Singlet-Triplet Energy Gaps in Divalent C_2H_2M and C_2H_6M (M = C, Si, Ge, Sn and Pb)

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Singlet-triplet energy gaps in cyclopropeneylidene, 1_C, and propaneylidene, 2_C, are calculated and compared with their analogues 1_M and 2_M (M = Si_{-s} *vs.* Si_{-t}), (M = Ge_{-s} *vs.* Ge_{-t}), (M = Sn_{-s} *vs.* Sn_{-t}) and (M = Pb_{-s} *vs.* Pb_{-t}); at B3LYP/6-311++G** level of theory. The change order of energy gaps between triplet (t) and singlet (s) states, ΔG_{t-s} for 1_M is: $1_{Si} > 1_C > 1_{Ge} > 1_{Sn} > 1_{Pb}$ while for 2_M, the opposite order is obtained: $2_{Pb} > 2_{Sn} > 2_{Ge} > 2_{Si} > 2_C$ (calculated *via* B3LYP/6-311++G**). Energy gaps, IG_{t-s}, of 1_M and 2_M appear linearly proportional to the size of the group 14 divalent elements (M) and the $\angle$ C-M-C angle.

Key Words: Carbenes, Silylenes, Germylenes, Stanylenes, Plumbylenes, Singlet-triplet energy gap.

INTRODUCTION

Highly reactive intermediates, carbenes, have attracted much attention in organic chemistry[1-5]. In past years, the chemistry of the bivalent and two-coordinate analogues of carbenes: silylenes, germylenes, stanylenes and plumbylenes have studied[6-12]. The presence of an electron pair in an σ orbital as well as an energetically low-lying unoccupied orbital of π-symmetry, leads to these reactive compounds react either as an electrophile or as a nucleophile towards appropriate substrates. The electrophilic character generally appears to dominate their reactivity[13].

The first silylene was synthesized by Denk *et al.*[5]. Their existence was first proposed as transient molecules in organometallic chemistry and later, they were observed in matrix at low temperature. The most important factor in the stabilization of singlet silylene is the π-electron donation from the substituent to the formally empty *p*-orbital of silicon[8,14-16].

Isolation of the plumbylene was reported by Lappert *et al.*[17,18]. However, the thermal instability and high light-sensitivity of many plumbylenes is studied earlier[19].

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Cyclopropenylidene and their divalent homologues species have three possible configurations. The triplet $\sigma\pi$ and the singlet π^2 are expected to participate in nucleophilic addition, whereas σ^2 should participate in electrophilic additions[20].

In follow up on previous works[21-23], in this work the calculations are carried out on cyclopropeneylidene, $\mathbf{1_C}$ and propaneylidene, $\mathbf{2_C}$. This calculations are studied and compared with their analogues $\mathbf{1_M}$ and $\mathbf{2_M}$ (M = Si, Ge, Sn and Pb) at B3LYP/6-311++G** level of theory (Table-1). The HOMO and LUMO orbitals and their differences are obtained by NBO analysis[24].

COMPUTATIONAL METHOD

Full geometry optimizations are carried out by HF and DFT methods[25,26]. These methods have been used *via* 6-311++G** basis set of the Gaussian 98 system[27]. For DFT calculations the Becke's hybrid three-parameters functional combined with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) with the 6-311++G** basis set is used. The 'Extrabasis' keyword is used for Sn and Pb atoms (Sn and Pb atoms are optimized by LANEL2DZ basis set)[28]. Thermodynamic functions such as thermal energies (E), thermal enthalpies (H), thermal Gibbs free energies (G) are multiplied by the suitable scaling factor and correction terms. To reach the most reliable relative energies, higher-level theoretical methods are used.

