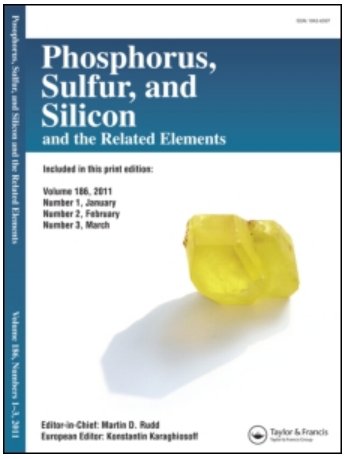

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E. Vessally[a]
[a] Payame Noor University (PNU), Zanjan, Iran

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AROMATIC CHARACTER STUDIES ON CALICENE AND ITS DERIVATIVES CONTAINING HEAVIER ATOMS VIA NUCLEAR INDEPENDENT CHEMICAL SHIFTS (NICS)

E. Vessally
Payame Noor University (PNU), Zanjan, Iran

DFT calculations were carried out on the molecular structure of calicene and its derivatives containing heavy atoms, 1_X and 2_X (X=C, Si, Ge and Sn), using 6-311+G** basis set in the GAUSSIAN 98 program. The aromatic character of 1_X and 2_X was investigated through the magnetic and the geometric criteria. From a geometric view, the molecules, 1_C, 1_{Si}, 1_{Ge}, 1_{Sn} and 2_{Si} have completed electron current in the three-member ring, while the molecules 2_{Ge} and 2_{Sn} have completed electron current in the five-member ring. Nuclear independent chemical shifts NICS (0.5) calculations indicated an aromatic character in both three and five rings of 1_X and 2_X, which was decreased from X=C to X=Sn (except for 1_{Sn}). However, a non-aromatic and an aromatic character at three- and five-membered ring were observed for 2_{Sn}, respectively.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Aromatic character; calicene; cyclopropenylidenecyclopentadiene; heavy atoms; molecular structure; NICS

INTRODUCTION

Calicene, triapentafulvalene, and cyclopropenylidenecyclopentadiene makes up a completely conjugated unsaturated molecule. The aromatic character with a dipolar electronic structure was reported for both rings of calicene. This molecule has never been synthesized, but the substituted species show high dipole moments.[1,2] The dipolar character of calicene could determine the chemical and spectroscopic properties of the molecule. Moreover, the rotation around the double bond between both rings can be made easier by the dipolar electronic structure.

Theoretical calculations have been carried out for calicene.[37] Semi-empirical SCF MO calculations have been conducted for calicene and its various possible benzo derivatives.[3] In another report, the ground-state electronic properties of calicene have been studied by the modified Huckel MO method in which the effects of the σ-bond

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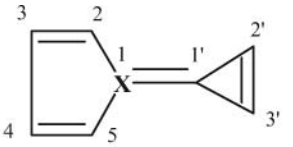
Address correspondence to E. Vessally, Payame Noor University (PNU), Zanjan, Iran. E-mail: e_vesali@yahoo.com

compressions are taken into account.[4] Finally, the ground and excited electronic state properties of calicene have been studied with a variety of density functional models by Ghigo et al.[5] As a continuation on our work,[8] in this article the aromatic character was calculated for calicene and its derivatives containing heavy atoms. The aromatic character is not a directly measurable or computable quantity. The aromatic character is generally evaluated on the basis of magnetic, energetic, and geometric criteria.[9–15] The magnetic criterion is measured through nuclear independent chemical shifts (NICS) calculations. The concept of NICS was introduced by Schleyer et al. in 1996 as a measure of the aromaticity and the anti-aromaticity (or non-aromaticity).[15a] It is based on a probe that is placed at or above the geometrical center of a conjugated ring. Its calculated isotropic NMR chemical shift indicates the aromatic properties of the ring, either as an individual moiety in a polycyclic compound or as a molecule. Initially, the probe was placed at the geometrical center of the molecules, but after realizing that in some systems the chemical shifts are influenced by the σ system (e.g., cyclopropane), it was placed 0.5 Å above the center [denoted as NICS (0.5)]. The method that has been used for the assignment of the aromatic character in many systems is generally very successful. In this article, NICS calculations were carried out on $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=C, Si, Ge and Sn). In molecules $\mathbf{1_X}$, the carbon atom at the five-membered ring was replaced with X (Si, Ge and Sn) atoms, while in molecules $\mathbf{2_X}$, the carbon atom at the three-membered ring was replaced with X atoms.

