

Theoretical study of heteroatom-containing compounds. From aromatic and polycyclic molecules to hollow cage clusters

Shigeru Nagase

Department of Chemistry, Faculty of Education, Yokohama National University
Yokohama 240, Japan

Abstract- By means of molecular orbital calculations, the compounds whose skeletons are made of the heavier group 14 or group 15 atoms are investigated. Included are the heavier analogues of aromatic, antiaromatic, and polycyclic carbon compounds. To characterize the properties of the heavier atom skeletons, the applicability of the important concepts such as aromaticity and strain established in carbon chemistry is discussed. It is found that substituents have remarkable effects on the aromaticity and strain of the heavier atom skeletons. Also investigated are the heavier analogues of hollow cage carbon clusters (fullerenes) of current interest.

INTRODUCTION

Carbon compounds have played a central role in organic chemistry. It is currently of considerable interest to replace the skeletal carbons by the heavier homologues (Si, Ge, Sn, and Pb) or neighboring atoms (P, As, Sb, and Bi) in the expectation of novel physical and chemical properties (for a review, see ref. 1). We report here the theoretical studies of the heavier analogues of aromatic, antiaromatic, and polycyclic carbon compounds as well as hollow cage carbon clusters. Aromaticity and strain are two important concepts and the usefulness is well established in carbon chemistry. Our primary concern is to investigate if these concepts are also applicable in the same way and clarify what is characteristic of the heavier analogues.

AROMATIC AND ANTIAROMATIC COMPOUNDS

Benzene (C_6H_6) is unique among conjugated compounds with respect to its stability and reactivity. This has been attributed to aromaticity or the cyclic delocalization of π electrons, as the $(4n + 2)$ Hückel rule suggests. Silicon is contiguous to carbon in group 14. Thus, it is no wonder to expect that hexasilabenzene (Si_6H_6) has also a planar hexagonal structure of D_{6h} symmetry since it contains 6π electrons.

However, it is found that the planar D_{6h} structure of Si_6H_6 is not a minimum but corresponds to a transition structure with one single imaginary b_{2g} frequency (refs. 2 and 3). Displacement along the b_{2g} vibrational mode leads to a minimum with a chair-like puckered structure of D_{3d} symmetry.

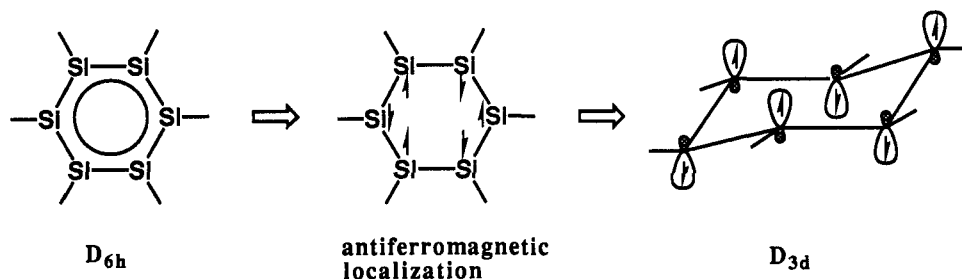


Fig. 1. Deformation from the planar D_{6h} to the non-planar D_{3d} structure in hexasilabenzene (ref. 1).

As Fig. 1 shows, the skeletal bonding of hexasilabenzene is characterized in terms of a spin density wave (alternative localization of α and β electrons) (ref. 2). A tendency of the antiferromagnetic localization of π electrons generates silyl radical character on each Si atom and leads to the preference of the non-planar D_{3d}

structure since silyl radicals take a pyramidal structure. This suggests that aromaticity is of limited value when it is applied to the heavier system. The preference of the non-planar D_{3d} structure is further enhanced as the skeletal atoms are replaced by the heavier Ge, Sn, and Pb atoms, the planar D_{6h} structures being 9.1 (Ge_6H_6), 23.1 (Sn_6H_6), and 63.3 (Pb_6H_6) kcal/mol less stable at the MP2/DZ+d//HF/DZ+d level (ref. 1). The pronounced preference of the non-planar D_{3d} structures is due to the increased tendency of π electrons to localize in an antiferromagnetic way: this is consistent with the fact that upon going to germlyl, stannyl, and plumblyl radicals, the pyramidal structures are progressively favored. Thus, planar hexagonal structures with 6π electrons have no special meaning in the heavier analogues, unlike in the case of C_6H_6 .

