

Spherical Sila- and Germa-Homoaromaticity

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Abstract: Guided by the $2(N + 1)^2$ electron-counting rule for spherical aromatic molecules, we have designed various spherical sila- and germa-homoaromatic systems rich in group 14 elements. Their aromaticity is revealed by density-functional computations of their structures and the nucleus-independent chemical shifts (NICS). Besides the formerly used endohedral inclusion strategy, spherical homoaromaticity is another way to stabilize silicon and germanium clusters.

Introduction

There has been considerable progress in investigating the effects of silicon and germanium substitution¹ on the aromaticity² of arenes with $4n + 2$ π -electrons. Among others, sila-³ and germa-aromatic^{3b,4} ions, stable neutral sila-⁵ and germa-naphthalene,⁶ sila-⁷ and germa-anthracene,⁸ sila-⁹ and germa-

benzene,¹⁰ and stable silylenes¹¹ have been synthesized; sila-¹² and germa-benzene,^{12a,b} silicon-substituted polycyclic systems,¹³ and silicon and germanium analogues of cyclopropenium ions¹⁴ have been studied theoretically.

However, homoaromaticity,¹⁵ well-established in organic chemistry, has received much less attention in silicon¹⁶ and germanium¹⁷ counterparts. Most recently, the $2(N + 1)^2$ electron-counting rule for spherical molecules¹⁸ has been employed to design a series of spherically homoaromatic hydrocarbons.¹⁹ Can this rule be applied to group 14 heavier analogues? We are

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motivated further by the recent focus on silicon and germanium clusters and their stabilization by endohedrally hosting a metal atom²⁰ or even a smaller cage.²¹ Another driving force may be aromatic stabilization, as demonstrated by some well-known Zintl ions including M_4^{4-} and $M_9^{2-/4-}$ ($M = \text{Si, Ge}$),^{18c} long used mercury amalgam,²² Al_4^{2-} dianion,²³ and its analogues,²⁴ and bimetallic Au_5Zn^+ .²⁵ Here, we apply the $2(N + 1)^2$ electron-counting rule to design various spherical sila- and germa-homoaromatic systems rich in group 14 elements.

Computational Methods

The full geometry optimizations and vibrational frequency analysis were performed at the B3LYP/6-31G* level of theory. The reported geometries are local minima, unless otherwise stated. Nucleus-independent chemical shifts (NICS, in ppm)²⁶ were computed at the centers of the cages using the GIAO-B3LYP/6-31G* method on the optimized geometries and were employed to evaluate the mobility of cage electrons. All of the calculations were carried out with the Gaussian 98 program.²⁷

Results and Discussion

Four-Center Two-Electron Systems. Schleyer's 1,3-dehydro-5,7-adamantenediyl dication ($\text{C}_{10}\text{H}_{12}^{2+}$, **1**)²⁸ is the best known 4c-2e spherical homoaromatic system. Replacing the

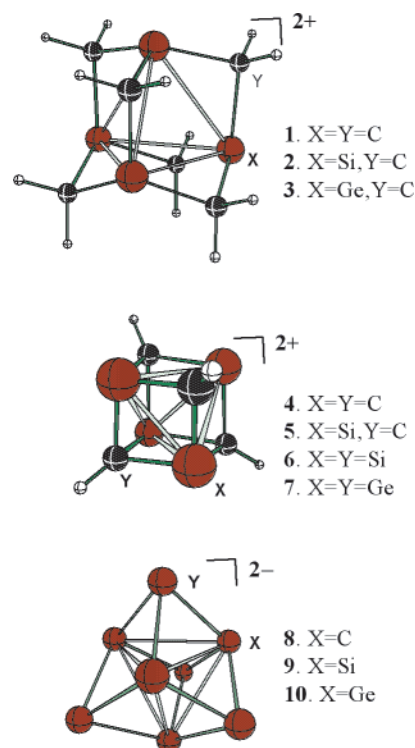


Figure 1. Molecular skeletons of four-center two-electron (4c-2e) homoaromatic systems.