COMPUTATIONAL METHODS

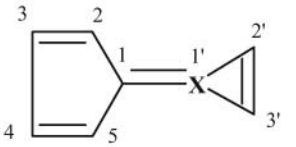
Full geometry optimizations were carried out on calicene and its derivatives $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=C, Si, Ge, and Sn) using B3LYP method (Figure 1).[16,17]

Basis set 6-311+G** is used in the GAUSSIAN 98 program.[18] Global minima were specified on corresponding energy surfaces at the B3LYP/6-311+G** level of theory. Energy surfaces scanning is done to obtain more accurate values of the electronic and thermal energies, E, enthalpies, H, and Gibbs free energies, G. For the Sn atom, the calculations were done via "Extrabasis" keyword (heteroatoms were optimized using LANL2DZ basis set).[19] To confirm the nature of the stationary species, frequency calculations were carried out. Only real frequency values were accepted due to the achievement of optimized structure. NICS calculations were carried out at the B3LYP/6-311++G(3df, 2p) level of theory.



$\mathbf{1_X}$

X = C, $\mathbf{1_C}$; X = Si, $\mathbf{1_{Si}}$; X = Ge, $\mathbf{1_{Ge}}$; X = Sn, $\mathbf{1_{Sn}}$



$\mathbf{2_X}$

X = Si, $\mathbf{2_{Si}}$; X = Ge, 2_{Ge}; X = Sn, $\mathbf{2_{Sn}}$

Figure 1 Calicene and its derivatives $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=C, Si, Ge, and Sn).

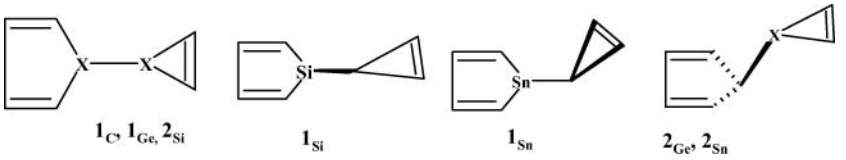


Figure 2 Full optimized conformations for calicene and its derivatives $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=C, Si, Ge, and Sn).

RESULTS AND DISCUSSIONS

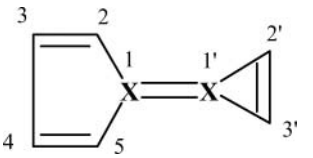
DFT calculations were carried out on the molecular structure of calicene, cyclopropenylidenecyclopentadiene, $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=C, Si, Ge and Sn), 5-cycloprop-2-enylidene-cyclopenta-1,3-diene, $\mathbf{1_C}$, 1-cycloprop-2-enylidene-1H-silole, $\mathbf{1_{Si}}$, 1-cycloprop-2-enylidene-1H-germole, $\mathbf{1_{Ge}}$, 1-cycloprop-2-enylidene-1H-stannole, $\mathbf{1_{Sn}}$, 1-cyclopenta-2,4-dienylidene-1H-silirene, $\mathbf{2_{Si}}$, 1-cyclopenta-2,4-dienylidene-1H-germirene, $\mathbf{2_{Ge}}$, and 1-cyclopenta-2,4-dienylidene-1H-stannirene, $\mathbf{2_{Sn}}$, at the B3LYP/6-311+G** level of theory (Figure 1). The fully optimized calculations showed both planar and nonplanar conformations as global minimum (Figure 2).

The fully optimized calculations indicated a planar structure for $\mathbf{1_C}$, $\mathbf{1_{Ge}}$, and $\mathbf{2_{Si}}$, while a nonplanar structure for $\mathbf{1_{Si}}$, $\mathbf{2_{Ge}}$, $\mathbf{1_{Sn}}$ and $\mathbf{2_{Sn}}$ was indicated as a global minimum (Figure 2 and Table I). The bond X−X, connecting two rings, was forced out of plane, and five-member ring was puckered for $\mathbf{1_{Si}}$, $\mathbf{2_{Ge}}$, and $\mathbf{1_{Sn}}$. (Figure 2 and Table I).