To enrich the chemistry of the heavier aromatic compounds, however, it is very important to control the non-planarization problem. For this purpose, the effects of substituents were investigated (ref. 4). Apparently, desirable substituents should increase the aromatic stabilization of the planar structure and suppress the non-planarization.

The aromatic stabilization energy of the planar Si_6H_6 is half as large as that of C_6H_6 (ref. 5). As TABLE 1 shows, the stabilization energy is decreased when the H atoms are substituted by CH_3 groups and the planar structure is highly destabilized upon substitution by F atoms. In contrast, the aromatic stabilization is significantly increased to 15.5 and 21.7 kcal/mol upon substitution by the BH_3 and SiH_3 groups, respectively. Interestingly, the aromatic stabilization energy of $Si_6(SiH_3)_6$ compares favorably with that (24.7 kcal/mol) of C_6H_6 .

TABLE 1. Aromatic stabilization energies of the planar hexasilabenzene at the HF/6-31G* level (ref. 4).

	kcal/mol ^a
Si_6H_6	11.8
Si_6F_6	-8.7
$Si_6(CH_3)_6$	8.5
$Si_6(BH_2)_6$	15.5
$Si_6(SiH_3)_6$	21.7

^aPositive values for stabilization.

TABLE 2. Relative energies (kcal/mol) of the planar and pyramidal structures of $(SiH_3)_2SiR$ at the HF/6-31G* level (ref. 4).

$(SiH_3)_2SiR$	planar	pyramidal
R = H	0.0	-2.6
R = F	0.0	-7.7
R = CH_3	0.0	-3.6
R = BH_2	0.0	no minimum
R = SiH_3	0.0	-1.0

In an attempt to see next the substituent effects on the suppression of pyramidalization, the $(SiH_3)_2SiR$ radical was calculated as a model. The calculated energy differences between the planar and pyramidal structures are shown in TABLE 2. When R = H, the pyramidal structure is 2.6 kcal/mol more stable than the planar structure. The preference of the pyramidal structure is enhanced to 7.7 and 3.6 kcal/mol with R = F and CH_3 , respectively. However, the pyramidal structure is only 1.0 kcal/mol more stable with R = SiH_3 . In case of R = BH_2 , no pyramidalization is caused and the radical takes a planar structure.

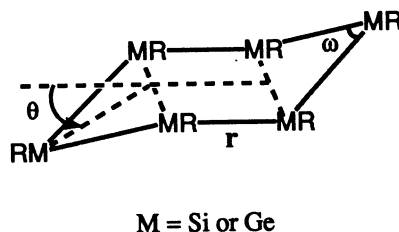
As is apparent from the results in TABLES 1 and 2, it is expected that the SiH_3 and BH_2 groups play an important role in both increasing the aromaticity and preventing the pyramidalization. To confirm this indeed, the structures of hexasilabenzene substituted by these groups were fully optimized, as summarized in TABLE 3. As expected, the SiH_3 - and BH_2 -substituted hexasilabenzene take a planar structure, as does benzene. The charge density analysis shows that the SiH_3 group acts as a good σ donor while the BH_2 group as a good π acceptor. In contrast, the CH_3 group of σ acceptor character has a little effect on the planarization while the planar structure is greatly disfavored with the F atom of σ acceptor and π donor character. These suggest that desirable substituents should have strong σ donor or π acceptor character.

Also shown in TABLE 3 are the SiH_3 -, GeH_3 -, and BH_2 -substituted hexagermanbenzenes. The σ donating effects of the SiH_3 and GeH_3 groups are now not sufficient for the complete planarization. However, it is interesting that the π accepting ability of the BH_2 group is still effective even for the germanium skeleton.

