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Citation: *The Journal of Chemical Physics* **117**, 9543 (2002); doi: 10.1063/1.1523899

View online: <http://dx.doi.org/10.1063/1.1523899>

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An *ab initio* investigation on aromaticities in semiconductor systems

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(Received 24 July 2002; accepted 1 October 2002)

Second-order Moller–Plesset perturbation theory investigations indicate that the highly strained three- and four-membered semiconductor ring systems $A_3R_3^+$, $A_2BR_3^+$, $GeSiCR_3^+$, A_3R_3Ha , and $A_4R_4^{2+}$ ($A, B=C, Si, Ge$; $R=H, SiH_3$; $Ha=F, Cl, Br$) exhibit aromaticities featured with the delocalized π orbitals perpendicular to the ring planes. © 2002 American Institute of Physics. [DOI: 10.1063/1.1523899]

The pioneer work of Robinson and co-workers on metallic ring system $Na_2[(Mes)_2C_6H_3Ga]_3$ ($Mes=2,4,6-Me_3C_6H_2$) possessing *metalloaromaticity* was first published in 1995^{1–4} and aromaticities in molecules containing 2 π electron three- or four-centered group 13 or 14 elemental cores have attracted considerable attention since then. The newly discovered square Al_4^{2-} (Ref. 5) and heterocyclic XAl_3^- ($X=Si, Ge, Sn, Pb$) (Ref. 6) have all been confirmed to exhibit characteristics of aromaticity in both experiments and theory. The long-sought free cyclotrimermerium cations $R_3Ge_3^+$ with a Ge_3 equilateral triangle at the center were recently observed in $[Ge_3(E'Bu_3)_3^+ BPh_4^-]$ (Ref. 7) and $[Ge_3(E'Bu_3)_3^+ BAr_4^-]$ ($E=Si, Ge$) (Ref. 8), analogous to cyclopropenium cation $C_3R_3^+$, the smallest aromatic molecule obtained so far. But cyclotrisilenium cation $R_3Si_3^+$, which was predicted aromatic in theory,⁹ has yet to be identified unambiguously in experiments, though stable cyclotrisilenes with a double $Si=Si$ bond have already been synthesized.^{10,11}

Theoretical investigations on aromaticities in systems containing group 14 elemental cores have so far been limited at density functional theory (DFT) level and some of the predictions reported obviously disagree with available experiments.^{7–9} The lowest-lying structure of model compound $Ge_3H_3^+$ was predicted to be an H-bridged chair (C_{3v}) employing Becke's three-parameter exchange functional and the nonlocal correlation potential provided by Lee *et al.* (B3LYP).⁹ In x-ray structural measurements, however, free cyclotrimermerium cation $(tBu_3Si)_3Ge_3^+$ was confirmed to form a Ge_3 equilateral triangle and the three Si atoms of tBu_3Si substituents were approximately within the same plane as the Ge_3 core.^{7–8} There is a long standing contro-

versy about the principal instability of excited states and charged ions within DFT and the possibility that DFT minima are only an artifact of the finite size of basis sets. In addition, there have been no theoretical predictions reported for systems containing binary A_2B , ternary $GeSiC$, or four-membered A_4 semiconductor cores. It is our position that, a systematical study on aromaticities in semiconductor systems with *ab initio* methods stricter than DFT is desirable at current stage. In this work, we present a second-order Moller–Plesset perturbation theory (MP2) investigation on aromaticities in three- and four-membered semiconductor ring systems $A_3R_3^+$, $A_2BR_3^+$, $GeSiCR_3^+$, A_3R_3Ha , and $A_4R_4^{2+}$ ($A, B=C, Si, Ge$; $R=H, SiH_3$; $Ha=F, Cl, Br$). Our optimized geometries fully support available experiments and shed new insight into the observations reported. The calculated negative nucleus independent chemical shifts (NICS) used as a criterion for aromatic cyclic delocalization clearly indicate that these model systems are aromatic.