The geometric parameters including bond length, bond, and dihedral angles were presented for $\mathbf{1_C}$, $\mathbf{1_{Si}}$, $\mathbf{1_{Ge}}$, $\mathbf{1_{Sn}}$, $\mathbf{2_{Si}}$, $\mathbf{2_{Ge}}$ and $\mathbf{2_{Sn}}$ in Table I and Figure 3). For $\mathbf{1_C}$ and $\mathbf{2_{Si}}$, the bond length X−X is a double bond (X=X). The electron current in the three-member ring of $\mathbf{1_C}$ and $\mathbf{2_{Si}}$ was completed, while the electron current in the five-member ring of $\mathbf{1_C}$ and $\mathbf{2_{Si}}$ was uncompleted and slightly completed, respectively. For $\mathbf{1_{Si}}$, the bond length X−X is a quasi double bond (X ═══ X). The bond length X−X is single bond for other compounds (X−X) (Table I).

The molecule, $\mathbf{1_C}$, $\mathbf{1_{Si}}$, $\mathbf{1_{Ge}}$, $\mathbf{1_{Sn}}$, and $\mathbf{2_{Si}}$ have complete electron current in the three-member ring, while $\mathbf{2_{Ge}}$ and $\mathbf{2_{Sn}}$ have complete electron current in the five-member ring.

Table I B3LYP/6-311+G** calculated bond length, dihedral angle, and mullikan charge on atoms of $\mathbf{1_X}$ and $\mathbf{2_X}$



Compound	Bond length X=X (Å)	Dihedral angle C_5-X_1-$X_{1'}$-$C_{3'}$ (Degree)	Mullikan charge on X atom	Mullikan charge on X atom
$\mathbf{1_C}$	1.351	0.000	0.01	0.99
$\mathbf{1_{Si}}$	1.754	23.902	0.72	–0.03
$\mathbf{1_{Ge}}$	1.921	69.802	0.54	0.12
$\mathbf{1_{Sn}}$	1.791	39.141	1.28	–0.57
$\mathbf{2_{Si}}$	1.727	0.020	–0.50	1.13
$\mathbf{2_{Ge}}$	1.807	0.000	–0.15	0.77
$\mathbf{2_{Sn}}$	1.764	66.665	0.06	1.12

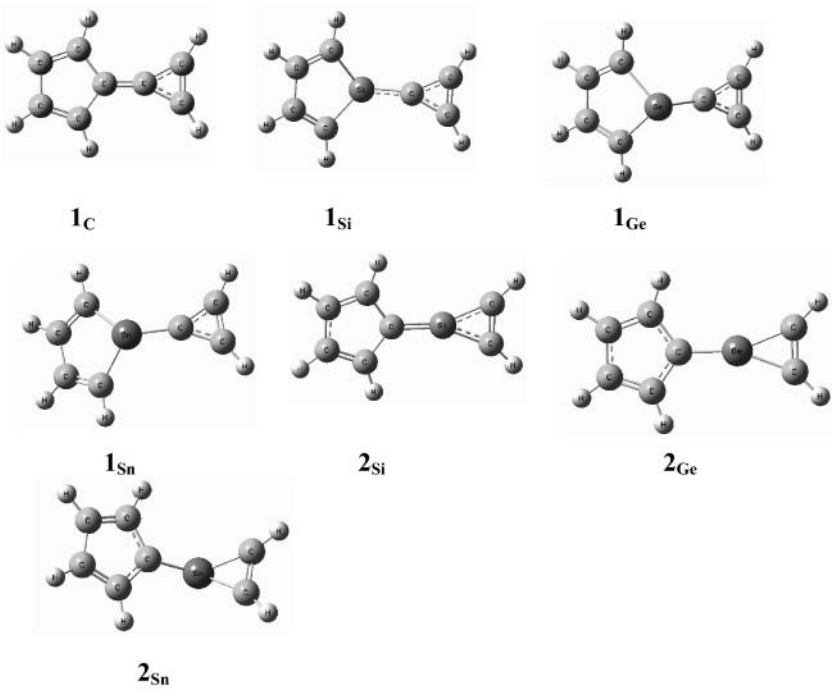


Figure 3 Bond types for full optimized conformations of calicene and its derivatives $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=C, Si, Ge and Sn) at the B3LYP/6-311+G** level of theory.