RESULTS AND DISCUSSION

Sum of electronic and thermal energies (E), thermal enthalpies (H), thermal Gibbs free energies (G) for singlet and triplet states of cyclopropeneylidene, $\mathbf{1_C}$ and propaneylidene, $\mathbf{2_C}$, are calculated and compared with their analogues $\mathbf{1_M}$ and $\mathbf{2_M}$ (M = Si, Ge, Sn and Pb) at B3LYP/6-311++G** level of theory (**Scheme-I** and Table-1). Except for $\mathbf{2_C}$, the singlet states of $\mathbf{1_M}$ and $\mathbf{2_M}$ are ground state and more stable than the corresponding triplet states, because the promotion energy essential to arrive at triplet configuration requires an increase in energy, larger than the accompanying decrease in electron-electron repulsion (Table-1).

Energy differences between singlet and their corresponding triplet states are calculated for $\mathbf{1_M}$ and $\mathbf{2_M}$ (M = C_{-s} *vs.* C_{-t}), (M = Si_{-s} *vs.* Si_{-t}), (M = Ge_{-s} *vs.* Ge_{-t}), (M = Sn_{-s} *vs.* Sn_{-t}) and (M = Pb_{-s} *vs.* Pb_{-t}), respectively (Table-2). The trend of energy differences between singlet and triplet, $\Delta G_{(t-s)}$, for $\mathbf{1_M}$ increase from M = C toward M = Si while decrease from M = Si toward M = Pb (Fig. 1). The B3LYP/6-311++G** calculated order of $\Delta G_{(t-s)}$ are: $\mathbf{1_{Si}}$ (67.835 kcal/mol) > $\mathbf{1_C}$ (46.558 kcal/mol) > $\mathbf{1_{Ge}}$ (36.266 kcal/mol) > $\mathbf{1_{Sn}}$ (25.701 kcal/mol) > $\mathbf{1_{Pb}}$ (18.065 kcal/mol). This order is related to the

TABLE-1

THERMODYNAMIC DATA CONSISTING OF THE SUM OF
ELECTRONIC AND THERMAL ENERGIES (E), THERMAL
ENTHALPIES (H), THERMAL GIBBS FREE ENERGIES (G), FOR
SINGLET (s) AND TRIPLET (t) STATES OF DIVALENT HCMCH
(1_{M-s}, 1_{M-t}) AND H_3CMCH_3 (2_{M-s}, 2_{M-t}) CALCULATED AT B3LYP/
6-311++G** LEVEL OF THEORY, WHERE M = C, Si, Ge, Sn AND Pb

Compd.(s)	B3LYP / 6-311++G(3df, 2p)		
	E	H	G
1_{C-s}	-72361.445	-72360.266	-72394.6010
1_{C-t}	-72313.069	-72311.890	-72348.0430
1_{Si-s}	-230165.623	-230164.444	-230200.7280
1_{Si-t}	-230095.795	-230094.616	-230132.8920
1_{Ge-s}	-1351827.138	-1351825.959	-1351864.0870
1_{Ge-t}	-1351786.184	-1351785.004	-1351827.8210
1_{Sn-s}	-50622.110	-50620.931	-50660.2360
1_{Sn-t}	-50591.576	-50590.397	-50634.5350
1_{Pb-s}	-50681.718	-50680.539	-50721.0510
1_{Pb-t}	-50659.147	-50657.968	-50702.9860
2_{C-s}	-73844.1140	-73842.936	-73881.4140
2_{C-t}	-73842.5740	-73841.395	-73882.4550
2_{Si-s}	-231656.2321	-231655.0533	-231695.8173
2_{Si-t}	-231627.7210	-231626.543	-231670.2980
2_{Ge-s}	-1353318.8860	-1353317.707	-1353363.3020
2_{Ge-t}	-1353286.7140	-1353285.535	-1353332.4010
2_{Sn-s}	-52117.1950	-52116.017	-52164.5970
2_{Sn-t}	-52086.7290	-52085.549	-52135.2050
2_{Pb-s}	-52177.5580	-52176.378	-52222.5940
2_{Pb-t}	-52138.4660	-52137.287	-52188.5160
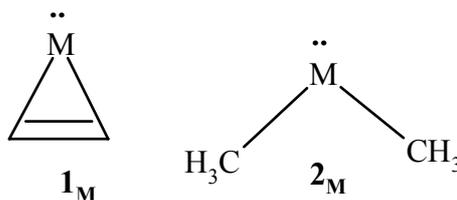
Scheme-I

strained structures of 1_M. The strain of cyclopropyl ring increase from C to
Pb, destabilizing the singlet state and also decrease difference energies,
$\Delta G_{(t-s)}$. The difference energies, $\Delta G_{(t-s)}$ for 1_{Si} are the most respected to other
1_M.