Initial structural optimizations and frequency analyses were performed using the MP2(FC)/6-31+G(d) method with the frozen core approximation (FC). The optimized structures were further refined by employing the MP2(FULL)/6-311+G(d) approach with the inclusion of all electrons in electron correlation calculation (FULL). To assess the aromatic/antiaromatic character of these systems, we calculated NICS values at the geometrical center of the ring's heavy atoms employing the gauge-independent atomic orbital (GIAO) approach at B3LYP/6-311+G(3df) level. NICS values are taken negative to follow the chemical convention. All calculations in this work were performed using the GAUSSIAN 98 package.¹² The NICS criterion, first introduced by Schleyer *et al.*,¹³ has been successfully applied in

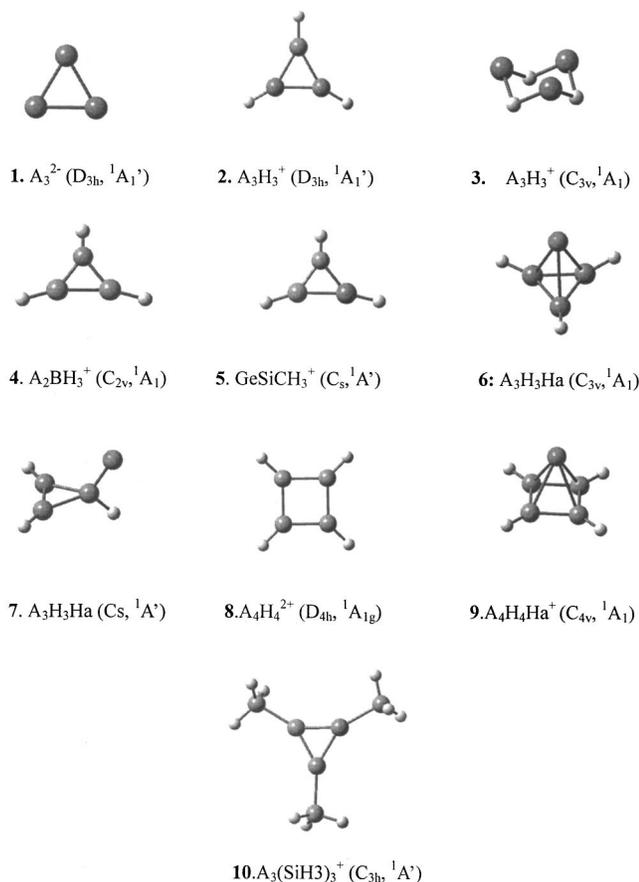


FIG. 1. Some of the optimized structures obtained for three- and four-membered ring systems. Atoms on rings represent A=C,Si,Ge, atoms on the 3-fold axis in **6** and 4-fold axis in **9** stand for Ha=F,Cl,Br,H atoms are presented as the smallest balls.

characterizing the aromaticity of $Ga_3H_3^{2-}$ and similar heterocyclic ring systems by Xie *et al.* in a series of works.²⁻⁴ The optimized geometries are shown in Fig. 1 and the doubly-occupied delocalized π orbitals (HOMOs) of some typical structures depicted in Fig. 2. The optimized bond parameters and calculated NICS values are tabulated in Tables I and II.

At MP2 level, analogous to cyclopropenium cation $C_3H_3^+$, both $Si_3H_3^+$ and $Ge_3H_3^+$ take the classical planar D_{3h} structure (**2**) as their lowest-lying state (D_{3h} , $^1A_1'$) and the A_2'' delocalized π orbitals as their HOMOs. D_{3h} $Si_3H_3^+$ and $Ge_3H_3^+$ are found to be 37.62 and 10.25 kcal/mol more stable than their H-bridged C_{3v} isomers (**3**) respectively. With a bigger basis of 6-311++(3df,2p), the MP2 energy difference between the two isomers for $Ge_3H_3^+$ is 8.41 kcal/mol. Our MP2 stability order is different from the B3LYP result reported in Ref. 9, which claimed that C_{3v} $Ge_3H_3^+$ is 17.4 kcal/mol more stable than D_{3h} $Ge_3H_3^+$.⁹ We performed a B3LYP/6-311++G(2d,2p) optimization which also indicated that the former lies 9.54 kcal/mol⁻¹ lower than the latter. The high stability of H-bridged C_{3v} structure for $Ge_3H_3^+$ at B3LYP level is quite unusual and surprising. We believe that our MP2 result is more reliable based on the following considerations. First, all electrons, including the core electrons, have been included in our MP2 optimization processes in electron correlation energy calculation, while