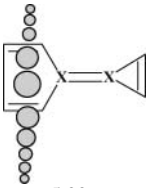
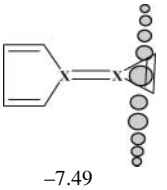
The sum of the electronic zero-point energies (ZPE), the thermal energy (E), the thermal enthalpy (H), and the thermal free energy (G) are presented at B3LYP/6-311+G** for calicene and its derivatives (see Table IV, which is available online in the Supplementary Materials).

The compound $\mathbf{1_X}$ could be energetically compared with $\mathbf{2_X}$. Molecules $\mathbf{2_{Si}}$ and $\mathbf{2_{Ge}}$ are more stable than $\mathbf{1_{Si}}$ and $\mathbf{1_{Ge}}$ ($\Delta G = 14.22$ and 8.40 kcal/mol, respectively) (Table II). It seems that replacement of heavy atoms at small ring (three-member ring) is more favorable than at large ring (five-member). This reason could be applied to describe the higher stable of $\mathbf{2_{Sn}}$ with respect to $\mathbf{1_{Sn}}$ ($\Delta G = 10.49$ kcal/mol). In addition to the above reason, the completed electron current in the two rings of $\mathbf{2_{Si}}$ leads to increased stability with respect to $\mathbf{1_{Si}}$.

Table II The zero-point energy gaps (ΔZPE), thermal energy gaps (ΔE), thermal enthalpy gaps (ΔH), and the thermal free energy gaps (ΔG) at the B3LYP/6-311+G** between $\mathbf{1_X}$ and $\mathbf{2_X}$

Compound	ΔZPE	ΔE	ΔH	ΔG
$\mathbf{1_C/2_C}$	14.31	14.42	14.43	14.22
$\mathbf{1_{Si}/2_{Si}}$	8.36	8.50	8.49	8.40
$\mathbf{1_{Ge}/2_{Ge}}$	9.97	9.84	9.85	10.49
$\mathbf{1_{Sn}/2_{Sn}}$	14.31	14.42	14.43	14.22

Table III Aromatic determination for both rings of $\mathbf{1_X}$ as well as $\mathbf{2_X}$ through NICS calculations (X=C, Si, Ge, and Sn) at the B3LYP/6-311++G(3df, 2p) Level

Compound	NICS (0)	NICS (0.5)	NICS (1.0)	NICS (1.5)	NICS (2.0)	NICS (2.5)
			Aromatic character at five-membered ring			
						
$\mathbf{1_C}$	–4.19	–4.90	–5.22	–4.21	–2.84	–1.85
$\mathbf{1_{Si}}$	–4.12	–4.61	–4.57	–3.66	–2.56	–1.60
$\mathbf{1_{Ge}}$	–3.28	–3.42	–5.22	–4.31	–2.70	–1.65
$\mathbf{1_{Sn}}$	–3.38	–5.10	–5.62	–4.67	–3.09	–1.77
$\mathbf{2_{Si}}$	–8.01	–8.33	–7.61	–5.58	–3.62	–2.33
$\mathbf{2_{Ge}}$	–8.01	–8.30	–7.48	–5.44	–3.53	–2.26
$\mathbf{2_{Sn}}$	–0.88	–0.16	–2.59	–3.20	–2.38	–1.60
			Aromatic character at three-membered ring			
						