TABLE-2

ENERGY DIFFERENCE BETWEEN SINGLET AND THEIR
CORRESPONDING TRIPLET STATES: ELECTRONIC AND THERMAL
ENERGIES, $\Delta E_{(t-s)}$; ELECTRONIC AND THERMAL ENTHALPIES,
$\Delta H_{(t-s)}$; ELECTRONIC AND THERMAL FREE ENERGIES, $\Delta G_{(t-s)}$, FOR
DIVALENT HCMCH ($\mathbf{1_{M-s}}$, $\mathbf{1_{M-t}}$), H_3CMCH_3 ($\mathbf{2_{M-s}}$, $\mathbf{2_{M-t}}$) LEVEL OF
THEORY, WHERE M = C, Si, Ge, Sn AND Pb

	B3LYP/6-311++G**		
	$\Delta E_{(t-s)}$	$\Delta H_{(t-s)}$	$\Delta G_{(t-s)}$
$\mathbf{1_C}$	48.376	48.376	46.558
$\mathbf{1_{Si}}$	69.828	69.828	67.835
$\mathbf{1_{Ge}}$	40.954	40.954	36.266
$\mathbf{1_{Sn}}$	30.534	30.534	25.701
$\mathbf{1_{Pb}}$	22.571	22.571	18.065
$\mathbf{2_C}$	1.541	1.541	-1.041
$\mathbf{2_{Si}}$	28.511	28.511	25.519
$\mathbf{2_{Ge}}$	32.172	32.172	30.901
$\mathbf{2_{Sn}}$	30.466	30.467	29.392
$\mathbf{2_{Pb}}$	39.092	39.091	34.078
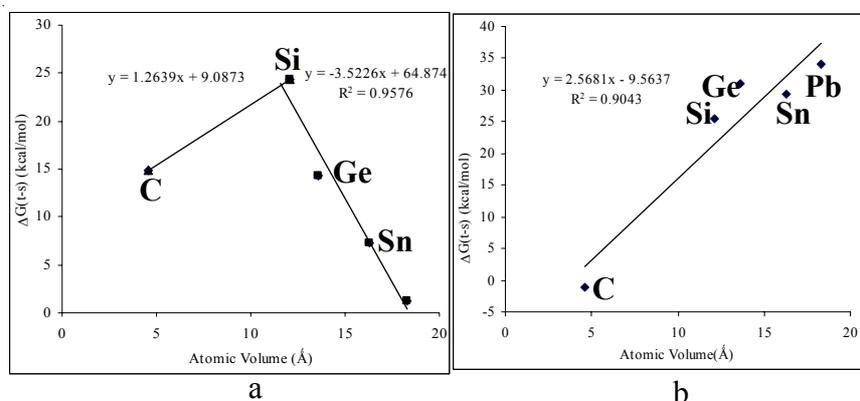
Fig. 1. Plot of $\Delta G_{(t-s)}$ *vs.* atomic volume for divalent HCMCH ($\mathbf{1_{M-s}}$, $\mathbf{1_{M-t}}$) and
H_3CMCH_3 ($\mathbf{2_{M-s}}$, $\mathbf{2_{M-t}}$), calculated at B3LYP/6-311++G** level of theory,
where M = C, Si, Ge, Sn and Pb

Generally, the amount of difference energies, $\Delta G_{(t-s)}$ for $\mathbf{1_M}$ could be
explained with the aromatic character shown in the **Scheme-II**. In fact,
$\mathbf{1_{M-s}}$ has a σ^2 center, which enables it to show an aromatic character (**Schemes
II** and **III**). It is seemed that $\mathbf{1_{M-s}}$ has greater aromatic character respected
to its triplet state $\mathbf{1_{M-t}}$ due to occupying one electron of triplet state in the π
orbital ($\sigma\pi$ configuration, **Schemes II** and **III**).