Table 1. The Homoconjugative Distances (Å), HOMO–LUMO Gaps (eV), and NICS Values (ppm) at the Cage Center of the 4c-2e Spherical Homoaromatic Systems (See Figure 1)

species	X–X	gap	NICS
1 ($\text{C}_{10}\text{H}_{12}^{2+}$, T_d)	2.103	6.48	–46.2
2 ($\text{C}_6\text{Si}_4\text{H}_{12}^{2+}$, T_d)	2.885	4.26	–29.2
3 ($\text{C}_6\text{Ge}_4\text{H}_{12}^{2+}$, T_d)	3.012	4.39	–33.2
4 ($\text{C}_8\text{H}_4^{2+}$, T_d)	1.975	5.77	–33.4
5 ($\text{C}_4\text{Si}_4\text{H}_4^{2+}$, T_d)	2.650	3.87	–14.4
6 ($\text{Si}_8\text{H}_4^{2+}$, T_d)	3.156	3.17	–8.0
7 ($\text{Ge}_8\text{H}_4^{2+}$, T_d)	3.370	2.81	–8.8
8 (C_8^{2-} , T_d)	2.067	3.99	–33.6
9 (Si_8^{2-} , T_d)	2.819	3.25	–18.5
10 (Ge_8^{2-} , T_d)	3.050	3.19	–17.0

carbon atoms by silicon and germanium atoms in the central C_4 homo-tetrahedron results in $\text{C}_6\text{Si}_4\text{H}_{12}^{2+}$ (**2**) and $\text{C}_6\text{Ge}_4\text{H}_{12}^{2+}$ (**3**). Their homoaromaticity is confirmed by the computed highly negative nucleus-independent chemical shift (NICS)²⁶ values at the cage center, –29.2 and –33.2 ppm, respectively. Most recently, the aromaticity of **2** has also been characterized by Laali et al.²⁹ by the same procedure. The homoconjugative Si–Si and Ge–Ge distances are 2.885 and 3.012 Å in **2** and **3**, respectively (Table 1), as compared with the single Si–Si and Ge–Ge bond lengths of 2.35 and 2.45 Å in the bulk, respectively.

Substituting the carbon atoms in the C_4 tetrahedron in the cubane-based spherically homoaromatic carbon cation $\text{C}_8\text{H}_4^{2+}$ (**4**, T_d)¹⁹ results in **5** with isolated sp^2 -Si-atoms at opposite corners. Its aromaticity is evidenced by the homoconjugative Si–Si distance of 2.650 Å in the Si_4 tetrahedron, and the –14.4 ppm NICS at the cage center. However, we failed to get SCF convergence for the Ge analogue.

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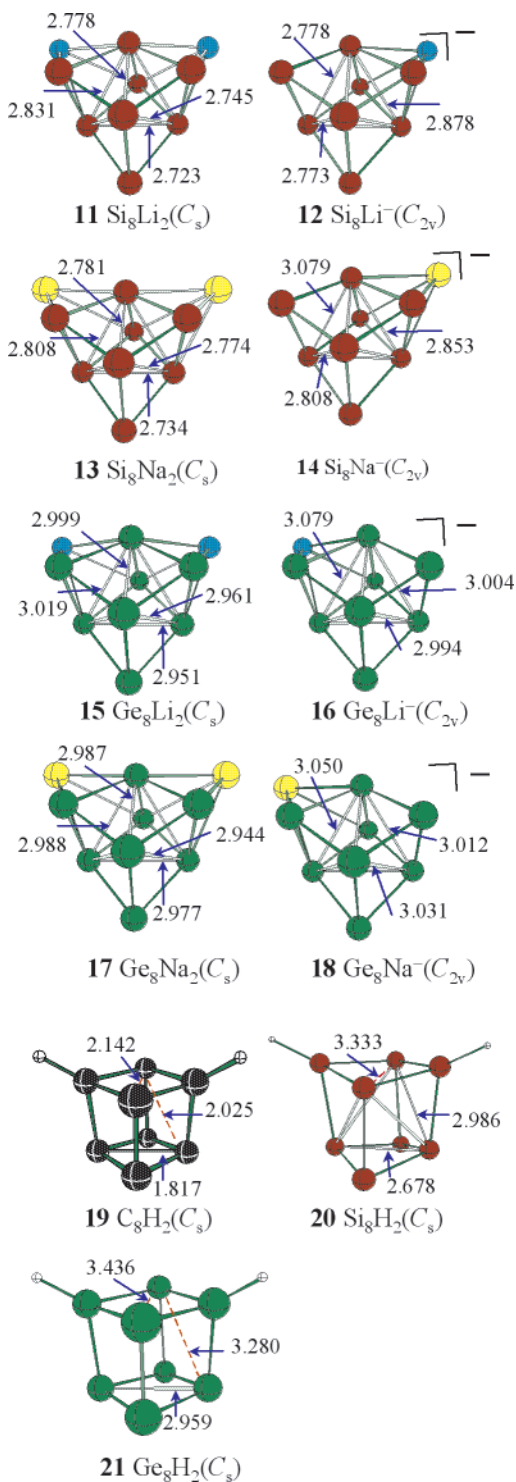