$\mathbf{1_C}$	–21.50	–19.20	–7.49	–2.49	–1.10	–0.70
$\mathbf{1_{Si}}$	–19.19	–11.22	–2.44	–0.43	–0.19	–0.23
$\mathbf{1_{Ge}}$	–18.69	–11.48	–4.83	–2.29	–1.34	–2.90
$\mathbf{1_{Sn}}$	–18.19	–18.12	–8.66	–3.40	–1.34	–0.58
$\mathbf{2_{Si}}$	–13.44	–14.87	–7.53	–2.42	–0.79	–0.44
$\mathbf{2_{Ge}}$	–11.13	–13.03	–7.19	–2.59	–0.95	–0.52
$\mathbf{2_{Sn}}$	–13.07	–5.08	–8.70	–3.30	–1.32	–0.95

The stability of $\mathbf{1_X}$ and $\mathbf{2_X}$ may be related to the aromatic character of each ring. Therefore, the aromatic character for two rings of $\mathbf{1_X}$ and $\mathbf{2_X}$ was determined through magnetic criterion. The NICS calculations were separately carried out for both rings of $\mathbf{1_X}$ as well as $\mathbf{2_X}$. All NICS calculations were done at the B3LYP/6-311+G** level of theory (Table III). Three and five-membered rings tend to have two and six electrons (according to Hückel's 4n + 2 rule) in the ring, respectively. NICS calculations showed interesting facts about correlation between the stability and the aromatic character of $\mathbf{1_X}$ as well as $\mathbf{2_X}$. NICS (0.5) calculations for $\mathbf{1_X}$ as well as $\mathbf{2_X}$ indicated the highest aromatic character at three-membered rings with respect to five-membered rings (Table III). A higher charge was found at X (C, Si, Ge, and Sn) atoms in $\mathbf{1_X}$ than in $\mathbf{2_X}$ (Table I). A higher charge at X (C, Si, Ge, and Sn) atoms may lead to a higher aromatic character in the three-membered ring.

DFT calculations indicated an aromatic character in both three- and five-membered rings of $\mathbf{1_X}$ and $\mathbf{2_X}$, which was decreased from X=C to X=Sn (except for $\mathbf{1_{Sn}}$). However, DFT calculations indicated a non-aromatic character for $\mathbf{2_{Sn}}$ at the five-membered ring while an aromatic character was indicated at the three-membered ring. The aromatic character was generally higher for $\mathbf{2_X}$ with respect to $\mathbf{1_X}$ (except for X=Sn). It may be concluded that

the replacement of heavy atoms at the small ring (three-member ring) generally raised the aromatic character with respect to replacement at the large ring (five-member), which leads to the stabilization of $\mathbf{2_X}$ with respect to $\mathbf{1_X}$. Unexpected aromatic character was obtained from $\mathbf{1_{Sn}}$ and $\mathbf{2_{Sn}}$. A higher aromatic character for both rings of $\mathbf{1_{Sn}}$ and a lower aromatic character for $\mathbf{2_{Sn}}$ are unexpected, respectively.

CONCLUSION

Full geometry optimizations indicated that the global minimum structure for $\mathbf{1_C}$, $\mathbf{1_{Ge}}$, and $\mathbf{2_{Si}}$ has planar conformation, while for $\mathbf{1_{Si}}$, $\mathbf{1_{Ge}}$ and $\mathbf{1_{Sn}}$, it has nonplanar conformation. Molecules $\mathbf{1_C}$, $\mathbf{1_{Si}}$, $\mathbf{1_{Ge}}$, $\mathbf{1_{Sn}}$, and $\mathbf{2_{Si}}$ have complete electron current in the three-membered ring, while molecules $\mathbf{2_{Ge}}$ and $\mathbf{2_{Sn}}$ have complete electron current in the five-membered ring. Molecules $\mathbf{2_{Si}}$, $\mathbf{2_{Ge}}$, and $\mathbf{2_{Sn}}$ are more stable than $\mathbf{1_{Si}}$, $\mathbf{1_{Ge}}$, and $\mathbf{1_{Sn}}$, respectively.

DFT calculations indicated an aromatic character in both three- and five-membered rings of $\mathbf{1_X}$ and $\mathbf{2_X}$, which was decreased from X=C to X=Sn (except for $\mathbf{1_{Sn}}$). Also, a non-aromatic character and an aromatic character at three- and five-membered ring were observed for $\mathbf{2_{Sn}}$.

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