1_{M-s}

1_{M-t}
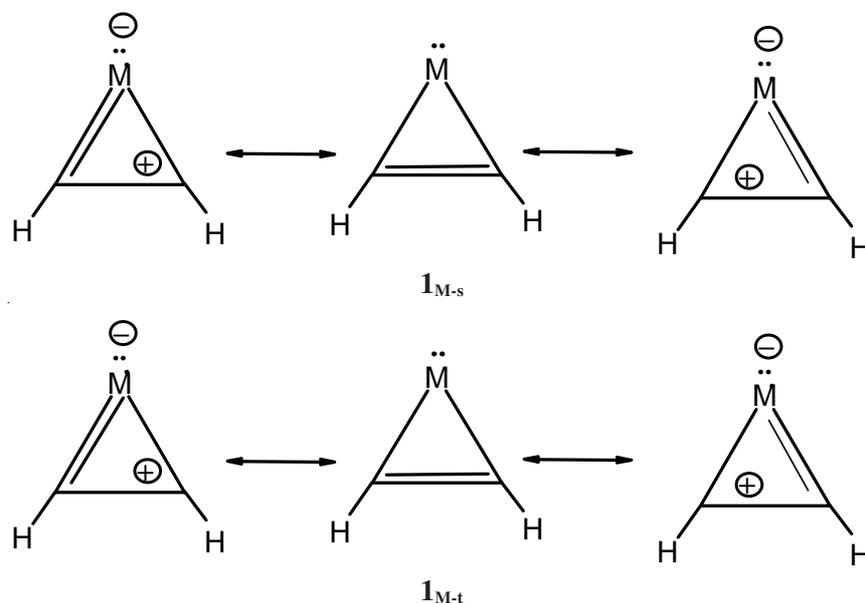
Scheme-II   Electron resonance and aromatic character of divalent
HCMCH (**1_{M-s}**, **1_{M-t}**) where M = C, Si, Ge, Sn and Pb
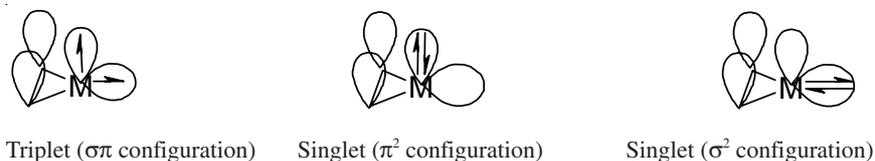
Triplet ($\sigma\pi$ configuration)   Singlet (π^2 configuration)   Singlet (σ^2 configuration)

Scheme-III. Three possible configurations of divalent HCMCH (**1_M**) where
M = C, Si, Ge, Sn and Pb

The difference energies, $\Delta G_{(t-s)}$, for **2_M** is ascending from C to Pb. The B3LYP/6-311++G** calculated order of changes is: **2_{Pb}** (34.078 kcal/mol) > **2_{Sn}** (30.901 kcal/mol) > **2_{Ge}** (29.392 kcal/mol) > **2_{Si}** (25.519 kcal/mol) > **2_C** (-1.041 kcal/mol). This order is due to the stabilization of the singlet states by the larger valence orbitals in acyclic carbenes and their analogous[1]. The larger size of the valence orbitals of plumbylenes, stanylenes, germylenes and silylenes, respectively, in comparison with carbenes leads to a decrease in the electron-electron repulsion of the lone pair of the singlet species. This in turn attenuates the lowering of energy upon separating these electrons in the triplet state. Therefore, the singlet state is stabilized from C to Pb and also the difference energies, $IG_{(t-s)}$ is increased (Table-2 and Fig. 1).