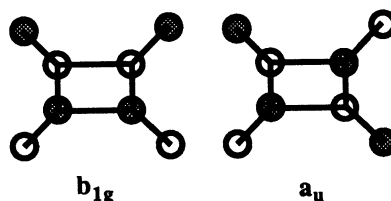
We now turn to the heavier analogues of cyclobutadiene (C_4H_4), a typical antiaromatic compound with 4π electrons. As the skeletal carbons are replaced by the heavier homologues, the planar D_{2h} structure is increasingly disfavored and two vibrational frequencies corresponding to out-of-plane b_{1g} and a_{1u} modes become imaginary (ref. 6). Reflecting antiaromaticity, the stabilization due to puckering is much larger than that in benzene and enhanced as the replacement atoms become heavier. The substituent effects on the two imaginary frequencies of Si_4H_4 and Ge_4H_4 are shown in TABLE 4. As in the case of benzene, the SiH_3 group is effective for the planarization of Si_4H_4 while the BH_2 group is effective for both Si_4H_4 and

TABLE 3. Optimized structures and energies of Si_6R_6 and Ge_6R_6 at the HF/6-31G* and HF/DZ+d levels, respectively (ref. 4).

R	r (Å)	θ (°)	ω (°)	ΔE (kcal/mol) ^a
Si_6R_6				
H	2.231	12.7	119.5	-0.4
F	2.278	50.3	111.2	-14.4
CH ₃	2.222	10.8	119.6	-0.2
SiH ₃	2.226	0.0	120.0	0.0 ^b
BH ₂	2.239	0.0	120.0	0.0 ^b
Ge_6R_6				
H	2.365	38.0	115.0	-5.2
SiH ₃	2.350	23.4	118.1	-0.8
GeH ₃	2.352	25.5	117.8	-1.0
BH ₂	2.341	0.0	120.0	0.0 ^b

^a $\Delta E = E$ (non-planar) - E (planar).^bNo minimum is located for the non-planar structure.TABLE 4. Two out-of-plane frequencies (cm^{-1}) of Si_4R_4 and Ge_4R_4 (ref. 4).^a

R	b_{1g}	a_u
Si_4R_4		
H	161i	134i
F	266i	259i
CH ₃	65i	115i
SiH ₃	54	21
BH ₂	110	164
Ge_4R_4		
H	338i	174i
SiH ₃	54i	54i
GeH ₃	48i	41i
BH ₂	89	99

^aHF/6-31G* for Si_4R_4 and HF/DZ for Ge_4R_4 .

Two out-of-plane vibrational modes.

Ge_4H_4 . However, more sophisticated calculations will be probably essential to the final confirmation of the planar structures since electron correlation tends to prefer a non-planar puckered structure.

It should be mentioned that the heavier group 15 (P, As, Sb, and Bi) analogues correspond to energy minima at the HF level, unlike the heavier group 14 analogues. The heavier atoms have a lower tendency to form hybrid orbitals and they rather maintain the atomic character even in compounds, known in terms of the so-called "inert (ns)² electron pair effect" originating from relativistic effects. This tendency is not especially unfavorable in forming double bonds for the heavier group 15 atoms; therefore, even the heaviest Bi atom can form double bonds, as already pointed out elsewhere (ref. 7). This contrasts with the fact that the heavier group 14 atoms must hybridize to form double bonds; as a result, Sn is very reluctant to form distinct double bonds and the heaviest Pb becomes unable to form double bonds (ref. 1).

POLYCYCLIC COMPOUNDS

Polycyclic compounds such as tetrahedrane, prismane, and cubane are highly strained and have long formed interesting synthetic targets. We have recently calculated that the strain energies decrease significantly when the skeletal carbons are replaced by the heavier homologues (Si, Ge, Sn, and Pb); the decrease in strain is progressively enhanced as the replacement atoms become heavier and the number of four-membered rings increases (or the number of three-membered rings decreases) (refs. 1 and 8-11). This is due to an increasing tendency of the heavier atoms to keep the (ns)²(np)² valence electron configuration even in compounds. It should be noted that the property of the heavier atoms becomes now favorable in

making 90° bond angles with low strain in four-membered rings, though it is still unfavorable in forming three-membered rings with bond angles of ca. 60°. Thus, the heavier group 14 analogues of cubane and prismane as well as bicyclo[2.2.0]hexane have been synthesized and isolated which contain four-membered rings (for a review of experiments, see ref. 12). However, the heavier polycyclic compounds consisting of only three-membered rings undergo bond-stretching or bond-breaking because of high strain. For example, the central bridge bonds of the heavier analogues of bicyclo[1.1.0]butane (refs. 10 and 13) and [1.1.1]propellane (refs. 11 and 14) are stretched to a great extent, as verified by the X-ray study of a pentastanna[1.1.1]propellane derivative (ref. 15). On the other hand, the heavier analogues of tetrahedrane collapse almost without a barrier by breaking the two skeletal bonds to an isomer with one four-membered ring (ref. 16).

