Energetic Property and Aromaticity in various Divalent Carbenes Derivatives: DFT and NMR Studies

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ABSTRACT

All parameters optimization singlet and triplet states of divalent three, five and six membered rings in carbenes structures when M= C, Si, Ge and Sn studied by using DFT method in B3LYP level of theory and 6-311++G (d, p) basis set. For this purpose we calculated values enthalpy gaps, ΔHs-t: thermal energy gaps, ΔEs-t: Gibbs free energy gaps, ΔGs-t: between singlet (s) and triplet (t) states by using *GAUSSIAN 03W* package of program in above structures. Obtained results show by changes of M atom in C_2H_4M, C_4H_8M and $C_6H_{12}M$ structures value of ΔGs-t, ΔHs-t, ΔEs-t and other parameters will change. In final we calculated value relative energy, HOMO and LUMO energies, chemical hardness η, chemical potential μ, dipole moment (D), Electrophilicity (ω) and Maximum amount of electronic charge transfer $\Delta Nmax$.

Key Words: Singlet-Triplet state, Divalent three, five and six-membered rings, NBO.

INTRODUCTION

An intermediate is a molecular entity which is neither a reactant nor a product; rather, it is formed from reactants during a chemical reaction that produces a final product. Intermediates are not products of chemical reaction but are separable [1]. Carbenes are intermediates that appear in two states: singlet or triplet. Therefore, they are referred to as amphiprotic compounds [2]. They are produces as intermediate in many chemical reactions and have been the subject of extensive studies [3]. A wide range of theoretical and experimental studies was carried out to determine why these compounds are formed in reactions [4-6]. Two major types of Carbenes are Silylene and Germylene. Silylenes are produced through different mechanisms such as thermal decomposition, photochemical mechanisms in silicon hydrates and organosylanes. They are also key intermediates in CVD. Cyclopentadienyldene, a five-membered ring Carbene, is a cyclic conjugated compound found in interstellar medium. The stable state of the five-membered ring for the singlet structures Silylenes and Germylenes was first synthesized and identified by Denk *et al* [7] and

their properties were compared to those of other carbenes. Spin multiplicity of carbenes and the arrangements of spins are among determinant factors in carbene reactivity and activity [8]. The multiplicity plays a key role in energy ratio of pi and sigma orbital in base, singlet, and triplet states. In addition, properties of singlet and triplet Carbenes can be examined in terms of electrons and spatial characteristics. Theoretical studies by E. Vessally *et al* and M.Z. Kassaee *et al* show that changes in ring size and type of substituent play a key role in reactivity and activity of carbenes in base state [9-12]. Research has indicated that type of substituent (electron donor or acceptor) influence energy level and stability of Carbenes. This can be easily verified by examining perturbation orbital diagram. In fact, σ-electron-withdrawing substituents inductively stabilize the nonbonding orbital by increasing its S character. This increases σ-pπ gap, leading to formation of singlet state. In contrast, σ-electron-donating substituents induce a small σ-pπ gap which favors the triplet state [13].

Mesomeric effects may influence stability of Carbenes as well. Depending on being electron donor (*e.g.* halogens) or electron acceptor (*e.g.* alkyls), substituents in Carbenes affect stability through mesomeric effects. Energy in unoccupied pπ orbital in Carbenes with electron-donating substituent increases chemical activity of symmetric compounds with lone electron pair. When σ orbital is not stabilized it has almost no charge, leading to increased σ-pπ gap [14]. The present study used quantum mechanics computations and density function theory (DFT) to determine whether variations in ring size for singlet and triplet states, in addition to type of substituent, influence Carbene structures. For this purpose, different parameters such as energy levels, chemical potential, chemical hardness, Electrophilicity, HOMO-LUMO gap were examined along with changes in bond angles and bond lengths. In some studies, Electrophilicity has been used to estimate aromaticity of structures. In order to calculate Electrophilicity, first we should determine Chemical hardness and Chemical potential, which both depend on HOMO-LUMO levels. In fact any change in Electronegativity may change µ, electronic chemical potential. These

parameters were calculated using Equations (1) to (6), where I denotes ionization potential and A is electron affinity [15-20].