TABLE-3

GEOMETRICAL PARAMETERS (BOND LENGTHS/Å, BOND ANGLES / DEGREES), MULLIKEN CHARGES AND TOTAL DIPOLE MOMENT OF DIVALENT HCMCH (1_{M-s}, 1_{M-t}) AND H$_3$CMCH$_3$ (2_{M-s}, 2_{M-t}), CALCULATED AT B3LYP/6-311++G** LEVEL OF THEORY, WHERE M = C, Si, Ge, Sn and Pb

Compound	Bond length (Å)			Bond angle (°)			Mulliken charges			Dipole moment
	$R_{1,2}$	$R_{2,3}$	$R_{3,1}$	$A_{1,2,3}$	$A_{2,3,1}$	$A_{2,1,3}$ (C-M_1-C)	M_1	C_2	C_3	
1_{C-s}	1.419	1.324	1.419	62.177	62.196	55.627	-0.481	0.241	0.241	3.488
1_{C-t}	1.452	1.334	1.452	62.652	62.647	54.701	-0.153	0.076	0.076	2.025
1_{Si-s}	1.835	1.341	1.835	68.564	68.579	42.858	0.292	-0.146	-0.146	0.951
1_{Si-t}	1.838	1.355	1.837	68.340	68.402	43.258	0.105	-0.053	-0.052	0.813
1_{Ge-s}	1.942	1.334	1.942	69.921	69.903	40.176	0.388	-0.194	-0.194	0.499
1_{Ge-t}	2.362	1.231	2.362	74.880	74.918	30.202	-0.050	0.025	0.025	1.908
1_{Sn-s}	2.128	1.332	2.129	71.796	71.743	36.461	0.530	-0.173	-0.356	0.497
1_{Sn-t}	2.813	1.211	2.815	77.465	77.683	24.852	-0.030	-0.285	0.315	1.650
1_{Pb-s}	2.199	1.326	2.200	72.494	72.407	35.099	0.447	-0.128	-0.319	1.320
1_{Pb-t}	2.902	1.209	2.900	78.043	77.908	24.049	-0.035	-0.311	0.347	1.223
2_{C-s}	1.471	2.448	1.470	–	–	112.641	-0.092	0.046	0.046	2.108
2_{C-t}	1.468	2.700	1.468	–	–	133.731	0.330	-0.165	-0.165	0.822
2_{Si-s}	1.916	2.891	1.915	–	–	97.952	0.358	-0.179	-0.179	1.238
2_{Si-t}	1.906	3.278	1.906	–	–	118.622	0.230	-0.115	-0.115	0.779
2_{Ge-s}	2.016	2.993	2.016	–	–	95.866	0.468	-0.234	-0.234	0.709
2_{Ge-t}	2.007	3.453	2.008	–	–	118.633	0.251	-0.126	-0.126	0.921
2_{Sn-s}	2.202	3.202	2.202	–	–	93.307	0.662	-0.331	-0.331	0.012
2_{Sn-t}	2.194	3.751	2.194	–	–	117.464	0.332	-0.166	-0.166	0.322
2_{Pb-s}	2.273	3.287	2.273	–	–	92.597	0.610	-0.305	-0.305	0.896
2_{Pb-t}	2.295	3.926	2.295	–	–	117.626	0.243	-0.122	-0.122	0.310

The geometrical parameters, charges on atoms and dipole moments of 1_M and 2_M are presented (Table-3). The $\angle C_2\text{-}M_1\text{-}C_3$ angles of 1_M (except M = C and Si) is larger for their singlet than their triplet states. Therefore, the suitable configuration for singlet state is π^2. However, for 1_C and 1_{Si} the configuration is σ^2 for constructing the aromatic character. In contrast, the $\angle C_2\text{-}M_1\text{-}C_3$ angle in the triplet state of 2_M is larger than singlet state. Then, the configuration of 2_M is σ^2. For both singlet and triplet states of 1_M and 2_M, the $C_2\text{-}M_1\text{-}C_3$ angle decrease from C to Pb. The B3LYP/6-311++G** calculated order of changes for singlet state are: 1_C (55.627°) > 1_{Si} (42.858°) > 1_{Ge} (40.176°) > 1_{Sn} (36.461°) > 1_{Pb} (35.099°) and 2_C (112.641°) > 2_{Si} (97.952°) > 2_{Ge} (95.866°) > 2_{Sn} (93.307°) > 2_{Pb} (92.597°). These orders reveal that the p character of 1_M and 2_M increase from C to Pb. Also, the $\angle C_2\text{-}C_3\text{-}M_1$ or $\angle C_3\text{-}C_2\text{-}M_1$ of 1_M reasonably increases with the decreasing of $\angle C_2\text{-}M_1\text{-}C_3$.