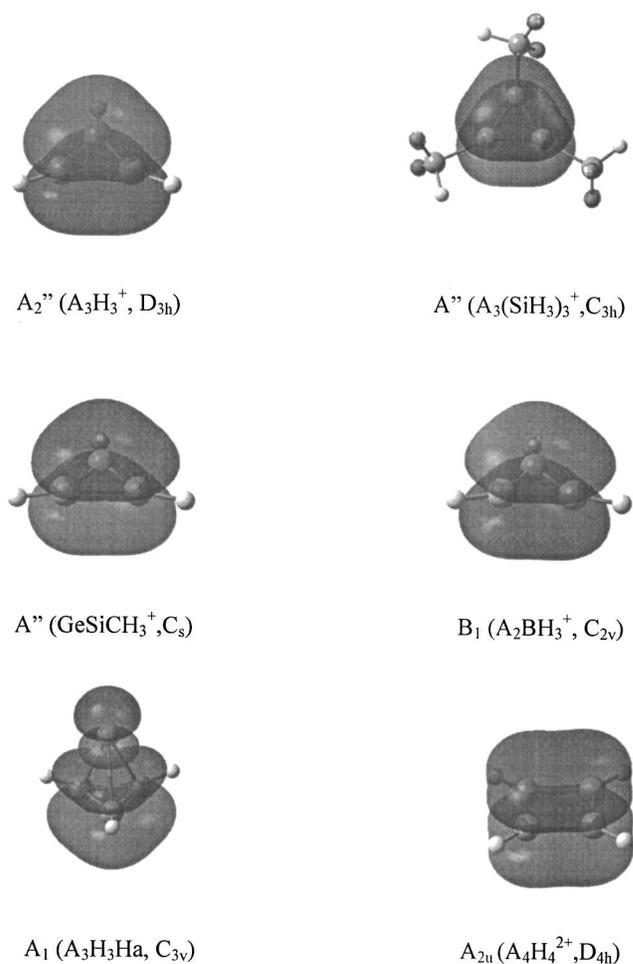


FIG. 2. The doubly occupied delocalized π orbitals (HOMOs) of D_{3h} $A_3H_3^+$, C_{3h} $A_3(SiH_3)_3^+$, C_s $GeSiCH_3^+$, C_{2v} $A_2BH_3^+$, C_{3v} A_3H_3Ha , and D_{4h} $A_4H_4^{2+}$ (A=Ge,Si,C). Atoms are presented in the same way as in Fig. 1.

the B3LYP optimization in Ref. 9 employed the valence-electron (pseudopotential) approximation. Second, MP2 method should be, in principle, more reliable for excited states and charged ions than B3LYP, which may produce artificial minima for such systems with finite basis sets. The high stability of the C_{3v} $Ge_3H_3^+$ at B3LYP may result from the specific functional forms treating electron correlation effect in B3LYP scheme and a sudden change of basis set for heavier group 14 elements starting from Ge.⁹ Finally and most importantly, our MP2 geometry for D_{3h} $Ge_3H_3^+$ agree very well with the observed Ge_3 equilateral triangle: The MP2 Ge-Ge bond length is 2.328 Å, much closer to the averaged experimental value of 2.326 Å in free germyl cation⁷ than corresponding B3LYP value of 2.361 Å.⁹ To further simulate the real compounds in which the A_3 equilateral triangle rings are incorporated,^{7,8} we replace the three H atoms with three SiH_3 groups and form a C_{3h} $A_3(SiH_3)_3^+$ model cation. As can be seen from Table I, only minor increase in A-A bond lengths in C_{3h} $A_3(SiH_3)_3^+$ is observed compared to D_{3h} $A_3H_3^+$ and the general bonding features, including the delocalized HOMO π bond (A'' , see Fig. 2), are well maintained. It should be noticed that the optimized

TABLE I. Optimized MP2 bond lengths (in Å) and calculated nucleus independent chemical shifts NICS at the ring center (in ppm) for A_3^{2-} anions (D_{3h}), $A_3H_3^+$ (D_{3h}) and $A_3(SiH_3)_3^+$ cations (C_{3h}), A_3H_3Ha neutrals (C_{3v}), and $A_4H_4^{2+}$ (D_{4h}) and $A_4H_4Ha^+$ (C_{4v}) cations ($A=C, Si, Ge; Ha=F, Cl, Br$). Absolute chemical shifts for H atoms are also tabulated.