In order to remove the disadvantage and enrich further the chemistry of the heavier polycycles, we investigated the substituent effects on the strain energies of three-membered as well as four-membered rings, with the CH₃ and SiH₃ groups as a representative (ref. 17). TABLE 5 shows the strain energies of cyclotrisilanes (*c*-Si₃R₃) and cyclopropanes (*c*-C₃H₆) calculated from the homodesmotic reactions. The calculated strain energy (28.7 kcal/mol) of *c*-C₃H₆ agrees well with the experimental value (27.5 kcal/mol); comparable accuracy would be expected for silicon compounds where experimental data are not available.

As well documented (ref. 18), the strain energy (38.9 kcal/mol) of *c*-Si₃H₆ is ca. 10 kcal/mol larger than that of *c*-C₃H₆. Upon substitution by the CH₃ group, it decreases only by 1.3 kcal/mol, though alkyl groups are usually employed as representative substituents in silicon chemistry. However, substitution by the SiH₃ group has a remarkable effect on the strain energy, *c*-Si₃(SiH₃)₆ becoming 10.8 kcal/mol less strained than the parent *c*-Si₃H₆. As a result, the strain energy (28.1 kcal/mol) of *c*-Si₃(SiH₃)₆ becomes almost equal to that (28.7 kcal/mol) of *c*-C₃H₆. In addition, it is 7.4 and 6.7 kcal/mol smaller than the strain energies of *c*-C₃(CH₃)₆ and *c*-C₃(SiH₃)₆, respectively. These findings are noteworthy since three-membered silicon rings have been widely believed to be more strained than the corresponding carbon rings and are at a disadvantage in forming polycycles.

TABLE 5. Strain energies (kcal/mol) calculated at the HF/6-31G* level (ref. 17).

	R = H	CH ₃	SiH ₃
Cyclopropanes (<i>c</i> -C ₃ R ₆ ; D _{3h})	28.7	35.5	34.8
Cyclotrisilanes (<i>c</i> -Si ₃ R ₆ ; D _{3h})	38.9	37.6	28.1
Tetrasilatetrahedranes (Si ₄ R ₄ ; T _d)	140.9	134.6	114.5
Hexasilaprismanes (Si ₆ R ₆ ; D _{3h})	113.8	105.6	95.7
Octasilacubanes (Si ₈ R ₈ ; O _h)	93.5	88.9	77.9

It is interesting to view the three-membered rings of cyclotrisilanes (*c*-Si₃R₆) as resulting from the interaction of three silylenes (:SiR₂) units. Two interaction modes (a and b) are shown in Fig. 2. As well-known, the parent :SiH₂ has a closed-shell singlet ground state which is ca. 21 kcal/mol more stable than the open-shell triplet state, in contrast to the triplet ground state of :CH₂ (ref. 18). Thus, mode a should be dominant in *c*-Si₃H₆ which leads to a closed-shell repulsion. The singlet-triplet energy difference is a little changed by CH₃ substitution. However, it becomes as small as ca. 4 kcal/mol in :Si(SiH₃)₂ (ref. 19). This marked singlet-triplet closeness is advantageous to open-shell interaction mode b and should lead to the stabilization of *c*-Si₃(SiH₃)₆. The energy closeness makes silicon atoms able to form hybrid orbitals with high p character; sufficiently high p character is essential for a description of the bent bond orbitals in three-membered rings (ref. 20).

To confirm the remarkable substituent effects in polycyclic compounds, the tetrahedrane system was investigated which consists of four three-membered rings. Tetrasilatetrahedrane (140.9 kcal/mol) is as highly strained as tetrahedrane (141.4 kcal/mol) (ref. 8). As TABLE 5 shows, substitution by the CH₃ group decreases the strain energy by 6.3 kcal/mol, the effect being relatively small. On the other hand, the relief of strain becomes as large as 26.4 kcal/mol upon SiH₃ substitution. This might suggest that the long-sought tetrasilatetrahedrane framework (ref. 12) can be an interesting synthetic target with proper substituents.

