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Singlet–Triplet Splitting and Stability of Divalent Five-Membered Ring C_4H_4M, C_4H_6M, and C_4H_8M (M = C, Si, Ge, Sn, and Pb)

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ABSTRACT: *The sum of electronic and thermal free energy differences between singlet and triplet states (ΔG_{t-s}) is calculated for C_4H_4M, C_4H_6M, and C_4H_8M (M = C, Si, Ge, Sn, and Pb) at B3LYP/6-311++G (3df,2p) level. Singlet–triplet splitting (ΔG_{t-s}) is compared for three analogs C_4H_4M, C_4H_6M, and C_4H_8M. The change order of ΔG_{t-s} is (except for M = C) $C_4H_6M > C_4H_8M > C_4H_4M$. The results of homodesmotic reaction energies show the most stability for singlet state of C_4H_6M with respect to C_4H_4M and C_4H_8M. In contrast, the triplet state of C_4H_4M (except for M = C) is the most stable with respect to C_4H_6M and C_4H_8M.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:245–251, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20428

INTRODUCTION

Carbenes are important intermediates in a variety of chemical reactions. They have been extensively studied both experimentally and theoretically [1–3]. Moreover, there has been significant synthetic interest in producing the silylene and germylene analogs of the carbene [4,5]. The reactivity of singlet and triplet states as well as the magnitude of the singlet–triplet splitting is of great importance and has received particular attention [6–11]. The stabilization effects for singlet and/or triplet states of carbenes are applied for heavier congeners of group 14 elements [12–14]. However, nonplanar isomers are found to have energy minima for most of these singlet cyclic conjugated carbenes, obtained through semiempirical studies [15]. Cyclopentylidene and cyclopentenylidene have been previously studied [16]. The isolation of the stable five-membered cyclic conjugated carbene, 1,3-di(1-adamantyl)imidazol-2-ylidene, was first reported by Arduengo et al. [17b]. Later, the stable five-membered cyclic singlet silylenes and the corresponding germylenes were synthesized and their physical properties were compared with the Arduengo-type carbenes [18–20].

Silylenes and germylenes have been the center of attention for more than the last two decades because of their importance of these group 14 electron-deficient radicals in chemical vapor deposition, semiconductor manufacturing, the photonics, and aerospace industries and other roles [21–24].

Considerable development has been made in the chemistry of stable organic derivatives of divalent tin [25]. The divalent of stanylenes has been suggested as intermediates in redox reactions of diazo compounds and other molecules [26]. Finally, isolation of the plumbylenes and the characterization of their derivatives are reported [27,28]. They are usually used as reactive intermediates in the preparation of plumbanes, R_4Pb. Plumbylenes are polymerized in the absence of suitable stabilizing groups on the lead atom [29]. The sterically demanding groups may be employed as a stabilizer for a variety of highly reactive plumbylenes [30]. Following up our work on the five-membered cyclic conjugated carbene [15],

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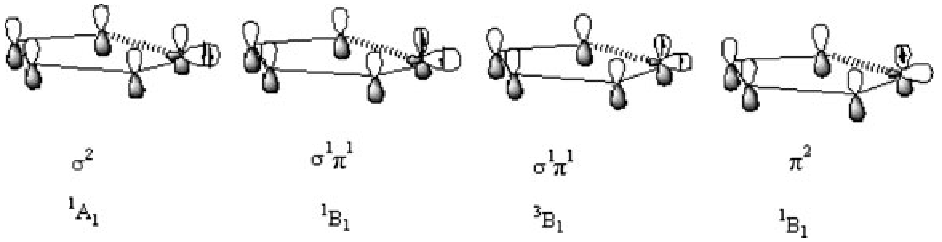
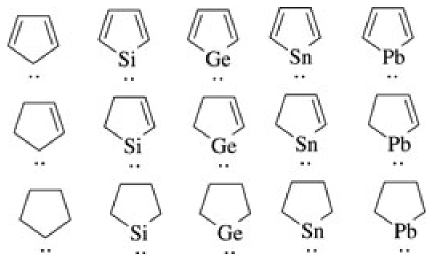


SCHEME 1 Four possible configurations for C_4H_4M, C_4H_6M, and C_4H_8M are σ^2 ($^1A_1$) singlet; $\sigma^1\pi^1$ ($^1B_1$) singlet; $\sigma^1\pi^1$ ($^3B_1$) triplet; and π^2 ($^1B_1$) singlet.