Figure 2. The B3LYP/6-31G* optimized spherical homoaromaticity stabilized silicon and germanium clusters.

The fully substituted analogues, **6** and **7**, based on the cubane framework are also possible. However, the homoconjugative distances in the tetrahedron are much longer (3.157 and 3.370 Å for **6** and **7**, respectively), and this reduces their aromaticity (the NICS at the center are -8.0 and -8.8 ppm, respectively).

Their isoelectronic analogues X_8^{2-} (**8–10**, T_d) ($X = \text{C}, \text{Si}, \text{Ge}$) also are homoaromatic (see Figure 1 and Table 1). Interestingly, the T_d homoaromatic isomers, **9** and **10**, are much more stable than the dianions of the lowest energy neutral

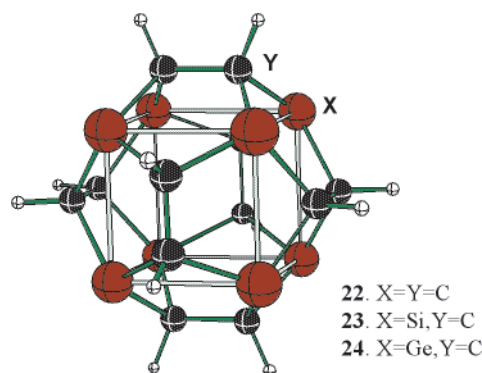


Figure 3. Molecular skeletons of eight-center eight-electron (8c-8e) homoaromatic systems.

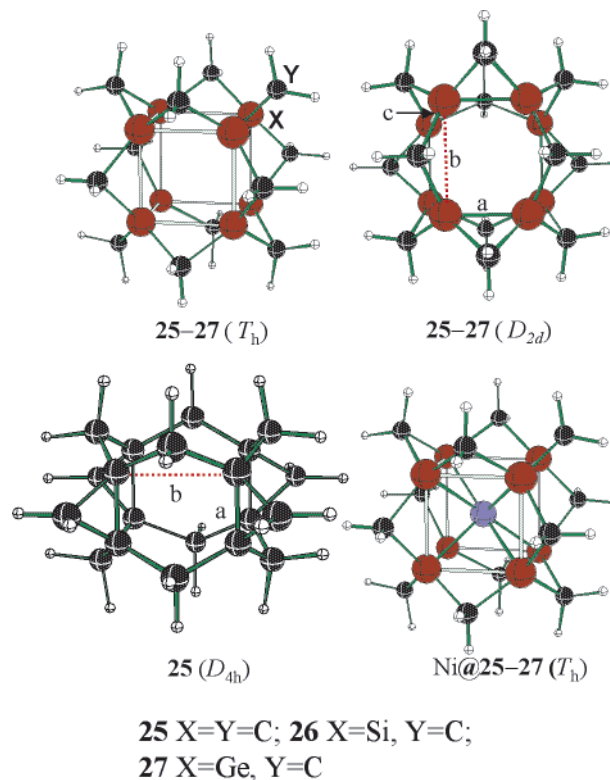
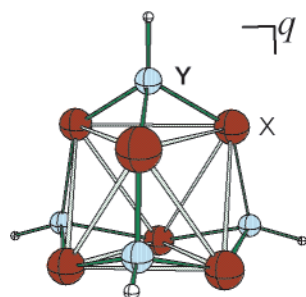


Figure 4. Molecular skeletons of the strain-free systems.

analogues³⁰ (see Supporting Information). The most stable neutral Si_8 isomer^{30a} is a distorted bicapped octahedron (C_{2h}), and a face-capped pentagonal bipyramid (C_s) is the global minimum for Ge_8 .^{30b} The two extra electrons in Si_8^{2-} and Ge_8^{2-} change the stability order of the neutral cluster isomers, which further confirms the homoaromatic stabilization from the two new π -electrons here because the underlying skeleton is not the most stable.

