

## Conformational Studies on Divalent Five-Membered Ring $C_4H_4M$ ( $M = C, Si, Ge, Sn$ and $Pb$ )

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Sum of electronic and thermal energy differences between singlet and triplet states,  $\Delta E_{t-s}$ ; enthalpy differences,  $\Delta H_{t-s}$ ; free energy differences,  $\Delta G_{t-s}$ , are calculated for  $C_5H_4$ ,  $C_4H_4Si$ ,  $C_4H_4Ge$ ,  $C_4H_4Sn$  and  $C_4H_4Pb$  at B3LYP/6-311++G (3df,2p) level of theory. Triplet state of carbene,  $C_5H_4$ , appears planar and ground state while its corresponding singlet state is non-planar. In contrast, its analogues,  $C_4H_4M$  ( $M = Si, Ge, Sn$  and  $Pb$ ) in both singlet and triplet states have planar structures with the ground state singlet. The order of energy differences between singlet and triplet,  $\Delta G_{t-s}$ , is: plumbylenes > stanylenes > germylenes > silylenes > carbene.

**Key Words:** Carbene, Silylene, Germylene, Stanylene, Plumbylene, Aromaticity.

### INTRODUCTION

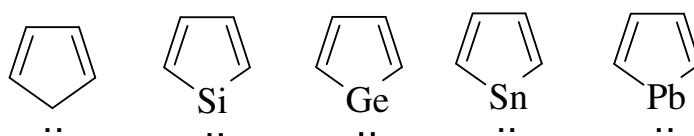
Divalent carbenes and their analogues are strongly reactive<sup>1</sup>. The cyclic completely conjugated species are important in the chemistry of divalent carbene intermediates<sup>2</sup>. These divalent structures were formerly described in terms of the Hückel ( $4n + 2$ ) rule<sup>3</sup>. However, non-planar isomers are found energy minima for most of these singlet cyclic conjugated carbenes through semi-empirical studies<sup>4</sup>. The isolation of the stable five membered cyclic conjugated carbene is firstly reported by Arduengo<sup>5</sup>. Later, the stable five membered cyclic singlet silylenes and germylenes were investigated<sup>6-12</sup>. Then, considerable development is made in the chemistry of divalent stanylenes<sup>13,14</sup>. Finally, the isolation of the plumbylenes and their derivatives are reported<sup>15-19</sup>. In this manuscript, the conformational structures on singlet and triplet states of  $C_4H_4M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ ) is discussed.

### EXPERIMENTAL

Full geometry optimizations of  $C_4H_4M$  ( $M = Si, Ge, Sn$  and  $Pb$ ) are carried out by DFT method using 6-311++G(3df,2p) basis set of the

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GAUSSIAN 98 system of programs<sup>20-22</sup> (**Scheme-I**). To find a global minimum on a specific surface, the all possible conformations of the given species are examined through scanning the specific dihedral angles at B3LYP/6-311++G(3df, 2p) level. This is for obtaining more accurate values of thermal energies (E) enthalpies (H) and Gibbs free energies (G). For stanylenes and plumblyenes, calculations are done using LANL2DZ basis set<sup>23</sup>.



**Scheme-I:** Homologues divalent species of  $C_4H_4M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ )

## RESULTS AND DISCUSSION

The energies (E), enthalpies (H) and free energies (G) is calculated for the group 14 divalent five member cyclic conjugated structures:  $C_5H_4$ ,  $C_4H_4Si$ ,  $C_4H_4Ge$ ,  $C_4H_4Sn$  and  $C_4H_4Pb$  at B3LYP/6-311++G (3df,2p) level of theory (Table-1). Sum of electronic and thermal energy differences between singlet and triplet states,  $\Delta E_{t-s}$ ; sum of electronic and thermal enthalpy differences between singlet and triplet states,  $\Delta H_{t-s}$ ; sum of electronic and thermal free energy differences between singlet and triplet states,  $\Delta G_{t-s}$ , are calculated at B3LYP/6-311++G (3df,2p) (Table-2). Geometrical parameters including bond lengths (R), bond angle (A) and dihedral angle (D) are calculated at B3LYP/6-311++G (3df,2p) level (Table-3).

