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Molecular Structure Studies on Calicene and Calicene-Like Containing Heavier Atoms Using DFT Calculations

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DFT calculations are carried out on molecular structure of calicene and calicene-like containing heavier atoms; 5-cycloprop-2-enylidene-cyclopenta-1,3-diene (CC), 1-cycloprop-2-enylidene-1*H*-silole (CSi), 1-cycloprop-2-enylidene-1*H*-germole (CGe), 1-cycloprop-2-enylidene-1*H*-stannole (CSn), 1-cyclopenta-2,4-dienylidene-1*H*-silirene (SiC), 1-siliren-1-ylidene-1*H*-silole (SiSi), 1-germol-1-ylidene-1*H*-silirene (SiGe), 1-cyclopenta-2,4-dienylidene-1*H*-germirene (GeC), 1-germiren-1-ylidene-1*H*-silole (GeSi), 1-germiren-1-ylidene-1*H*-germole (GeGe), 1-cyclopenta-2,4-dienylidene-1*H*-stannirene (SnC), 1-stanniren-1-ylidene-1*H*-silole (SnSi), at B3LYP/6-311++G** level of theory. The stability of conformations are discussed and compared.

Key Words: Cyclopropenylidenecyclopentadiene, Calicene, Molecular structure, Heavier atoms.

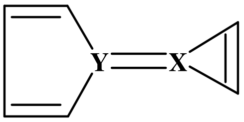
INTRODUCTION

Calicene, triapentafulvalene, cyclopropenylidenecyclopentadiene, is a completely conjugated unsaturated molecule. The two rings, connected by a double bond, can assume aromatic character with a dipolar electronic structure. This molecule has never been synthesized but the substituted species show quite 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 the two rings can be make easier by the dipolar electronic structure.

Theoretical calculations have been carried out for calicene[3-7]. Semi-empirical SCF MO calculations have been done 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 Hückel MO method in which the effects of σ-bond compression 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.*[7]. In present work, the molecular structure studies carried out on calicene and calicene-like containing heavier atoms using DFT calculations.

EXPERIMENTAL

Full geometry optimizations are carried out on calicene and calicene-like by B3LYP method (Fig. 1)[8,9]. This is using 6-311++G** basis set of the GAUSSIAN 98 system of program[10]. Global minima are specified on corresponding energy surfaces through relax scan at B3LYP/6-311++G** level of theory. Energy surfaces scanning is for obtaining more accurate values of electronic and thermal energies (E), enthalpies (H) and Gibbs free energies (G). For Sn atom, the calculations are done *via* 'Extrabasis' keyword (hetero-atoms are optimized using LANL2DZ basis set)[11]. To confirm the nature of the stationary species, frequency calculations are carried out. For minimum state structures, only real frequency values are accepted.

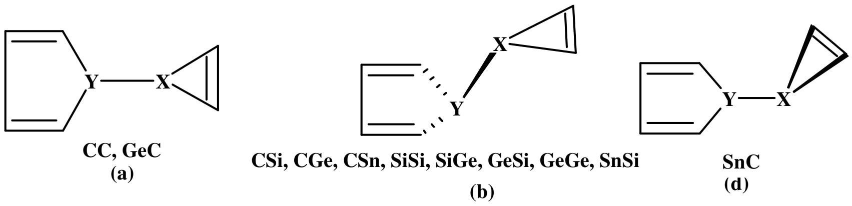


X = C, Y=C, **CC**; X = C, Y=Si, **CSi**; X = C, Y=Ge, **CGe**;
X = C, Y=Sn, **CSn**; X = Si, Y=C, **SiC**; X = Si, Y=Si, **SiSi**;
X = Si, Y=Ge, **SiGe**; X = Ge, Y=C, **GeC**; X = Ge, Y=Si, **GeSi**;
X = Ge, Y=Ge, **GeGe**; X = Sn, Y=C, **SnC**; X = Sn, Y=Si,**SnSi**;