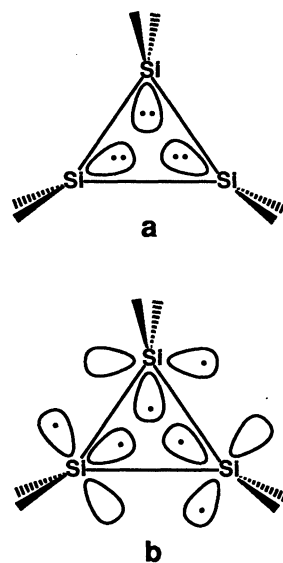


Fig. 2. Two interaction modes of three silylene units (ref. 17).

Also shown in TABLE 5 are the strain energies of the cubane system. The strain energy (93.5 kcal/mol) of octasilacubane consisting of only four-membered rings is already 65 kcal/mol smaller than that (158.6 kcal/mol) of cubane (ref. 8). Upon substitution by the CH_3 and SiH_3 groups, the strain energy is further decreased to 88.9 and 77.9 kcal/mol, respectively, the effect of the SiH_3 group being again larger. This reflects the fact that the strain energy (14.7 kcal/mol) of the SiH_3 -substituted cyclotetrasilane ($c\text{-Si}_4(\text{SiH}_3)_8$) is smaller than that (16.7 kcal/mol) of the parent $c\text{-Si}_4\text{H}_8$; in fact, the strain energy of $c\text{-Si}_4(\text{SiH}_3)_8$ differs little from the strain energy per four-membered ring (13.0 kcal/mol) of $\text{Si}_8(\text{SiH}_3)_8$. As TABLE 5 shows, the advantage of SiH_3 over CH_3 substitution is also true for the prismane (Si_6R_6) system which contains both three-membered and four-membered rings: the strain energies decrease in the order 113.8 ($\text{R} = \text{H}$) > 105.6 ($\text{R} = \text{CH}_3$) > 95.7 ($\text{R} = \text{SiH}_3$) in kcal/mol. The charges analysis shows that the SiH_3 group is a good electropositive substituent while the CH_3 group is electronegative in silicon compounds.

It appears that electropositive substituents such as silyl groups are much more effective for the relief of strain than alkyl groups. The choice of substitution is also important for the stabilization of the still heavier Ge, Sn, and Pb skeletons. According to the calculations at the HF/DZ level, the strain energies of octastannacubanes (Sn_8R_8) are 77.0 ($\text{R} = \text{H}$), 75.7 ($\text{R} = \text{CH}_3$), 65.0 ($\text{R} = \text{SiH}_3$), 62.0 ($\text{R} = \text{GeH}_3$), and 58.4 ($\text{R} = \text{SnH}_3$) kcal/mol (ref. 17). Although these values tend to be overestimated by ca. 6 kcal/mol because of the omission of d polarization functions, it appears that the effects of substituents are remarkable also for the tin skeleton; the more electropositive the substituents, the larger the effects. This was also true for the silicon skeleton: upon going from $\text{Si}_8(\text{SiH}_3)_8$ to $\text{Si}_8(\text{SnH}_3)_8$ the strain energy is decreased by 5.2 kcal/mol at the HF/DZ level.

HOLLOW CAGE CLUSTERS

There is currently intense interest in the properties of semiconductor clusters. Among these, silicon clusters attract special attention (refs. 21 and 22). However, the determination of specific structures remains elusive except for very small clusters. In view of recent great progress in the chemistry of buckminsterfullerene (C_{60}), the structural characterization of the Si_{60} cluster is most attractive and fruitful.

It has been observed that silicon cluster ions fragment mainly by loss of Si_6 and Si_{10} units (refs. 23 and 24). In order to explain the observed fragmentation pattern into Si_{10} units, successive stacking of six planar naphthalene-like plates in a quasigraphitic cylinder has been proposed for the structure of the Si_{60} cluster (ref. 25). This stacked naphthalene structure (2 in Fig. 3) is expected to be significantly stabilized by electronic conjugation within the plates, and most silicon atoms are tetracoordinated with dangling bonds accommodated by inter-plate bonding. In this context, a cylindrical structure (3 in Fig. 3) with a stack of ten planar benzene-like rings has also been suggested which may account for the selective fragmentation of silicon cluster ions by sequential loss of Si_6 units. In contrast to these cylindrically stacked structures based on the fragmentation data of the positive cluster ions, we have suggested the buckminsterfullerene structure (1 in Fig. 3) of the Si_{60} cluster from the *ab initio* calculations (ref. 26). Since hollow spherical cage structures have never been explicitly considered for silicon clusters, it is of crucial interest to clarify the thermodynamic stability.