The isoelectronic species of Si_8^{2-} and Ge_8^{2-} , neutral Si_8M_2 and Ge_8M_2 , as well as Si_8M^- and Ge_8M^- ($M = \text{Li}$ and Na) (**11–18**) are particularly enchanting. They are aromatic, as indicated by their homoconjugative distances and very significantly negative NICS values (Figure 2 and Table 2). They also have large HOMO–LUMO gap energies. Moreover, the vertical ionization potentials of Si_8M_2 and Ge_8M_2 ($M = \text{Li}$ and Na) are similar to that of C_{60} (calc. 7.21 eV at B3LYP/6-31G*; exp. 7.57 ± 0.01 eV³¹), suggesting their possible existence as viable

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28. X=Y=C, $q=4+$
 29. X=Si, Y=C, $q=4+$
 30. X=Ge, Y=C, $q=4+$
 31. X=Y=Si, $q=4+$
 32. X=Y=Ge, $q=4+$
 33. X=C, Y=B, $q=0$
 34. X=Si, Y=B, $q=0$
 35. X=Ge, Y=B, $q=0$

Figure 5. Molecular skeletons of six-center eight-electron (6c-8e) homoaromatic systems.

Table 2. HOMO–LUMO Gaps (eV) and NICS Values (ppm) at the Cage Center of the Homoaromaticity Stabilized Si_8 and Ge_8 Clusters, and the Vertical Ionization Potentials (VIP, eV) of the Binary Metal Clusters (See Figure 2)

species	gap	NICS	VIP
11 (Si_8Li_2 , C_s)	3.09	−21.1	7.11
12 (Si_8Li^+ , C_{2v})	2.81	−20.8	3.06
13 (Si_8Na_2 , C_s)	2.72	−13.8	6.55
14 (Si_8Na^+ , C_{2v})	2.10	−16.0	2.83
15 (Ge_8Li_2 , C_s)	3.06	−20.7	7.23
16 (Ge_8Li^+ , C_{2v})	2.78	−20.0	3.19
17 (Ge_8Na_2 , C_s)	2.69	−11.8	6.34
18 (Ge_8Na^+ , C_{2v})	2.10	−14.2	2.78
19 (C_8H_2 , C_s)	3.82	−27.0	
20 (Si_8H_2 , C_s)	2.85	−18.2	
21 (Ge_8H_2 , C_s)	2.59	−19.3	

species. These data strongly suggest that spherical homoaromaticity is another way to stabilize silicon and germanium clusters, besides the endohedrally doping strategy used before.^{20,21}

The neutral nonclassical hydroadducts are also interesting. The 1,3-minima, **19–21** (Figure 2 and Table 2), are more stable than the 1,2- and 1,4-minima (see Supporting Information) because only 1,3 substitution is compatible with the homoaromaticity. The NICS values at the pseudo- T_d symmetrical X_4 cage centers, −27.0 (C_8H_2), −18.2 (Si_8H_2), and −19.3 ppm (Ge_8H_2), confirm that they are truly neutral homoaromatic systems.

Eight-Center Eight-Electron Systems. Substituting the carbon atoms in the conjugated carbon cube in the homoaromatic $\text{C}_{20}\text{H}_{12}$ (**22**, T_h)¹⁹ leads to **23** and **24**. As expected, the neutral eight-center, eight- π -electron (8c-8e) species **23** and **24** are highly aromatic, as indicated by the very negative NICS of −33.0 and −33.7 ppm, and the homoconjugation distances of 2.991 and 3.045 Å, respectively (Table 3). Moreover, the much greater stability of the singlets to their high-spin nonet states (by 53.3 and 91.3 kcal/mol at MP2/6-31G*) also indicates the high stabilization energies of **23** and **24**.