Clusters	Structure	Bond length			Chemical shifts	
		A–A	A–H	A–Ha	NICS	H
C_3^{2-}	1	1.442			+195	
$C_3H_3^+$	2	1.372	1.082		–23	21
C_3H_3F	6	1.368	1.076	2.275	–24	23
C_3H_3Cl	6	1.369	1.077	2.776	–18	22
C_3H_3Br	6	1.370	1.078	2.943	–17	22
$C_3(SiH_3)_3^+$	10	1.392	1.473	1.908	–20	27
			(Si–H)	(C–Si)		(H–Si)
Si_3^{2-}	1	2.329			–5	
$Si_3H_3^+$	2	2.196	1.477		–23	24
$Si_3H_3^+$	3	2.543	1.671		–	–
Si_3H_3F	6	2.189	1.478	2.451	–23	24
Si_3H_3Cl	6	2.184	1.478	3.028	–20	24
Si_3H_3Br	6	2.184	1.478	3.172	–7	24
$Si_3(SiH_3)_3^+$	10	2.219	1.477	2.367	–17	27
			(Si'–H)	(Si–Si')		(H–Si)
Ge_3^{2-}	1	2.492			–6	
$Ge_3H_3^+$	2	2.328	1.532		–19	22
$Ge_3H_3^+$	3	2.722	1.770		–	–
Ge_3H_3F	6	2.316	1.533	2.486	–19	21
Ge_3H_3Cl	6	2.317	1.533	3.036	–16	22
Ge_3H_3Br	6	2.318	1.533	3.208	–14	22
$Ge_3(SiH_3)_3^+$	10	2.343	1.474	2.416	–14	27
			(Si–H)	(Ge–Si)		(H–Si)
$Si_4H_4^{2+}$	8	2.269	1.475		–8	22
$Si_4H_4F^+$	9	2.251	1.476	2.353	–13	23
$Si_4H_4Cl^+$	9	2.242	1.474	2.893	–4	23
$Ge_4H_4^{2+}$	8	2.371	1.526		–6	20
$Ge_4H_4F^+$	9	2.348	1.526	2.432	–11	22
$Ge_4H_4Cl^+$	9	2.345	1.524	2.905	–4	22

Ge–Ge and Ge–Si bond lengths of 2.343 and 2.416 Å in $Ge_3(SiH_3)_3^+$ agree quite well with corresponding averaged values of 2.326 and 2.443 Å observed in $[Ge_3(Si^tBu_3)_3^+BPh_4^-]$ and 2.335 and 2.438 Å obtained in $[Ge_3(Si^tBu_3)_3^+BAr_4^-]$, in which the three Si atoms of tBu_3Si substituents are approximately coplanar with the Ge_3 equilateral triangle.^{7,8} It is also worth noting that the positive charge on $Ge_3(SiH_3)_3^+$ is mainly distributed on the three exo-Si atoms (+0.448 each), different from $Ge_3H_3^+$ in which the three Ge atoms on the ring evenly share the unit positive charge. Similar situation happens to $Si_3(SiH_3)_3^+$. We believe

the results obtained for $C_3(SiH_3)_3^+$ and $Si_3(SiH_3)_3^+$ can also serve as useful references in future experimental identification of analogous cations. The fact that the MP2 Si–Si distance of 2.219 Å in $Si_3(SiH_3)_3^+$ is between the averaged Si–Si single bond length of 2.367 Å and Si=Si double bond length of 2.138 Å in cyclotrisilene¹⁰ well demonstrates the bond length equalization effect of aromatic bonding in $Si_3(SiH_3)_3^+$.