SCHEME 2 Homologues divalent species of group 14 in the periodic table: singlet and triplet of cyclic unsaturated and/or saturated carbenes, silylenes, germylenes, stanylenes, and plumbylenes.

in this paper we have comparatively studied the singlet–triplet splitting for C_4H_4M, C_4H_6M, and/or C_4H_8M (M = C, Si, Ge, Sn and Pb) (Schemes 1 and 2).

COMPUTATIONAL METHODS

Geometry optimizations of C_4H_4M, C_4H_6M, and/or C_4H_8M are carried out by using the DFT (B3LYP) method, using 6-311++G (3df,2p) basis set of the Gaussian 98 system of programs (Schemes 1 and 2 and Table 1) [31–33]. 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. Therefore, the global minimum of structures is only presented in this paper. For stanylenes and plumbylenes, heteroatoms' calculation is optimized using LANL2DZ basis set [34]. Vibrational analyses on the stationary points have been performed at B3LYP/6–311++G (3df, 2p) level of theory.

RESULTS AND DISCUSSION

The electronic and thermal free energies (*G*) are calculated for the divalent five-membered cyclic conjugated and/or unconjugated structures, C_4H_4M, C_4H_6M, and C_4H_8M (M = C, Si, Ge, Sn and Pb) at B3LYP/6-311++G (3df,2p) level of theory (Table 1). The sum of electronic and thermal free energy differences between singlet and triplet states (ΔG_{t-s}) is calculated at B3LYP/6-311++G (3df,2p) (Table 2).

For the estimation of stabilization energies (SE), various "isodesmic and/or homodesmotic" reactions are applied (Scheme 3 and Tables 3–6) [11,24].

A triplet state of carbene, C_5H_4, appears planar and ground state, whereas its corresponding singlet

TABLE 1 Sum of Electronic Energy and Thermal Correction to Gibbs Free Energy (*G*) (AU) at B3LYP/6-311++G (3df,2p) Level for the Singlet (s) and Triplet (t) States of C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb)

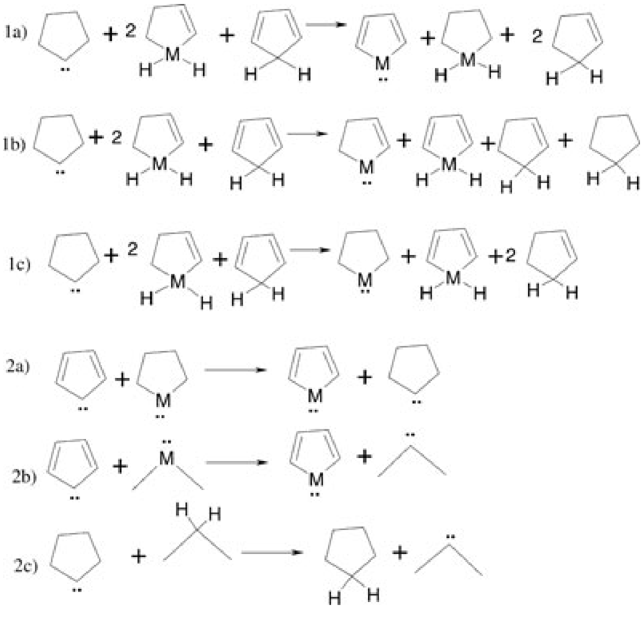
	C_4H_4M		*C_4H_6M*		*C_4H_8M*	
Compound	*G*	*ZPE*	*G*	*ZPE*	*G*	*ZPE*
$M = C_{(s)}$	−192.7714	41.5338	−193.9963	56.3650	−195.1921	70.6670
$M = Si_{(s)}$	−438.9282	43.4122	−445.4784	54.2589	−446.6767	68.5325
$M = Ge_{(s)}$	−2231.7691	39.4341	−2232.9911	53.7579	−2234.1906	68.1579
$M = Sn_{(s)}$	−158.1427	39.1200	−159.3603	53.3204	−160.5605	67.7513
$M = Pb_{(s)}$	−158.2384	38.8535	−159.3867	53.6439	−160.6556	67.4809
$M = C_{(t)}$	−192.7872	41.8555	−193.9894	56.6395	−195.1790	71.6651
$M = Si_{(t)}$	−444.2307	40.1650	−438.8939	43.5420	−446.628627	69.50462
$M = Ge_{(t)}$	−2231.7327	39.4264	−2232.9303	53.9099	−2234.1371	68.8863
$M = Sn_{(t)}$	−158.0995	38.0598	−159.3006	53.4895	−160.5104	68.2614
$M = Pb_{(t)}$	−158.1931	37.7219	−159.3891	52.0535	−160.5980	67.4329