The $C_1\text{-}C_2$ or $C_2\text{-}C_3$ bond length of 1_M and 2_M increase from C to Pb due to decreasing s character of hybridization of M atoms. The B3LYP/6-311++G** calculated order of $C_1\text{-}C_2$ bond length changes for singlet state are: 1_C (1.419 Å) < 1_{Si} (1.835 Å) < 1_{Ge} (1.942 Å) < 1_{Sn} (2.128 Å) < 1_{Pb} (2.199 Å) and 2_C (1.471Å) < 2_{Si} (1.916 Å) < 2_{Ge} (2.016 Å) < 2_{Sn} (2.202 Å) < 2_{Pb} (2.273 Å).

The increasing trend of charge on M_1 in 1_M and 2_M from C to Pb is related to electropositivity trend of heteroatom M = Pb (Table-3). The B3LYP/6-311++G** calculated order of Mulliken Charge changes on M atom for singlet state are: 1_C (-0.481) < 1_{Si} (0.292) < 1_{Ge} (0.388) < 1_{Pb} (0.447) < 1_{Sn} (0.53) and 2_C (-0.092) < 2_{Si} (0.358) < 2_{Ge} (0.468) < 2_{Pb} (0.610) < 2_{Sn} (0.662).
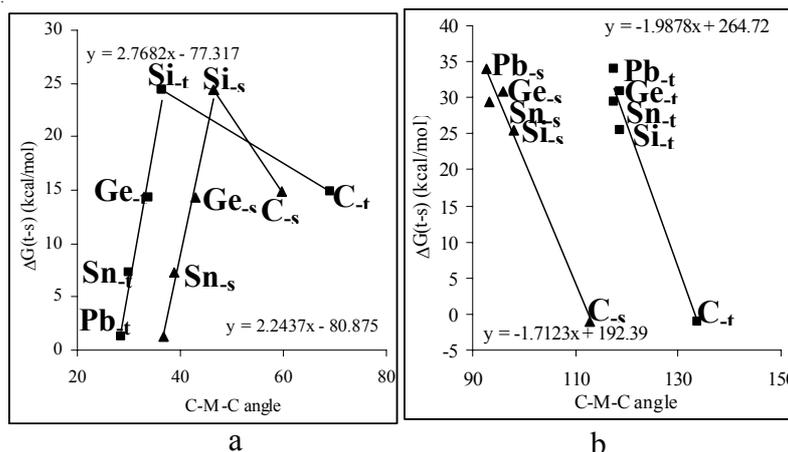
Fig. 2. Correlations between $\Delta G_{(t-s)}$ and the $\angle$C-M-C angle (A₁) for divalent HCMCH ($1_{M\text{-}s}$, $1_{M\text{-}t}$) and H₃CMCH₃ ($2_{M\text{-}s}$, $2_{M\text{-}t}$) calculated at B3LYP/6-311++G** level of theory where M=C, Si, Ge, Sn and Pb

HOMO, LUMO eigen values and their diferences, $\Delta_{(LUMO-HOMO)}$ of $\mathbf{1_M}$ and $\mathbf{2_M}$ (where M = C, Si, Ge, Sn and Pb) are extracted with B3LYP/ 6-311++G** level (Table-4). Except for $\mathbf{2_{M-s}}$ and $\mathbf{2_{M-s}}$ the HOMO eigen values and differences between HOMO and LUMO, D(LUMO-HOMO), for both singlet and triplet state of $\mathbf{1_M}$ and $\mathbf{2_M}$ decrease from C to Pb. This order is due to the electropositivity of heteroatom.

