

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Table 5. Relative Energies (kcal/mol) of Si_{60} and Ge_{60} Isomers, NICS(0) Values at the Cage Centers (ppm), and the NICS (sum) at All the Ring Centers.

	I_h	T_h	T	C_i
Si_{60}				
RE[a]	91.3	56.2	4.7	0.0
NICS(0)[b]	−1.4	−6.9	−6.0	−7.8
NICS(sum)[b]	−7.7	−65.8	−34.1	−56.7
Ge_{60}				
RE[c]	206.4	86.8	4.8	0.0
NICS(0)[d]	−1.5	−8.6	−6.5	−7.8
NICS(sum)[d]	3.5	−54.9	−4.3	−19.7

[a]B3LYP/6-31G*.
[b]GIAO-HF/3-21G//B3LYP/6-31G*.
[c]B3LYP/LanL2DZ.
[d]GIAO-HF/LanL2DZ//B3LYP/LanL2DZ.

Supplementary Material Available

Total energies at HF, DFT, and DFTB levels, and Gaussian archive entries for DFT optimized structures are given.

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