TABLE 2 Sum of Electronic Energy and Thermal Correction to Gibbs Free Energy Differences (ΔG_{s-t}) between Singlet (s) and Triplet (t) States (in kcal/mol) at B3LYP/6-311++G (3df,2p) for C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb)

	ΔG_{s-t}		
Compound	C_4H_4M	$C_4H_{six}M$	C_4H_8M
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

state is nonplanar. In contrast, its analogs, C_4H_4M (M = Si, Ge, Sn and Pb) in both singlet and triplet states, have planar structures with the ground state singlet. The structures of C_4H_6M and C_4H_8M are nonplanar in both singlet and triplet states.

The energy differences between singlet and the corresponding triplet states (ΔG_{t-s}) of C_4H_4M, C_4H_6M, and C_4H_8M generally increase in absolute magnitude from M = C to M = Pb (Table 2). These changes in singlet–triplet splitting (ΔG_{t-s}) are consistent with those simple analogs such as :CH_2, :SiH_2, :GeH_2, :SnH_2, and :PbH_2 [28]. Plumbylenes with the largest valence orbitals and bond length (R_1) have more stable singlet states and a larger ΔG_{t-s}. A lower electronegativity for lead also increases the size of the AOs and lengthens the M—H bonds. Therefore, heavier atoms prefer to have nonbonding electrons in atomic orbitals with a higher percentage of s-character. The higher s-character of nonbonding electrons leads to an increase in the singlet–triplet splitting and stability of singlet state [27]. The electron–electron repulsion is diminished with the larger size of the lone pair orbital. Diminishing of the repulsion raises the stability for both the singlet and triplet states of C_4H_4M, C_4H_6M, and C_4H_8M from M = C to M = Pb. This stabilizing effect is more for the singlet state than the triplet state. The change order of singlet–triplet splitting (ΔG_{t-s}) is plumbylenes > stanylenes > germylenes > silylenes.



SCHEME 3 Two series isodesmic and/or homodesmic formal equations for stabilization energies (SE) estimation of C_4H_4M, C_4H_6M, and C_4H_8M (where M = C, Si, Ge, Sn, and Pb).

Singlet–triplet splitting (ΔG_{t-s}) is also compared along with three analogs C_4H_4M, C_4H_6M, and C_4H_8M. ΔG_{t-s} of C_5H_4 (9.598) is the maximum with respect to C_5H_6(−4.744) and C_5H_8 (−9.000) (Table 2). This order is attributed to the instability of the singlet state or the stability of triplet state for C_5H_4 with respect to C_5H_6 and C_5H_8. Moreover, except for M = C, the change order of ΔG_{t-s} with negative sign is $C_4H_6M > C_4H_8M > C_4H_4M$. This order is related to the stability of singlet state or the instability of triplet state for C_4H_6M with respect to C_4H_8M and C_4H_4M. Whether increasing the stability of the singlet state or increasing the instability of the triplet state responsible to increase ΔG_{t-s} is not known. Thus, various homodesmotic and/or isodesmic reactions are applied to determine the stability energies of the singlet and triplet states for C_4H_4M, C_4H_6M, and C_4H_8M [24]. These reaction schemes demand only equal numbers of formal single and double bonds in products and reactants. Systems with negative stability energies SE are most stable, whereas those with positive SE are unstable. Four series of homodesmotic and/or "isodesmic" reactions and relative SE energies are presented (Scheme 3 and Tables 3–6). Homodesmotic reactions (Eqs. (1a)–(1c)) are based on cyclic olefin and conjugated unsaturated analogs [24]. The homodesmotic reactions (Eq. (1)) are discussed in three possible forms (see Eqs. (1a)–(1c)) (Tables 3–5). The results of homodesmotic reaction energies of Eqs. (1a)–(1c) show the most stability for the singlet state of C_4H_6M with respect to C_4H_4M and C_4H_8M. The most stability of C_4H_6M shows an effective conjugation of one double bond with the carbonic center, whereas this conjugation is not occurred for two double bonds and/or for the lack of double bonds. On the other hands, the triplet state of C_4H_4M (except for M = C) is the most stable with respect to C_4H_6M and C_4H_8M. The stability for the triplet state of C_4H_4M is due to effective sharing of one electron of carbene center ($\sigma^1\pi^1$