The “strain-free cubical octaradical” **25** (T_h) proposed by Hoffmann et al.³² is an interesting counterpart. However, singlet **25** (T_h) is not a local minimum, even though the NICS of −15.8

Table 3. The Relative Energies (E_{rel} , kcal/mol, Given with ZPE), Homoconjugative Distances (X–X, Å), HOMO–LUMO Gaps (eV), and NICS Values (ppm) at the Cage Center of the 8c-8e Spherical Homoaromatic Systems Based on the Dodecahedrane Framework (See Figure 3)

species		E_{rel}	X–X	gap	NICS
22 ($\text{C}_{20}\text{H}_{12}$, T_h)	singlet	0.0 (0.0) ^a	2.249	2.47	−32.2
	nonet	−4.8 (82.9) ^a	2.410		−2.9
23 ($\text{C}_{12}\text{Si}_8\text{H}_{12}$, T_h)	singlet	0.0	2.991	2.052	−33.0
	nonet	53.3	3.030		2.1
24 ($\text{C}_{12}\text{Ge}_8\text{H}_{12}$, T_h)	singlet	0.0	3.045	2.260	−33.7
	nonet	91.3	3.089		7.4

^a Energy data in the parentheses are at MP2/6-31G* level with B3LYP/6-31G* ZPE.

Table 4. The Relative Energy (E_{rel} , kcal/mol, Given with ZPE), Number of Imaginary Frequencies (NIMAG), Homoconjugative Distance (X–X, Å), HOMO–LUMO Gap (eV), and NICS Value (ppm) at the Cage Center of the 8c-8e Spherical Homoaromatic Systems Based on the Strain-Free Cubical Framework (See Figure 4)

species	symmetry	E_{rel}	NIMAG	X–X	gap	NICS
25 ($\text{C}_{20}\text{H}_{24}$)	T_h (nonet)	−3.2 (70.4) ^a	0	2.259		−2.0
	T_h	0.0 (0.0) ^a	3	2.458	2.00	−15.8
	D_{2d}	−188.3	0		8.57	0.9
	D_{4h}	−195.3	0		8.45	−0.3
26 ($\text{C}_{12}\text{Si}_8\text{H}_{24}$)	T_h (nonet)	66.5	0	3.479		0.5
	T_h	0.0	3	2.621	2.05	−20.3
	D_{2d}	−73.4	0		4.82	−0.9
27 ($\text{C}_{12}\text{Ge}_8\text{H}_{24}$)	T_h (nonet)	101.2	0	3.551		−0.4
	T_h	0.0	3	2.702	3.56	−18.6
	D_{2d}	−75.3	0		4.70	−0.8
	D_{2d}		<i>a</i>	<i>b</i>	<i>c</i>	
25		1.533	2.477		2.575	
26		2.214	3.140		2.925	
27		2.307	3.190		2.992	
	D_{4h}		<i>a</i>	<i>b</i>		
25		1.526			2.549	

^a Energy data in the parentheses are at MP2/6-31G* level with B3LYP/6-31G* ZPE.

ppm at the cage center suggests delocalized bonding. Mode following of the first imaginary frequency leads to a true minimum with D_{2d} symmetry, which is 188.3 kcal/mol more stable than **25**. Its classical D_{4h} isomer, also a local minimum, has even lower energy (Table 4). However, these lower symmetry minima are nonaromatic as indicated by their NICS values. The nonet state of **25** is a local T_h minimum, but its energy is much higher than the best singlet. These DFT computations agree well with Hoffmann’s conclusion based on the extended Hückel computations.³²

The same situation holds true for its silicon (**26**) and germanium (**27**) analogues: the T_h symmetry aromatic singlets are higher order saddle points (NImag = 3), which distort to their more stable but nonaromatic D_{2d} isomers; the T_h symmetrical high spin nonets are much higher in energy and are nonaromatic.