Fig. 1. Calicene and calicene-like compounds

RESULTS AND DISCUSSION

DFT calculations are carried out on molecular structure of calicene, cyclopropenylidenecyclopentadiene; 5-cycloprop-2-enylidene-cyclopenta-1,3-diene (CC) and calicene-like containing heavier atoms; 1-cycloprop-2-enylidene-1*H*-silole (CSi), 1-cycloprop-2-enylidene-1*H*-germole (CGe), 1-cycloprop-2-enylidene-1*H*-stannole (CSn), 1-cyclopenta-2,4-dienylidene-1*H*-silirene (SiC), 1-siliren-1-ylidene-1*H*-silole (SiSi), 1-germol-1-ylidene-1*H*-silirene (SiGe), 1-cyclopenta-2,4-dienylidene-1*H*-germirene (GeC), 1-germiren-1-ylidene-1*H*-silole (GeSi), 1-germiren-1-ylidene-1*H*-germole (GeGe), 1-cyclopenta-2,4-dienylidene-1*H*-stannirene (SnC), 1-stanniren-1-ylidene-1*H*-silole (SnSi), at B3LYP/6-311++G** level of theory (Fig. 1). The fully optimized calculations suggest both planar and non-planar conformations as global minimum (Fig. 2). The fully optimized calculations suggest planar conformer as global minimum for CC, CGe and SiC (Fig. 2a) and non-planar conformer as global minimum for CSi, CGe, CSn, SiSi, SiGe, GeSi, GeGe and SnSi (Fig. 2b). The bond X-Y, connecting two rings, is forced out of plane and five-member ring is puckered for CSi, CGe, CSn, SiSi, SiGe, GeSi, GeGe and SnSi. For molecule SnC the bond X-Y is occurred in a straight line attached to five-member ring and three-member ring is occurred as bisected of molecule (Fig. 2c).



CC, GeC
(a)

CSi, CGe, CSn, SiSi, SiGe, GeSi, GeGe, SnSi
(b)

SnC
(d)

Fig. 2. Full optimized conformations for calicene and calicene-like compounds

The types of bonds are presented for CC, CSi, CGe, CSn, SiC, SiSi, SiGe, GeC, GeSi, GeGe, SnC and SnSi (Fig. 3). For CC and SiC, the bond length X-Y is double bond (X=Y). The electron current in the three-member ring of CC and SiC is completed while the electron current in the five-member ring of CC and SiC is incompleted and partial completed, respectively. For CSi, the bond length X-Y is quasi double bond (X–Y). The bond length X-Y

