

## Conformational Studies on Divalent Rings $C_4H_nM$ ( $n = 4, 6$ and $8$ ; $M = C, Si, Ge, Sn$ and $Pb$ )

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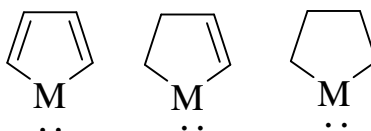
In this work, the correlation between geometry and energy of structures were studied. Geometrical parameters including bond lengths and XYZ coordinated of optimized structures,  $C_4H_4M$ ,  $C_4H_6M$  and  $C_4H_8M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ ) were calculated. The change order of  $\Delta G_{t-s}$  is (except for  $M = C$ ):  $C_4H_6M > C_4H_8M > C_4H_4M$ .

**Key Words:** Molecular structure, Carbene, Silylene, Germylene, Stanylene, Plumbylene,  $C_4H_4M$ ,  $C_4H_6M$  and  $C_4H_8M$ , Singlet-triplet splitting.

### INTRODUCTION

Carbenes are important intermediates in a variety of chemical reactions<sup>1-3</sup>. Moreover, there has been significant synthetic interest in producing the silylene and germylene analogues of the carbene<sup>4,5</sup>. The reactivity of singlet and triplet states as well as the magnitude of the singlet-triplet splitting are of great importance and have received particular attention<sup>6-11</sup>. The stabilization effects for singlet and/or triplet states of carbenes are applied for heavier congeners of group 14 elements<sup>12-14</sup>. However, non-planar isomers are found for most of these singlet cyclic conjugated carbenes through semi-empirical studies<sup>15</sup>.

Following up our work on five membered cyclic conjugated carbene<sup>15</sup>, we studied the conformational studies for  $C_4H_4M$ ,  $C_4H_6M$  and/or  $C_4H_8M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ ) (**Scheme-I**).



**Scheme-I:** Singlet and triplet states of  $C_4H_4M$ ,  $C_4H_6M$  and  $C_4H_8M$  ( $M = C, Si, Ge, Sn$  and  $Pb$ )

### EXPERIMENTAL

Geometry optimizations of  $C_4H_4M$ ,  $C_4H_6M$  and/or  $C_4H_8M$  are carried out by DFT (B3LYP) method using 6-311++G (3df, 2p) basis set of the GAUSSIAN 98 system of programs (**Scheme-I** and Table-1)<sup>16-19</sup>. To find a global minimum on a

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specific surface, all possible conformations of the given species are examined through scanning the specific dihedral angles. Therefore, the global minimum of structures is only presented in this paper. For stanylenes and plumbylenes hetero-atoms calculation are optimized using LANL2DZ basis set<sup>20</sup>. Vibrational analysis on the stationary points have been performed at B3LYP/6-311++G (3df, 2p) level of theory.

TABLE-1  
GEOMETRICAL PARAMETERS INCLUDING BOND LENGTH (DEGREE) FOR  
SINGLET AND TRIPLET STATES OF C<sub>4</sub>H<sub>6</sub>MH<sub>2</sub>, C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M AND C<sub>4</sub>H<sub>8</sub>M  
(M = C, Si, Ge, Sn and Pb)

Compound	C <sub>4</sub> H <sub>6</sub> MH <sub>2</sub> =C-MH <sub>2</sub>	C <sub>4</sub> H <sub>4</sub> M: =C-M:	C <sub>4</sub> H <sub>6</sub> M: =C-M:	C <sub>4</sub> H <sub>8</sub> M: -HC-M:
M = C <sub>(s)</sub>	1.51	1.39	1.45	1.48
M = Si <sub>(s)</sub>	1.87	1.43	1.38	1.49
M = Ge <sub>(s)</sub>	1.95	1.93	1.89	1.93
M = Sn <sub>(s)</sub>	2.12	1.84	1.84	1.93
M = Pb <sub>(s)</sub>	2.22	2.26	1.98	2.03
M = C <sub>(t)</sub>	1.51	1.94	1.94	2.04
M = Si <sub>(t)</sub>	1.87	2.20	2.16	2.21
M = Ge <sub>(t)</sub>	1.95	2.19	2.14	2.23
M = Sn <sub>(t)</sub>	2.12	2.27	2.28	2.28
M = Pb <sub>(t)</sub>	2.22	2.25	2.24	2.34