However, it is possible to stabilize the high symmetrical “strain-free cubical octaradical”. Nickel endohedrally complexed in the cage realizes the closed valence 18-electron shell and stabilizes the T_h symmetrical strain-free cage. All of the T_h symmetrical nickel complexes are local minima, with large HOMO–LUMO gaps (3.00, 5.10, and 4.65 eV, for Ni@**25**, Ni@**26**, and Ni@**27**, respectively). There are also strong interactions between Ni and the cubical atoms, their distances

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Table 5. The Homoconjugative Distances (X–X, Å), HOMO–LUMO Gaps (eV), and NICS Values (ppm) at the Cage Center of the 6c-8e Spherical Homoaromatic Systems (See Figure 5)

species	X–X	gap	NICS
28 (C ₁₀ H ₄ ⁴⁺ , T _d)	2.207	4.69	–58.6
29 (C ₄ Si ₆ H ₄ ⁴⁺ , T _d)	3.201	1.44	–17.1
30 (C ₄ Ge ₆ H ₄ ⁴⁺ , T _d)	3.296	2.47	–18.6
31 (Si ₁₀ H ₄ ⁴⁺ , T _d)	3.759	2.55	–25.4
32 (Ge ₁₀ H ₄ ⁴⁺ , T _d)	3.760	2.84	–32.9
33 (C ₆ B ₄ H ₄ , T _d)	1.871	7.28	–38.0
34 (Si ₆ B ₄ H ₄ , T _d)	2.958	3.48	–41.6
35 (Ge ₆ B ₄ H ₄ , T _d)	2.974	3.84	–42.5

are 2.047 (Ni–C), 2.312 (Ni–Si), and 2.398 Å (Ni–Ge), respectively, in Ni@**25**, Ni@**26**, and Ni@**27**.

Six-Center Eight-Electron Systems. Like C₁₀H₄⁴⁺ (**28**, T_d),¹⁹ 6c-8e systems Si₆C₄H₄⁴⁺ (**29**, T_d) and Si₆Ge₄H₄⁴⁺ (**30**, T_d) can be obtained by bridging four nonadjacent delta-faces of a silicon octahedron by CH groups and removing four electrons. The eight electrons are delocalized over six centers in overall T_d symmetry. The homoconjugation distances are 3.201 and 3.296 Å, and the NICS values at the cage centers are –17.1 and –18.6 ppm, for **29** and **30**, respectively, strongly indicating their high degree of electron delocalization (Table 5).

The fully inorganic cages Si₁₀H₄⁴⁺ (**31**, T_d) and Ge₁₀H₄⁴⁺ (**32**, T_d) are also highly aromatic (NICS –25.4 and –32.9 ppm, respectively). Although the distances between the heavier atoms (3.759 and 3.760 Å, respectively) are quite long, the silicon and germanium orbital radial extensions are larger than carbon's, and the 6c-8e systems are effectively homoaromatic, following the 2(N + 1)² rule¹⁸ for spherical aromaticity.

More realistic synthetic targets than the tetracations are their neutral isoelectronic T_d analogues. Similar to C₆B₄H₄ (**33**, T_d), Si₆B₄H₄ (**34**, T_d) and Ge₆B₄H₄ (**35**, T_d) have even larger NICS (–41.6 and –42.5 ppm, respectively) at the cage center; the homoconjugative separations are 2.958 and 2.974 Å, respectively.

Concluding Remarks

Guided by the 2(N + 1)² electron-counting rule,^{18,19} we have designed a series of spherical sila- and germa-homoaromatic systems. Their significant homoaromaticity has been demonstrated by the highly negative NICS values at their cage centers. These novel homoaromatic compounds with well-delocalized electrons in the heavier group 14 elements present new synthetic targets, in particular the spherical homoaromaticity stabilized silicon and germanium clusters Si₈M₂ and Ge₈M₂ (M = Li and Na). Moreover, several precursors are available such as the derivatives of 1,3,5,7-tetrasiladamantane³³ as well as the polyhedral silicon and germanium compounds, Si₈R₈³⁴ and Ge₈R₈.^{34b,35}

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Supporting Information Available: Total energies and zero-point energies, and structures and relative energies of Si₈^{2–} and Ge₈^{2–} isomers, as well as C₈H₂, Si₈H₂, and Ge₈H₂ isomers (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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