Similar to $A_3H_3^+$, the lowest-lying binary C_{2v} $A_2BH_3^+$ (**4**) and ternary C_s $GeSiCH_3^+$ (**5**) contain three-membered

TABLE II. Optimized bond lengths r (in Å) and bond angles α (in degree) at MP2(FULL)/6-311+(d) level and the calculated nucleus independent chemical shifts (NICS in ppm) at ring the centers for $A_2BH_3^+$ and $GeSiCH_3^+$ cations using the GIAO approach at B3LYP/6-311+(3df) level.

Cluster	Structure	Bond parameter			NICS
		r (A–A)	r (A–B)	α (A–B–A)	
$GeSi_2H_3^+$	4	2.201	2.258	58.4°	–22
$Ge_2SiH_3^+$	4	2.326	2.262	61.9°	–20
$Si_2CH_3^+$	4	2.145	1.775	74.4°	–21
$Ge_2CH_3^+$	4	2.278	1.863	75.2°	–16
$SiC_2H_3^+$	4	1.393	1.747	46.9°	–19
$GeC_2H_3^+$	4	1.375	1.835	44.8°	–15
$GeSiCH_3^+$	5	1.870	1.770	74.6°	–19
		(C–Ge)	(C–Si)	(Ge–C–Si)	

semiconductor cores and exhibit characteristics of delocalized 2-electron π orbitals (B_1 and A'' respectively). Existence of the delocalized π bond results in obvious bond length and bond angle equalization¹³ in cations relative to corresponding neutral A_2B and $GeSiC$. Typical situation happens in $GeSiCH_3^+$, in which the $Ge-C-Si$ bond angle is decreased from 113° at MP2 in $GeSiC$ (126° at CISD¹⁴) to 75° in $GeSiCH_3^+$ and corresponding $Ge-Si$ distance decreased from 2.920 to typical covalent bond length of 2.208 Å. All the other $A_2BH_3^+$ cations contain A_2B isosceles triangle rings with covalent $A-A$ and $A-B$ interaction distances between corresponding single bond and double bond lengths.

With one face-capping halogen anion added along the three-fold axis of a D_{3h} $A_3H_3^+$ cation, the C_{3v} A_3H_3Ha neutrals (**6**) result ($Ha=F, Cl, Br$). These high symmetry structures are not expected to be thermodynamically stable towards structural distortion. Their bond parameters tabulated in Table I, however, indicate that the $A_3H_3^+$ structural units are well maintained in these neutrals and $A-Ha$ interactions in A_3H_3Ha are basically ionic. As can be seen from Fig. 2, A_3H_3Ha neutrals exhibit clear characteristics of delocalized π orbital (A_1 , HOMO), similar to the A_2' orbital (HOMO) in D_{3h} $A_3H_3^+$. The global minima of A_3H_3Ha turned out to be the C_s halogen-substituted cyclic rings with one $A-A$ double bond and two $A-A$ single bonds (**7**). The optimized MP2 bond lengths $r_{Ge-Ge}=2.409$ Å, $r_{Ge=Ge}=2.261$ Å, and $r_{Ge-Br}=2.341$ Å for model compound C_s Ge_3H_3Br agree fairly well with corresponding observed average values of 2.420, 2.274 and 2.425 Å for bromine-substituted cyclotrigermene,¹⁵ considering the fact that the big tBu_3Si ligands in real compounds are simply replaced with H atoms in our model calculation. The $Ge-Br$ single bond in C_s Ge_3H_3Br is much shorter than the ionic interaction distance of 3.208 Å in C_{3v} Ge_3H_3Br .