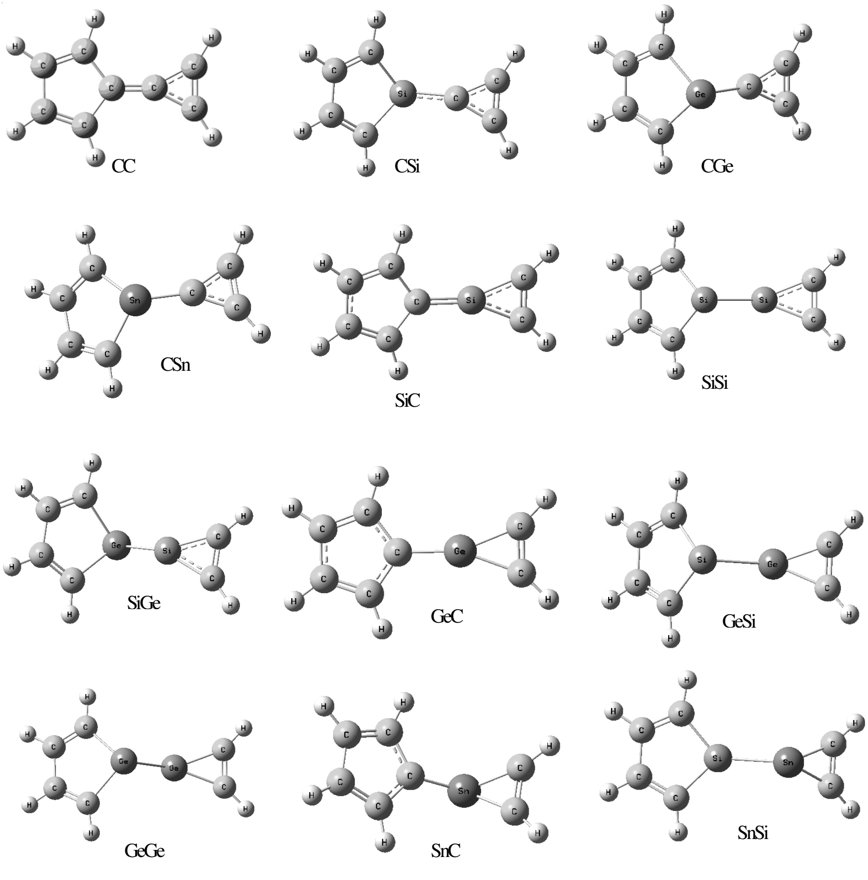


Fig. 3. Bond types for full optimized conformations of calicene and calicene-like compounds at B3LYP/6-311++G** level of theory

is single bond for other compounds (X-Y). Molecules, CC, CSi, CGe, CSn, SiC, SiSi and SiGe have completed electron current in the three-member ring while the molecules GeC and SnC have completed electron current in the five-member ring. The molecules, GeSi, GeGe and SnSi do not show any completed electron current in the both rings. Therefore, CC, CSi, CGe, CSn, SiC, SiSi and SiGe have aromatic character in the three-member ring more than for their corresponding five-member ring while GeC and SnC have aromatic character in the five-member ring more than for their corresponding three-member ring.

Sum of electronic zero-point energies (ZPE), thermal energy (E); thermal enthalpy (H) and thermal free energy (G) are presented at B3LYP/6-311++G (3df,2p) for calicene-like compounds (Table-1). The molecules which have same molecule formula could be energetically compared. Therefore, the compounds CSi, CGe, CSn and SiGe are energetically compared with SiC, GeC, SnC and GeSi, respectively. Molecules SiC and GeC are more stable than CSi and CGe (14.21 and 8.40 kcal/mol), respectively. It is seemed that the occurring of a heavy atom on small ring (three-member ring) is favour than large ring (five-member). This reason could be applied to describe the higher stable of SnC respect to CSn (10.49 kcal/mol). However, the higher stable of SiGe respect to GeSi (3.40 kcal/mol) may attributed to possibility of building a completed electron current system in the three-member ring of SiGe (Fig. 3). In spite of the above reason, the completed electron current in the two rings of SiC leads to increase its stability respect to CSi.

TABLE-1
SUM OF ELECTRONIC ZERO-POINT ENERGIES (ZPE), THERMAL ENERGIES (E), THERMAL ENTHALPIES (H) AND THERMAL FREE ENERGY (G) AT B3LYP/6-311++G ** FOR CALICENE-LIKE COMPOUNDS

Compound	ZPE	E	H	G
CC	-191449.71	-191445.62	-191445.04	-191468.76
CSi	-347615.51	-347610.61	-347610.02	-347636.03
CGe	-1458047.54	-1458042.35	-1458041.77	-1458068.75
CSn	-3873990.99	-3873986.85	-3873986.26	-3874010.95
SiC	-347629.82	-347625.03	-347624.45	-347650.25
SiSi	-503814.62	-503809.17	-503808.58	-503836.31
SiGe	-1614257.35	-1614251.56	-1614250.97	-1614280.17
GeC	-1458055.90	-1458050.85	-1458050.26	-1458077.15
GeSi	-1614254.11	-1614248.36	-1614247.78	-1614276.76
GeGe	-2724697.76	-2724691.67	-2724691.08	-2724721.44
SnC	-3874000.96	-3873996.69	-3873996.11	-3874021.44
SnSi	-4030144.57	-4030139.46	-4030138.87	-4030166.38

Conclusion

Full geometry optimizations are carried out on calicene and calicene-like by DFT method using 6-311++G** basis set of the GAUSSIAN 98 system of programs. Global minimum structures for CC, CGe and SiC have planar conformation while for CSi, CGe, CSn, SiSi, SiGe, GeSi, GeGe and SnSi have non-planar conformation. Molecules, CC, CSi, CGe, CSn, SiC, SiSi and SiGe have completed electron current in the three-member ring while the molecules, GeC and SnC have completed electron current in the five-member ring completed. Molecules SiC, SiGe, GeC and SnC are more stable than CSi, GeSi, CGe and CSn, respectively.

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