TABLE 3 Stabilization Energies (SE) Estimation (kcal/mol) for Singlet (s) and Triplet (t) States of C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb) through the Homodesmotic Reaction (1a) at B3LYP/6-311++G (3df, 2p)

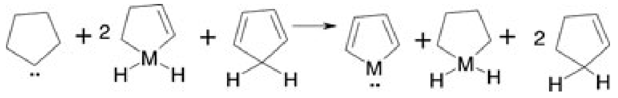
*Compound **1a***							*SE (kcal/mol)*
M = $C_{(s)}$	−195.1921	−195.3819	−194.1563	−192.7714	−196.5770	−195.3819	7.7
M = $Si_{(s)}$	−195.1921	−446.7880	−194.1563	−438.9282	−448.0177	−195.3819	−27.5
M = $Ge_{(s)}$	−195.1921	−2234.2692	−194.1563	−2231.7691	−2235.501	−195.3819	−47.2
M = $Sn_{(s)}$	−195.1921	−160.6150	−194.1563	−158.1427	−161.847	−195.3819	−71.4
M = $Pb_{(s)}$	−195.1921	−160.6731	−194.1563	−158.2384	−161.907	−195.3819	−84.2
M = $C_{(t)}$	−192.7872	−195.3819	−194.1563	−192.7872	−196.5770	−195.3819	−10.9
M = $Si_{(t)}$	−192.7872	−446.7880	−194.1563	−444.2307	−448.0177	−195.3819	−21.6
M = $Ge_{(t)}$	−192.7872	−2234.2692	−194.1563	−2231.7327	−2235.501	−195.3819	−33.4
M = $Sn_{(t)}$	−192.7872	−160.6150	−194.1563	−158.0995	−161.847	−195.3819	−54.4
M = $Pb_{(t)}$	−192.7872	−160.6731	−194.1563	−158.1931	−161.907	−195.3819	−65.9

TABLE 4 Stabilization Energies (SE) Estimation for Singlet (s) and Triplet (t) States of C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb) through the Homodesmotic Reaction (1b) at B3LYP/6-311++G (3df, 2p)

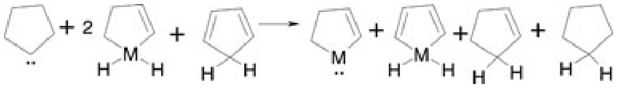
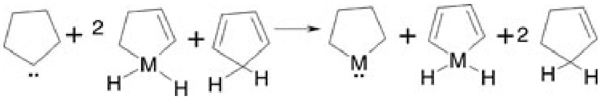
*Compound **1b***								*SE (kcal/mol)*
M = $C_{(s)}$	−195.1921	−195.3819	−194.1563	−193.9963	−194.1563	−195.3819	−196.5770	−6.8
M = $Si_{(s)}$	−195.1921	−446.7880	−194.1563	−445.4784	−445.5550	−195.3819	−196.5770	−35.8
M = $Ge_{(s)}$	−195.1921	−2234.2692	−194.1563	−2232.9911	−2233.0363	−195.3819	−196.5770	−53.6
M = $Sn_{(s)}$	−195.1921	−160.6150	−194.1563	−159.3603	−159.3827	−195.3819	−196.5770	−75.0
M = $Pb_{(s)}$	−195.1921	−160.6731	−194.1563	−159.3867	−159.4409	−195.3819	−196.5770	−84.5
M = $C_{(t)}$	−192.7872	−195.3819	−194.1563	−193.9894	−194.1563	−195.3819	−196.5770	−11.1
M = $Si_{(t)}$	−192.7872	−446.7880	−194.1563	−438.8939	−445.5550	−195.3819	−196.5770	−10.7
M = $Ge_{(t)}$	−192.7872	−2234.2692	−194.1563	−2232.9303	−2233.0363	−195.3819	−196.5770	−24.3
M = $Sn_{(t)}$	−192.7872	−160.6150	−194.1563	−159.3006	−159.3827	−195.3819	−196.5770	−46.3
M = $Pb_{(t)}$	−192.7872	−160.6731	−194.1563	−159.3891	−159.4409	−195.3819	−196.5770	−54.9