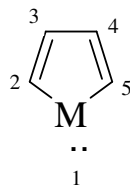
TABLE-1  
SUM OF ELECTRONIC AND THERMAL ENERGY (E); SUM OF ELECTRONIC AND THERMAL ENTHALPY (H); SUM OF ELECTRONIC AND THERMAL FREE ENERGY (G) AT B3LYP/6-311++G (3df,2p) FOR SINGLET (s) AND TRIPLET (t) STATES OF  $C_4H_4M$  ( $M = C, Si, Ge, Sn$  AND  $Pb$ )

Compound	E	H	G
$M = C_{(s)}$	-120903.597	-120903.004	-120922.939
$M = Si_{(s)}$	-278709.981	-278709.389	-278729.872
$M = Ge_{(s)}$	-1400374.331	-1400373.739	-1400396.049
$M = Sn_{(s)}$	-99173.673	-99173.081	-99195.803
$M = Pb_{(s)}$	-99233.427	-99232.834	-99256.134
$M = C_{(t)}$	-120912.846	-120912.253	-120932.537
$M = Si_{(t)}$	-278694.397	-278693.805	-278715.021
$M = Ge_{(t)}$	-1400351.716	-1400351.123	-1400373.264
$M = Sn_{(t)}$	-99147.353	-99146.760	-99169.598
$M = Pb_{(t)}$	-99205.360	-99204.768	-99228.831

TABLE-2  
SUM OF ELECTRONIC AND THERMAL ENERGY DIFFERENCES BETWEEN SINGLET (s) AND TRIPLET (t) STATES  $\Delta E_{s-t}$ ; ELECTRONIC AND THERMAL ENTHALPY DIFFERENCES  $\Delta H_{s-t}$ ; ELECTRONIC AND THERMAL FREE ENERGY DIFFERENCES  $\Delta G_{s-t}$ , at B3LYP/6-311++G(3df,2p) FOR  $C_4H_4M$  (M = C, Si, Ge, Sn AND Pb)

Compound	$\Delta E_{s-t}$	$\Delta H_{s-t}$	$\Delta G_{s-t}$
M = C	9.249	9.249	9.598
M = Si	-15.584	-15.584	-14.851
M = Ge	-22.616	-22.616	-22.786
M = Sn	-26.319	-26.320	-26.205
M = Pb	-28.067	-28.067	-27.304

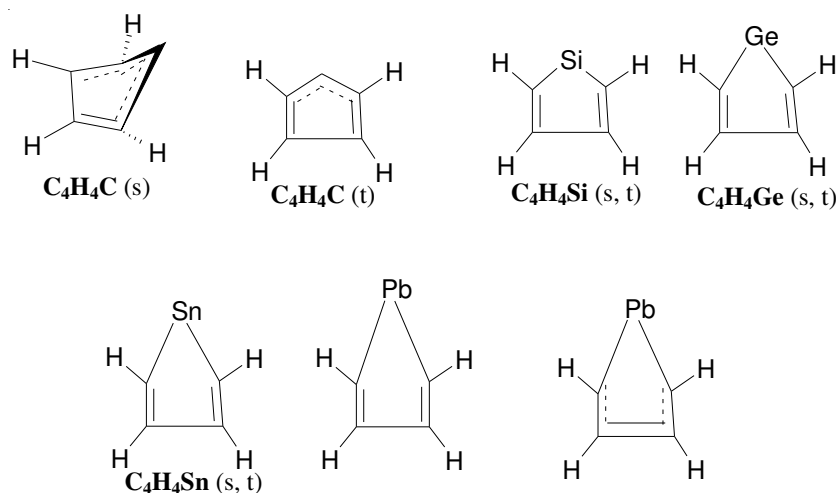
TABLE-3  
BOND LENGTHS (Å), BOND ANGLE (°) AND DIHEDRAL ANGLE (°) AT B3LYP/6-311++G (3df,2p) FOR  $C_4H_4M$  (M = C, Si, Ge, Sn AND Pb)