## RESULTS AND DISCUSSION

In present studies, the correlation between geometry and energy of structures were studied. Geometrical parameters including bond lengths, bond angles and XYZ coordinated of optimized structures, C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M and C<sub>4</sub>H<sub>8</sub>M (M = C, Si, Ge, Sn and Pb) were calculated (Table-1 and table in supplementary section). Sum of electronic and thermal free energy differences between singlet and triplet states,  $\Delta G_{t-s}$ , are calculated. All calculation were carried out at B3LYP/311++G (3df, 2p) level of theory.

Singlet state of carbene, C<sub>4</sub>H<sub>4</sub>C, appears non-planar and ground state while its corresponding triplet state is planar. In contrast, both singlet and triplet states of its analogues, C<sub>4</sub>H<sub>4</sub>M (M = Si, Ge, Sn and Pb) have planar structures with the ground state singlet. The structures of C<sub>4</sub>H<sub>6</sub>M and C<sub>4</sub>H<sub>8</sub>M are non-planar in both singlet and triplet states.

The free energy differences between singlet and the corresponding triplet states,  $\Delta G_{t-s}$ , of C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M and C<sub>4</sub>H<sub>8</sub>M generally increase in absolute magnitude from M = C to M = Pb (Table-2). The change order of singlet-triplet splitting,  $\Delta G_{t-s}$ : plumbylenes > stanylenes > germlylenes > silylenes > carbene.

Singlet-triplet splitting,  $\Delta G_{t-s}$ , was also compared along with three analogues C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M and C<sub>4</sub>H<sub>8</sub>M.  $\Delta G_{t-s}$  of C<sub>4</sub>H<sub>4</sub>C is the most with respect to C<sub>4</sub>H<sub>6</sub>C and C<sub>4</sub>H<sub>8</sub>C (Table-2). This order attributed to the instability of singlet or the stability of

TABLE-2  
SUM OF ELECTRONIC AND THERMAL FREE ENERGY SPLITTING,  $\Delta G_{s-t}$ , BETWEEN SINGLET AND TRIPLET STATES, kcal/mol, AT B3LYP/6-311++G (3df,2p) FOR C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M AND C<sub>4</sub>H<sub>8</sub>M (WHERE M = C, Si, Ge, Sn and Pb)

Compound	$\Delta G_{s-t}$ (C <sub>4</sub> H <sub>4</sub> M)	$\Delta G_{s-t}$ (C <sub>4</sub> H <sub>6</sub> M)	$\Delta G_{s-t}$ (C <sub>4</sub> H <sub>8</sub> M)
M=C	9.598	-4.744	-9.000
M=Si	-14.851	-34.098	-31.118
M=Ge	-22.786	-38.318	-34.106
M=Sn	-26.205	-37.645	-31.954
M=Pb	-27.304	-38.597	-36.074

TABLE-3  
XYZ COORDINATED OF OPTIMIZED STRUCTURES, C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M AND C<sub>4</sub>H<sub>8</sub>M (M = C, Si, Ge, Sn and Pb)