TABLE 5 Stabilization Energies (SE) Estimation for the Singlet (s) and Triplet (t) States of C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb) through the Homodesmic Reaction (1c) at B3LYP/6-311++G (3df, 2p)

*Compound **1c***							*SE (kcal/mol)*
M = $C_{(s)}$	−195.1921	−195.3819	−194.1563	−195.1590	−194.1563	−195.3819	0.0
M = $Si_{(s)}$	−195.1921	−446.7880	−194.1563	−446.6415	−445.5550	−195.3819	−30.8
M = $Ge_{(s)}$	−195.1921	−2234.2692	−194.1563	−2234.1540	−2233.0363	−195.3819	−49.2
M = $Sn_{(s)}$	−195.1921	−160.6150	−194.1563	−160.5229	−159.3827	−195.3819	−71.0
M = $Pb_{(s)}$	−195.1921	−160.6731	−194.1563	−160.6170	−159.4409	−195.3819	−82.5
M = $C_{(t)}$	−192.7872	−195.3819	−194.1563	−195.1447	−194.1563	−195.3819	0.0
M = $Si_{(t)}$	−192.7872	−446.7880	−194.1563	−446.5926	−445.5550	−195.3819	−8.7
M = $Ge_{(t)}$	−192.7872	−2234.2692	−194.1563	−2234.0997	−2233.0363	−195.3819	−24.1
M = $Sn_{(t)}$	−192.7872	−160.6150	−194.1563	−160.4718	−159.3827	−195.3819	−48.0
M = $Pb_{(t)}$	−192.7872	−160.6731	−194.1563	−160.5580	−159.4409	−195.3819	−55.4

($^3B_1$)) in the electron resonance of the ring rather than others. Therefore, the singlet state of C_4H_4M uses the configuration (σ^2 ($^1A_1$) for the carbenic center instead of π^2 ($^1B_1$) and is unable to the effectively share the ring and destabilizing the singlet state.

Equation (2a) measures the effect of the cyclic heterocarbene being conjugated with the π system

TABLE 6 Stabilization Energies (SE) Estimation (kcal/mol) for the Singlet (s) and Triplet (t) States of C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb) through Three Isodesmic Equations

	SE			
Compound	*Eq. (2a)*	*Eq. (2b)*	*Eq. (2c)*	*Eq. (2a) – Eq. (2b)*
M = $C_{(s)}$	0.0	0.0	4.2	0.0
M = $Si_{(s)}$	1.7	7.1	–	−5.4
M = $Ge_{(s)}$	0.9	6.1	–	−5.2
M = $Sn_{(s)}$	−1.3	7.2	–	−8.5
M = $Pb_{(s)}$	−1.7	6.4	–	−8.1
M = $C_{(t)}$	0.0	0.0	−4.9	0.0
M = $Si_{(t)}$	4.2	4.9	–	−0.7
M = $Ge_{(t)}$	8.3	7.1	–	1.2
M = $Sn_{(t)}$	11.5	12.5	–	−1.0
M = $Pb_{(t)}$	8.2	4.7	–	4.0

TABLE 7 Geometrical Parameter, Bond Length (degrees) for the Singlet (s) and Triplet (t) States of $C_4H_6MH_2$, C_4H_4M, C_4H_6M, and C_4H_8M (Where M = C, Si, Ge, Sn, and Pb) through Three Isodesmic Equations