TABLE-4
HOMO AND LUMO EIGENVALUES (eV) AND THEIR DIFFERENCES, $\Delta_{(LUMO-HOMO)}$, OF DIVALENT HCMCH ($\mathbf{1_{M-s}}$, $\mathbf{1_{M-t}}$) AND H$_3$CMCH$_3$ ($\mathbf{2_{M-s}}$, $\mathbf{2_{M-t}}$), CALCULATED AT B3LYP/6-311++G** LEVEL OF THEORY, WHERE M = C, Si, Ge, Sn and Pb

Comd.	Singlet			Triplet		
	HOMO	LUMO	$\Delta_{(LUMO-HOMO)}$	HOMO	LUMO	$\Delta_{(LUMO-HOMO)}$
$\mathbf{1_C}$	-0.243	-0.049	0.194	-0.168	-0.018	0.151
$\mathbf{1_{Si}}$	-0.255	-0.065	0.190	-0.146	-0.039	0.107
$\mathbf{1_{Ge}}$	-0.244	-0.073	0.171	-0.154	-0.029	0.125
$\mathbf{1_{Sn}}$	-0.221	-0.079	0.142	-0.153	-0.061	0.092
$\mathbf{1_{Pb}}$	-0.204	-0.076	0.128	-0.147	-0.062	0.085
$\mathbf{2_C}$	-0.207	-0.073	0.134	-0.187	-0.008	0.179
$\mathbf{2_{Si}}$	-0.214	-0.090	0.125	-0.159	-0.011	0.148
$\mathbf{2_{Ge}}$	-0.219	-0.093	0.126	-0.156	-0.013	0.142
$\mathbf{2_{Sn}}$	-0.211	-0.093	0.118	-0.153	-0.016	0.137
$\mathbf{2_{Pb}}$	-0.214	-0.088	0.126	-0.143	-0.019	0.124

Correlations between $\Delta G_{(t-s)}$ and atomic volume are plotted for $\mathbf{1_M}$ and $\mathbf{2_M}$ (M = Si, Ge, Sn and Pb) (Fig. 1). The $\Delta G_{(t-s)}$ *vs.* atomic volume is decreased from Si to Pb for 1M through destabilization of singlet state due to increasing the strain of two rings. The contour of $\mathbf{1_M}$ is the same because of similar structure.

Relationship between $\Delta G_{(t-s)}$ and the $\angle$C-M-C angle figure out for both singlet and triplet state of $\mathbf{1_M}$ and $\mathbf{2_M}$ (Fig. 2). The $\Delta G(t-s)$ vs. the $\angle$C-M-C angle is increased from Pb to Si for $\mathbf{1_M}$ and decreased from Pb to C for $\mathbf{2_M}$.

Conclusion

Singlet-triplet energy gaps in cyclopropeneylidene $\mathbf{1_C}$ and propaneylidene $\mathbf{2_C}$, have been calculated and compared with their analogues $\mathbf{1_M}$ and $\mathbf{2_M}$ (M = Si$_{-s}$ *vs.* Si$_{-t}$), (M = Ge$_{-s}$ *vs.* Ge$_{-t}$), (M = Sn$_{-s}$ *vs.* Sn$_{-t}$) and (M = Pb$_{-s}$ *vs.* Pb$_{-t}$) at B3LYP/6-311++G** level of theory. The B3LYP/6-311++G** calculated order of changes of IG$_{(t-s)}$ is: $\mathbf{1_{Si}} > \mathbf{1_C} > \mathbf{1_{Ge}} > \mathbf{1_{Sn}} > \mathbf{1_{Pb}}$. The reverse order is obtained for $\mathbf{2_M}$: $\mathbf{2_{Pb}} > \mathbf{2_{Sn}} > \mathbf{2_{Ge}} > \mathbf{2_{Si}} > \mathbf{2_C}$. Except for $\mathbf{1_C}$, linear relationships between IG$_{(t-s)}$ *vs.* atomic volume and also the $\angle$C-M-C angles is found.

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