Compd.	Atom(s)	C <sub>4</sub> H <sub>4</sub> M			C <sub>4</sub> H <sub>6</sub> M			C <sub>4</sub> H <sub>8</sub> M		
		X	Y	Z	X	Y	Z	X	Y	Z
M=C <sub>(s)</sub>	M1	0.129	-1.093	0.229	-0.167	-1.362	0.000	0.000	1.360	-0.375
	C2	1.243	-0.359	-0.159	-1.224	-0.371	0.000	-1.096	0.370	-0.519
	C3	0.634	0.894	-0.019	-0.757	0.907	0.000	-0.769	-0.931	0.256
	C4	-0.832	0.797	-0.025	0.731	0.958	0.000	0.768	-0.931	0.256
	C5	-1.150	-0.533	-0.083	1.091	-0.547	0.000	1.095	0.583	0.256
M=Si <sub>(s)</sub>	M1	1.375	0.000	0.000	1.422	-0.045	0.000	-1.040	-1.024	0.000
	C2	-0.023	-1.331	0.000	0.151	1.347	0.000	0.886	-1.024	0.000
	C3	-1.233	0.750	0.000	-1.127	0.909	0.000	0.416	1.395	-0.314
	C4	-0.023	1.331	0.000	-1.388	-0.568	0.000	1.401	0.395	0.314
	C5	-0.023	-1.331	0.000	-0.038	-1.314	0.000	-1.011	0.902	0.000
M=Ge <sub>(s)</sub>	M1	1.008	0.000	0.000	1.055	-0.011	-0.001	-0.797	-0.751	0.000
	C2	-0.494	1.360	0.000	-0.341	1.387	0.001	-0.676	1.273	0.000
	C3	-1.687	-0.749	0.000	-1.596	0.893	0.000	0.771	1.683	-0.324
	C4	-1.687	0.749	0.000	-1.825	-0.591	-0.002	1.726	0.669	0.324
	C5	-0.494	-1.360	0.000	-0.482	-1.343	0.002	1.231	-0.751	0.000
M=Sn <sub>(s)</sub>	M1	0.840	0.000	0.000	0.885	-0.005	-0.004	-0.694	-0.607	0.000
	C2	-0.848	1.414	0.000	-0.707	1.451	0.016	-0.401	1.586	0.000
	C3	-2.014	-0.747	0.000	-1.933	0.892	0.003	1.076	1.859	-0.339
	C4	-2.014	0.747	0.000	-2.148	-0.599	-0.022	1.985	0.821	0.339
	C5	-0.848	-1.414	0.000	-0.832	-1.401	0.025	1.519	-0.607	0.000
M=Pb <sub>(s)</sub>	M1	-0.612	0.000	0.000	-0.649	-0.003	-0.003	-0.518	-0.442	0.000
	C2	1.145	-1.431	0.000	1.014	1.470	0.025	-0.155	1.810	0.000
	C3	2.300	0.746	0.000	2.228	0.891	0.003	1.326	2.033	-0.344
	C4	2.300	-0.746	0.000	2.438	-0.602	-0.033	2.218	0.985	0.344
	C5	1.144	1.432	-0.001	1.135	-1.420	0.037	1.763	-0.442	0.000
M=C <sub>(t)</sub>	M1	0.001	-1.215	0.000	-0.107	-1.265	0.000	0.000	1.231	-0.404
	C2	1.189	-0.427	0.000	-1.233	-0.469	0.000	1.172	0.629	0.287
	C3	0.741	0.871	0.000	-0.837	0.864	0.000	0.773	-0.877	0.287
	C4	-0.741	0.871	0.000	0.674	0.974	0.000	-0.773	-0.877	0.287
	C5	-1.188	-0.427	0.000	1.184	-0.514	0.000	-1.172	0.337	-0.604

M=Si <sub>(t)</sub>	M1	-1.259	0.000	0.000	-0.916	-0.975	0.000	-0.889	-1.033	0.000
	C2	-0.033	-1.370	0.000	-1.130	0.853	0.000	-1.176	0.876	0.000
	C3	1.176	0.732	0.000	0.094	1.422	0.000	0.252	1.366	-0.332
	C4	1.176	-0.732	0.000	1.340	0.549	-0.001	1.314	0.452	0.332
	C5	-0.033	1.370	0.000	1.013	-0.975	0.000	1.041	-1.033	0.000
M=Ge <sub>(t)</sub>	M1	0.929	0.000	0.000	0.996	-0.025	-0.022	-0.694	-0.759	0.000
	C2	-0.411	-1.399	0.000	-0.262	1.450	0.048	-0.875	1.273	0.000
	C3	-1.595	0.734	0.000	-1.504	0.941	0.030	0.571	1.663	-0.337
	C4	-1.595	-0.734	0.000	-1.746	-0.563	-0.093	1.606	0.716	0.337
	C5	-0.411	1.399	0.000	-0.484	-1.427	0.106	1.346	-0.759	0.000
M=Sn <sub>(t)</sub>	M1	0.780	0.000	0.000	-0.847	-0.010	0.018	-0.624	-0.615	0.000
	C2	0.781	1.390	0.000	0.650	1.512	-0.074	-0.592	1.610	0.000
	C3	2.001	0.714	0.000	1.848	0.922	-0.032	0.882	1.846	-0.350
	C4	2.001	0.714	0.000	2.049	-0.589	0.135	1.859	0.855	0.350
	C5	0.781	1.390	0.000	0.827	-1.475	-0.150	1.601	-0.615	0.000
M=Pb <sub>(t)</sub>	M1	-0.631	0.000	0.000	0.698	0.045	0.058	-0.477	-0.436	0.107
	C2	1.151	1.381	0.000	1.038	1.574	0.100	1.856	-0.436	0.107
	C3	2.407	-0.693	0.000	2.192	0.903	0.034	2.091	1.065	0.107
	C4	2.407	0.693	0.000	2.352	-0.615	0.363	1.135	1.884	-0.826
	C5	1.151	-1.381	0.000	1.170	4.377	0.194	-0.334	1.829	-0.447