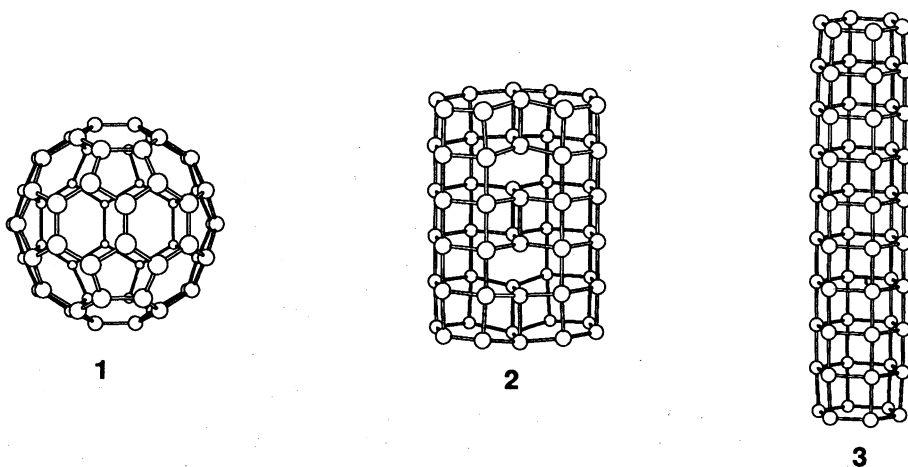


Fig. 3. The fullerene (I_h , 1), stacked naphthalene (D_{2h} , 2), and stacked benzene (C_{2v} , 3) structures optimized for the Si_{60} cluster (ref. 27). These are drawn with the same scale.

Thus, we have recently undertaken the molecular orbital calculations of the relative stabilities of the Si_{60} isomers (1, 2, and 3) (ref. 27). Geometries were fully optimized with the semi-empirical AM1 method (ref. 28). As for the cylindrically stacked structures, 2 was calculated to be 70 kcal/mol more stable than 3. Structure 2 of D_{2h} symmetry corresponds to an energy minimum on the Si_{60} potential energy surface. However, 2 is 158 kcal/mol less stable than 1. This may not be surprising since 2 contains many bond angles which deviate greatly from the normal tetrahedral value of 109.5° and is thereby highly strained. Since such strain energies tend to be considerably underestimated by the AM1 method, single point calculations at the HF/DZ level (with effective core-potentials (ref. 29) on Si) were carried out on the AM1 optimized geometries. As expected, the single point calculations make the energy difference favoring 1 over 2 as huge as 606 kcal/mol. This huge energy difference does suggest that the buckminsterfullerene structure is much more favorable for the Si_{60} cluster. The same trends were also calculated for different cluster sizes; for example, fullerene forms are more stable than stacked naphthalene ones by 115 and 127 kcal/mol for the Si_{30} and Si_{50} clusters at the AM1 level, respectively. Thus, we do not think that fragmentation data provide much information on the stable structures of silicon clusters.

Despite the strong support for the fullerene structure of Si_{60} , there is not yet direct experimental evidence. However, a recent saturation study of the Si_{60}^+ ion with ammonia by Jarrold et al. (ref. 30) seems noteworthy to us which shows that most of the silicon atoms are surface atoms. Particularly interesting is the observation that the average number of ammonia molecules absorbed rapidly onto Si_{60}^+ is close to 6 (see Fig. 13 in ref. 30). This may imply the fullerene structure, though not considered in this way by the authors, since it is closely related to the recent observation that amines (HNRR') react readily with C_{60} to give the amino addition products $\text{C}_{60}(\text{HNRR}')_n$ (predominantly $n = 6$): buckminsterfullerene consists of six independent pyraclycene units to which the amines can be added most easily (ref. 31).

In an attempt to assess further the stability of the fullerene structure of Si_{60} , the smaller silicon-based fullerenes were calculated for comparison, as shown in Fig. 4 (ref. 27).