	$C_4H_6MH_2$	*C_4H_4M:*	*C_4H_6M:*	*C_4H_6M:*
Compound	*=C—XH2*	*=C—X:*	*=C—X:*	*—HC—X:*
M = $C_{(s)}$	1.512	1.389	1.449	1.484
M = $Si_{(s)}$	1.512	1.426	1.380	1.487
M = $Ge_{(s)}$	1.868	1.930	1.885	1.926
M = $Sn_{(s)}$	1.868	1.838	1.840	1.930
M = $Pb_{(s)}$	1.950	2.260	1.976	2.028
M = $C_{(t)}$	1.950	1.938	1.940	2.040
M = $Si_{(t)}$	2.123	2.202	2.158	2.212
M = $Ge_{(t)}$	2.123	2.193	2.137	2.225
M = $Sn_{(t)}$	2.216	2.266	2.279	2.281
M = $Pb_{(t)}$	2.216	2.254	2.235	2.336

of the five-membered ring with respect to the cyclic heterocarbene (using as reference the corresponding stabilization in the C case) (Table 6). The stability of singlet state for C_4H_4M is generally increased from M = Si to M = Pb (Table 6). In contrast, stability of the triplet state for C_4H_4M is generally decreased from M = C to M = Pb (Table 6).

Equation (2b) measures the effect of the heterocarbene being cyclic and fully conjugated with respect to the acyclic heterocarbene (using as reference the corresponding stabilization in the C case). It seems that the acyclic heterocarbenes for both singlet and triplet states are energetically more stable than the heterocarbene being cyclic and fully conjugated of C_4H_4M.

The difference between Eqs. (2a) and (2b) is the "desire" of the heterocarbene to be (or not to be) part of a cyclic (a five-membered ring) structure (using as reference the C case). It appears that the cyclic heterocarbenes, C_4H_8M, for the singlet state are energetically less stable than C_4H_8C.

The "desire" of carbene to be cyclic or not cyclic can be estimated from the energy of the Eq. (2c). For the singlet state, the "desire" of carbene to be part of a five-membered ring (Eq. (2c)) as compared with the acyclic dimethylcarbene whereas for the triplet state, the five-membered carbene is less stable than an acyclic carbene.

From the difference of Eqs. (2a) and (2b) and the result of Eq. (2c), we can conclude that except for the singlet state of C_4H_8C, the other singlet state of heterocarbenes (in the form of C_4H_8M:, where M = Si, Ge, Sn, and Pb) prefers an acyclic structure. Also, the triplet state of heterocarbenes C_4H_8M: (where M = C, Si, Ge, Sn, and Pb) prefers an acyclic structure.

To discuss about a possible strong conjugation between M: and double bonds apart from the energetic criterion, the geometrical parameter is discussed (Table 7). 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 H2M—C=C compound). The bond length =C—C: for the triplet state and specially the singlet state of C_4H_4C: is shortest among the other analogs, showing the strongest conjugation between M: and an adjacent C=C bond. Surprisingly, the bond length =C—C: for the singlet state of C_4H_6Si: is shortest among the other analogs whereas the bond length =C—C: for the triplet state of C_4H_6Si: is near to the other analogs. The bond length =C—C: for both the triplet and singlet states of C_4H_6M: (where M = Ge, Sn, and Pb) is similar to each other.

CONCLUSION

The singlet and triplet splittings (ΔG_{t-s}) of C_4H_4M, C_4H_6M, and C_4H_8M (M = C, Si, Ge, Sn, and Pb) are calculated at B3LYP/6-311++G (3df,2p) level of theory. ΔG_{t-s} of C_5H_4 is the maximum with respect to $C_5H_6$and C_5H_8. However, the change order of ΔG_{t-s} is $C_4H_6M > C_4H_8M > C_4H_4M$. The homodesmotic reaction energy calculations indicate that the singlet state of C_4H_6M and the triplet state of C_4H_4M are the most stable with respect to other analogs.

SUPPLEMENTARY INFORMATION

Data related to XYZ coordinated of optimized structures, C_4H_4M, C_4H_6M, and C_4H_8M (M = C, Si, Ge, Sn, and Pb) and computed frequencies (from the vibrational analyses) (cm^{-1}) and IR intensity (KM/mol) for both singlet and triplet states of C_4H_4M are available from the first author (e_vesali@yahoo.com) on request.

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