triplet state for C<sub>4</sub>H<sub>4</sub>C respect to C<sub>4</sub>H<sub>6</sub>C and C<sub>4</sub>H<sub>8</sub>C. Moreover, except for M=C, the change order of  $\Delta G_{t-s}$  with negative sign is: C<sub>4</sub>H<sub>6</sub>M > C<sub>4</sub>H<sub>8</sub>M > C<sub>4</sub>H<sub>4</sub>M. This order is related to the stability of singlet or the instability of triplet state for C<sub>4</sub>H<sub>6</sub>M respect to C<sub>4</sub>H<sub>8</sub>M and C<sub>4</sub>H<sub>4</sub>M.

To discuss about a possible strong conjugation between M: and double bonds apart from the energetic criterion, the geometrical parameter is discussed (Table-1). Stronger conjugation between M: and an adjacent C=C bond should lead to a shorter M-C bond (as compared with the M-C bond in the corresponding H<sub>2</sub>M-C=C compound). The bond length =C-C: for triplet state and specially singlet state of C<sub>4</sub>H<sub>4</sub>C: is shortest among the other analogues (C<sub>4</sub>H<sub>6</sub>C: and C<sub>4</sub>H<sub>8</sub>C:), showing strongest conjugation between C: and an adjacent C=C bond. Surprisingly, the bond length =C-Si: for the singlet state of C<sub>4</sub>H<sub>6</sub>Si: is shortest among the other analogues (C<sub>4</sub>H<sub>4</sub>C: and C<sub>4</sub>H<sub>8</sub>C:) while the bond length =C-Si: for triplet state of C<sub>4</sub>H<sub>6</sub>Si: is near to the other analogues. The bond length =C-C: for both triplet and singlet states of C<sub>4</sub>H<sub>6</sub>M: (M = Ge, Sn and Pb) is more or less similar to each other.

## Conclusion

Singlet and triplet splittings,  $\Delta G_{t-s}$ , of C<sub>4</sub>H<sub>4</sub>M, C<sub>4</sub>H<sub>6</sub>M and C<sub>4</sub>H<sub>8</sub>M (M = C, Si, Ge, Sn and Pb) are calculated at B3LYP/6-311++G (3df, 2p) level of theory. The change order of  $\Delta G_{t-s}$  is: C<sub>4</sub>H<sub>6</sub>M > C<sub>4</sub>H<sub>8</sub>M > C<sub>4</sub>H<sub>4</sub>M. The bond length =C-C: for triplet state and specially singlet state of C<sub>4</sub>H<sub>4</sub>C: is shortest among the other analogues (C<sub>4</sub>H<sub>6</sub>C: and C<sub>4</sub>H<sub>8</sub>C:), showing strongest conjugation between C: and an adjacent

C=C bond. Surprisingly, the bond length =C–Si: for the singlet state of C<sub>4</sub>H<sub>6</sub>Si: is shortest among the other analogues (C<sub>4</sub>H<sub>4</sub>C: and C<sub>4</sub>H<sub>8</sub>C:) while the bond length =C–Si: for triplet state of C<sub>4</sub>H<sub>6</sub>Si: is near to the other analogues.

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