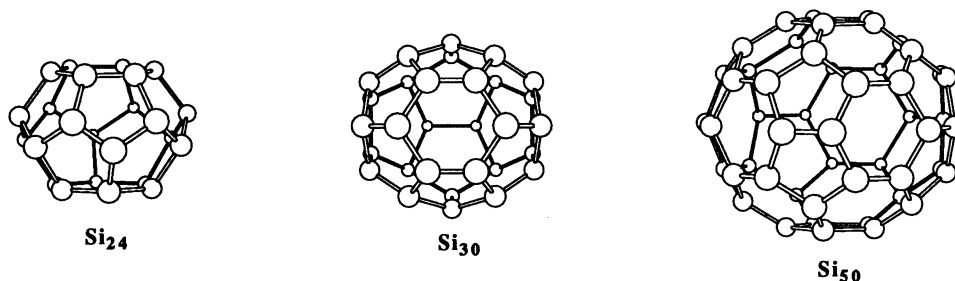


Fig. 4. The optimized fullerene structures of Si_{24} (D_3), Si_{30} (C_{2v}), and Si_{50} (D_{5h}) (ref. 27).

The binding energy per atom of Si_{60} is 1.3, 4.7, and 6.7 kcal/mol larger than those of Si_{50} , Si_{30} , and Si_{24} at the AM1 level, respectively. This trend is further enhanced at the HF/DZ//AM1 level; the value of Si_{60} becomes 2.1, 6.6, and 9.3 kcal/mol larger than those of Si_{50} , Si_{30} , and Si_{24} , indicating that Si_{60} is more strongly bound and thermodynamically stable. This greater stability of Si_{60} is explained in terms of the so-called "isolated pentagon rule" (ref. 32). To construct closed fullerene structures, twelve pentagons are always needed with any number of hexagons. However, the fusion of pentagons is energetically unfavorable as a result of increased strain and induced antiaromatic character (ref. 32). As is apparent from Fig. 4, the number of adjacent pentagons increases upon going to Si_{50} , Si_{30} , and Si_{24} , while pentagons are all separated by hexagons and uniformly distributed in the most spherical Si_{60} . To make comparison with carbon clusters, the binding energies per atom of fullerenes were calculated at the AM1 level. Upon going from C_{60} to C_{50} , C_{30} , and C_{24} , the binding energies per atom decrease by 4.2, 16.0, and 21.5 kcal/mol, respectively. These decreases in the binding energies (especially for C_{30} and C_{24}) are larger than those calculated for the corresponding silicon-based fullerenes. This is ascribed to the fact that fullerenes undergo higher strain and antiaromaticity owing to adjacent pentagons than the silicon analogues.

To make the effect of adjacent pentagons clearer, an isomer of Si_{60} was calculated, as shown in Fig. 5 (ref. 27). The C_{2v} isomer with two pairs of adjacent pentagons is easily obtained by the local two-atom transformation (ref. 33) without changing the number of pentagons and hexagons. The structural defects introduce an energy destabilization of 16.3 (AM1) and 21.1 (HF/DZ//AM1) kcal/mol. However, these destabilization energies due to edge-sharing pentagons are half as large as the values of 47.8 (AM1) and 48.9 (HF/3-21G) (ref. 34) kcal/mol calculated for C_{60} . This suggests that the isolated pentagon rule becomes less severe in silicon-based fullerenes and may enrich the chemistry of silicon clusters.

The full hydrogenation of Si_{60} leads to the saturated $\text{Si}_{60}\text{H}_{60}$ molecule (an exohedral complex), as shown in Fig. 6. The strain energies of 114 (AM1) and 207 (HF/DZ//HF/DZ) kcal/mol calculated from the homodesmotic reactions for $\text{Si}_{60}\text{H}_{60}$ are much smaller than that of 530 (AM1) kcal/mol for $\text{C}_{60}\text{H}_{60}$. This may reflect that Si_{60} itself also is significantly less strained than C_{60} .

TABLE 6. Stabilization energies (ΔE), HOMO-LUMO levels, and charge densities (Q) on the guest atoms for the endohedral complexes of C_{60} , Si_{60} , and Ge_{60} .