The big negative NICS values listed in Tables I and II calculated at the geometrical center of the three-membered rings clearly indicate the aromatic characteristics of D_{3h} $A_3H_3^+$, C_{2v} $A_2BH_3^+$, C_s $GeSiCH_3^+$, C_{3h} $A_3(SiH_3)_3^+$ and C_{3v} A_3H_3Ha . In most cases, these semiconductor systems have NICS values higher than the SCF value of -15 reported for $M_2Ga_3H_3$ in magnitudes.² As a general trend, the absolute NICS values decrease from $Ha=F, Cl$, to Br for the same semiconductor core while the absolute chemical shifts of H atoms directly bonded to the central ring remain almost unchanged (in a narrow range of 21–24). We also calculated the aromatic stabilization energies (ASEs) of $A_3H_3^+$ following Eq. (1) in Ref. 9. Our MP2 ASE values are 66.10 for $A=C$, 37.82 for $A=Si$, and 36.43 kcal/mol for $A=Ge$, respectively, generally agreeing with corresponding B3LYP values of 58.7, 35.6, and 31.9 kcal/mol.⁹ The biggest difference happens at $Ge_3H_3^+$: The ASE of $Ge_3H_3^+$ is very close to that of $Si_3H_3^+$ at MP2 (the difference is less than 3.7%, coinciding with the 4%–5% difference in covalent radii between Si and Ge) and MP2 ASE value for D_{3h} $Ge_3H_3^+$ is significantly higher than corresponding B3LYP value for C_{3v} $Ge_3H_3^+$ (14.2%). This ASE difference has its origin in relative energy determinations at different theoretical levels: $Ge_3H_3^+$ and $Si_3H_3^+$ share the same lowest-lying structure D_{3h}

(**2**) at MP2, while for $Ge_3H_3^+$ at B3LYP, the H-bridged C_{3v} chair (**3**) lies lower than D_{3h} ring. Comparing the variations of ASE and NICS values with semiconductor cores, we find that both values roughly decrease from $A=C, Si$, to Ge . However, unlike in the case of five-membered ring heterocycles,¹³ the two indicators of aromaticity for semiconductor systems do not vary proportionally. For example, $C_3H_3^+$ and $Si_3H_3^+$ have almost the same NICS values (-23 ppm), but the former possesses much higher aromatic stabilization energy than the latter.

D_{4h} $A_4H_4^{2+}$ (**8**) and C_{4v} $A_4H_4Ha^+$ (**9**) cations, both containing square A_4 rings and delocalized π orbitals (HOMOs), have relatively smaller NICS values at the four-membered ring center compared to the three-membered ring systems discussed above. Optimization of rhombic D_{2h} $A_4H_4^{2+}$ produced the same result as D_{4h} $A_4H_4^{2+}$. NICS reaches its maximum values of -10 for $A=Si$ and -9 for $A=Ge$ at a point on the four-fold axis 0.8 Å above the A_4 square, where the local shielding effect of nearby σ peripheral bonds on A_4 ring is minimized. This NICS value variation reflects the π electron toroid density distribution above and beneath the molecular plane. It is expected that with H atoms replaced with suitable substituents and the introduction of necessary counterions, a square A_4 core or its near-planed distortion may be maintained in complexes through effective steric hindrance of big ligands.

In summary, MP2 investigations performed in this work show that the classical three-membered ring structures are favored for semiconductor systems $A_3H_3^+$ (D_{3h}), $A_3(SiH_3)_3^+$ (C_{3h}), $A_2BH_3^+$ (C_{2v}) and $GeSiCH_3^+$ (C_s) ($A=C, Si, Ge$). These high symmetry structures can be regarded as D_{3h} A_3^{2-} (**1**),¹⁶ C_{2v} A_2B^{2-} or C_s $GeSiC^{2-}$ rings triply coordinated with three H^+ or three SiH_3^+ cations at the lone pairs, while the left two valence electrons form a delocalized π bond utilizing the three empty p orbitals perpendicular to the three-membered ring. Similar delocalized π orbitals exist in pyramid C_{3v} A_3H_3Ha neutrals. The existence of ring currents and the aromatic characteristics of these systems are supported by large NICS values at the ring centers. The lowest-lying D_{3h} structure at MP2 provides the first reliable *ab initio* evidence for D_{3h} $Ge_3H_3^+$ observed in recent experiments. Theoretical predictions for weaker aromaticity in $A_4H_4^{2+}$ and $A_4H_4Ha^+$ containing square A_4 cores are also presented. Preliminary investigations also indicate that, at B3PW91/6-31G(d) level, the bicapped antisquare prism Ge_{10}^{2-} (D_{4d}) exhibits spherical aromaticity as indicated by the big negative NICS value of -50.8 ppm at the cage center.

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