Compound	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	$A_{2,1,3}$	$D_{2,1,3,4}$
M = C <sub>(s)</sub>	1.410	1.401	1.470	116.798	-30.213
M = Si <sub>(s)</sub>	1.853	1.349	1.499	92.319	0.000
M = Ge <sub>(s)</sub>	2.026	1.341	1.498	84.363	0.000
M = Sn <sub>(s)</sub>	2.202	1.343	1.495	79.905	0.000
M = Pb <sub>(s)</sub>	2.266	1.344	1.492	78.363	0.000
M = C <sub>(t)</sub>	1.426	1.373	1.482	112.912	0.000
M = Si <sub>(t)</sub>	1.838	1.367	1.465	96.340	0.000
M = Ge <sub>(t)</sub>	1.938	1.358	1.468	92.455	0.000
M = Sn <sub>(t)</sub>	2.187	1.433	1.386	77.025	0.000
M = Pb <sub>(t)</sub>	2.254	1.432	1.386	75.538	-0.043

Triplet state of carbene ( $C_5H_4$ ) appears planar and ground state while its corresponding singlet state is non-planar (**Scheme-II** and Tables 1-3). In contrast, its analogues,  $C_4H_4M$ , (M = Si, Ge, Sn and Pb) in both singlet and triplet states have planar structures with the ground state singlet.

This issue that carbene,  $C_5H_4$ , is ground state triplet while silylene, germylene, stanylene and plumbylene are ground state singlets is well explained by evaluation of HOMO-LUMO energies<sup>24,25</sup>.  $\Delta(\text{LUMO-HOMO})$  for divalent compounds,  $C_4H_4M$  (M = C, Si, Ge, Sn and Pb) is increased from M = C to M = Pb; showing stabilization of singlet respect to triplet state.



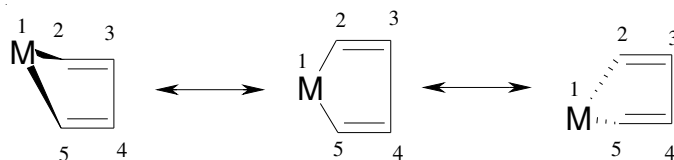
**Scheme-II:** Optimized structures for singlet (s) and triplet (t) states of  $C_4H_4M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ )

Heavier atoms prefer to have non-bonding electrons in atomic orbitals with a higher percentage of s-character. The higher s-character in the  $2a_1$  orbital of  $C_4H_4M$  ( $M = Si, Ge, Sn$  and  $Pb$ ) relative to  $C_3H_4$  suggests a relatively lower energy of this orbital and a higher HOMO-LUMO gap in  $C_4H_4M$ .

One of the factors to rising of  $\Delta G_{s-t}$ , is the electron-electron repulsion between the lone pair electrons for the singlet state. The larger size of heavier divalent atoms diminishes the electron-electron repulsion of lone pair electrons; favouring the singlet state for  $C_4H_4M$  ( $M = Si, Ge, Sn$  and  $Pb$ ) respect to  $C_4H_4C$ <sup>26</sup>.

The order of energy differences between singlet and the corresponding triplet,  $\Delta G_{t-s}$ , is: plumbylenes > stanylenes > germlylenes > silylenes > carbene. This singlet-triplet splitting,  $\Delta G_{t-s}$ , order is similar to the simple analogues<sup>27</sup>  $:CH_2$ ,  $:SiH_2$ ,  $:GeH_2$ ,  $:SnH_2$  and  $:PbH_2$ .

In order to confirm global minima, energy surface studies are necessary, since puckering of cyclopenta-2,4-dienylidene rings may alter positions of the global minima. Puckering progression are presented for  $M$ -cyclopenta-2,4-dienylidene ring as a function of dihedral angle  $D_{2,1,5,4}$  ( $M = C, Si, Ge, Sn$  and  $Pb$ ) (**Scheme-III**). The puckering energy appears higher for triplet states than their corresponding singlet states. The order of puckering energy barriers for both singlet and triplet states is: carbenes > silylenes > germlylenes > stanylenes > plumbylenes. Nevertheless, the puckering energy barriers are higher for triplet states compared to their corresponding singlet states.



**Scheme-III:** Puckering progression for  $C_4H_4M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ ) as a function of dihedral angle  $D_{2,1,5,4}$

### Conclusion

Triplet state of carbene ( $C_3H_4$ ) appears planar and ground state while its corresponding singlet state is non-planar. In contrast, its analogues,  $C_4H_4M$ , ( $M = Si, Ge, Sn$  and  $Pb$ ) in both singlet and triplet states have planar structures with the ground state singlet. The order of singlet-triplet splitting ( $\Delta G_{t-s}$ ) is: plumblylenes > stanylenes > germylenes > silylenes > carbene.

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