	ΔE (kcal/mol)	HOMO (eV)	LUMO (eV)	Q
C_{60}^{a}		-8.0	-0.3	
C_{60}Ne	0.4	-8.0	-0.3	
C_{60}F^-	-39.8	-4.5	3.1	
C_{60}Na^+	-6.7	-11.4	-3.8	
$\text{Si}_{60}^{\text{b}}$		-6.5	-2.1	
Si_{60}Ne	-0.0	-6.5	-2.1	0.000
Si_{60}F^-	2.2	-4.2	0.2	-0.994
$\text{Si}_{60}\text{Na}^+$	-20.3	-8.8	-4.4	1.059
$\text{Ge}_{60}^{\text{c}}$		-6.1	-2.0	
Ge_{60}Ne	-0.0	-6.1	-2.0	0.000
Ge_{60}F^-	3.9	-4.0	0.2	-0.996
$\text{Ge}_{60}\text{Na}^+$	-23.3	-8.3	-4.1	1.100

^a ref. 36. ^b ref. 26. ^c ref. 37 (Ge-Ge = 2.315 and 2.398 Å).

The diameter (11.092 Å) of the hollow spherical cage of Si_{60} (ref. 26) is much larger than that (7.113 Å) of C_{60} (ref. 35). In addition, the electrons of Si_{60} are more polarizable, as expected from the smaller HOMO-LUMO gap. In an attempt to provide insight into the inside of the cage, an atom or an ion with ten electrons was placed at the center of the cage to form an endohedral complex. As TABLE 6 shows, the gain in stabilization is as large as 20.3 kcal/mol in $\text{Si}_{60}\text{Na}^+$ while Si_{60}F^- is destabilized only by 2.2 kcal/mol. Cations are highly stabilized in the Si_{60} cage, forming a super atom. This is in sharp contrast with the trend calculated for the C_{60} cage (ref. 36): C_{60}F^- is stabilized to a much greater extent than C_{60}Na^+ , a negatively charged core being favored in C_{60} . The orbitals of the guest ions are a little mixed with those of the cage. Correspondingly, the charge transfer between the ions and cage is negligible, as shown in TABLE 6. This suggests that the interactions in the endohedral complexes are electrostatic in origin and due to polarization. In this context, it is not surprising that there is no significant interaction in the neutral Si_{60}Ne and C_{60}Ne . The HOMO and LUMO of Si_{60} and C_{60} are stabilized in the presence of cations while they are destabilized by anions; neutral species has no effect on the HOMO and LUMO levels. Also shown in TABLE 6 are the endohedral complexes of Ge_{60} (diameter = 11.736 Å) (ref. 37). The Ge_{60} cage is much more similar to the Si_{60} cage than to the C_{60} cage.

It is expected that silicon-based fullerenes are successfully subjected to experimental tests and open a new field of silicon clusters. In addition, it should be mentioned that the higher silicon-based fullerenes such as Si_{70} , Si_{78} , and Si_{84} with a larger number of hexagons are even more stable in a thermodynamic sense than Si_{60} , as shown in Fig. 7 (ref. 38).

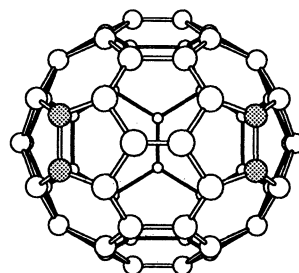


Fig. 5. A C_{2v} isomer of Si_{60} . Atoms at the fused pentagonal positions are dotted (ref.27).

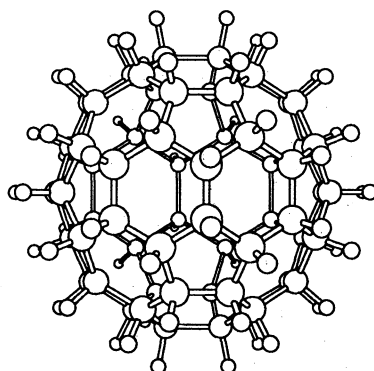


Fig. 6. $\text{Si}_{60}\text{H}_{60}$ (I_h).

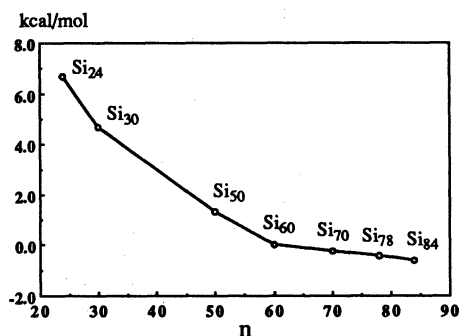


Fig. 7. The binding energies per atom of Si_n relative to Si_{60} as a function of n .

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