$$\mu = (\varepsilon_H + \varepsilon_L)/2 \qquad ...(1)$$

$$\eta = \varepsilon_L - \varepsilon_H \qquad ...(2)$$

$$\omega = \mu^2/2\eta = \div^2/2\eta \qquad ...(3)$$

$$\chi = -\mu = -(\delta_N/\delta_N)_{V(r)} \approx (I+A)/2 \approx -1/2\,(\varepsilon_{HOMO} + \varepsilon_{LUMO}) \qquad ...(4)$$

$$\eta = (\delta_{2E}/\delta_{N2})_{V(r)} = (I-A) \approx (\varepsilon_{LUMO} - \varepsilon_{HOMO}) \qquad ...(5)$$

$$\Delta N_{max} = -\mu/\eta \qquad ...(6)$$

Computational details

Density functional theory (DFT) calculations of divalent three, five and seven membered rings in Carbenes structures were conducted in which geometries, energies, Electrophilicity index, chemical hardness and chemical potential were obtained at the B3LYP/6-311++G(d,p) level [21]. However, for the Sn atom in different molecules, the calculations were carried out by using a LANL2DZ basis set and for Carbons and Hydrogens atoms in the same molecule, the 6-311++G (d, p) basis set was used [22, 23]. For all of structure, value of energy level are calculated self consistent field calculation used closed-shell (RB3LYP) for the singlet state and un restricted open-shell (UB3LYP) for the triplet state. Calculations of the independent chemical shifts (NICS) for various divalent three, five and seven membered rings structures were carried out using the gauge invariant atomic orbital (GIAO) approach in which NICS values were calculated at the centre (NICS(0)) and also at 1Å above the ring (NICS (1)) using GIAO-B3LYP/6-31++G (d, p) method [24, 25]. All calculations were conducted using *GAUSSIAN 03W* program package and obtained parameters are calculated in gas phase condition, 298 K temperature and 1 atm pressure [26].

RESULTS AND DISCUSSION

Prior to any discussion, it should be mentioned that we have carried out all required calculations and obtained parameters needed for discussion (Fig 1). For this purpose, we examined

several basic parameters such as energetic properties, Chemical potential, Chemical hardness, Electrophilicity, and Nuclear Magnetic Resonance (NMR).

Energetic properties

We first obtained thermal energy, enthalpy, and Gibbs free energy for each individual structure to calculate thermal energy gap, enthalpy gap, and Gibbs free energy gap for different cases. Results

found for thermal energy, enthalpy, and Gibbs free energy indicate that as the element M or ring size changes, energy levels change as well. As we know, thermodynamic quantities cannot be measured in absolute value; rather the variations (Δ) in the quantities should be measured. An increase in ΔG_{s-t} results in higher stability for singlet state (σ orbital) and reduces stability in triplet state (π orbital). Generally, stability can be determined based on ΔG_{s-t} for singlet and triplet states. In other

Table 1: Gibbs free energy, G (Kcal/mol), Gibbs free energy gaps, ΔGs-t (Kcal/mol), zero point vibrational energy, ZPVE (Kcal/mol) and dipole moments (Debye) for the singlet and triplet states of divalent three , five and seven membered rings at B3LYP/6-311++G (d, p) level of theory

Compound	M	G	ΔG_{s-t}	ZPVE	Dipole moment
3- membered ring	Singlet state				
	C	-72399.987	-51.2723	20.18030	3.4921
	Si	-230203.603	-77.1762	18.50829	0.9478
	Ge	-1351865.579	-85.3688	17.95828	0.5014
	Sn	-3792112.913	-62.0359	20.28143	1.6395
	Triplet state				
	C	-72348.715	-	16.49056	1.6622
	Si	-230126.427	-	14.62160	0.6385
	Ge	-1351780.210	-	13.36034	0.8277
	Sn	-3792050.877	-	18.26155	1.4837
5-membered ring	Singlet state				
	C	-120964.110	9.8304	41.16717	1.0240
	Si	-278769.152	-14.4218	39.75111	1.5607
	Ge	-1400435.046	-22.8033	39.42524	0.9196
	Sn	-3840712.150	-9.6158	42.79679	1.5637
	Triplet state				
	C	-120973.940	-	41.86836	0.9326
	Si	-278754.730	-	40.17282	0.1641
	Ge	-1400412.243	-	39.42306	0.1029
	Sn	-3840702.534	-	41.46413	0.1233
7-membered ring	Singlet state				
	C	-169575.990	-19.6194	64.66343	1.2502
	Si	-327347.319	-29.5427	62.35140	3.1815
	Ge	-1449009.782	-37.4642	61.75189	2.4569
	Sn	-3889306.078	-22.5799	65.22605	3.3134
	Triplet state				
	C	-169556.371	-	62.12689	0.7446
	Si	-327317.776	-	60.92402	0.4088
	Ge	-1448972.318	-	60.81023	0.8743
	Sn	-3889283.498	-	65.68332	1.2634

words, in singlet state, stability is improved when M is substituted with these atoms: Ge> Si> Sn> C. However, ring size has different effects on energy level. Stability of singlet state varies as follows based on ring size: 3-membered ring> 7-membered ring> 5-membered ring (Tables 1 and 2) Similar results were found for other energy levels, such as enthalpy and thermal energy.

Nucleus independent chemical shifts (NICS) indices

NICS indicates a type of chemical shift which is directly associated with aromaticity. The more negative is this value, the more aromatic a compound is expected to be. NICS was measured at ring center, one angstrom above the center, and two angstrom above the center, as reported in Table 3 (Fig 2 to 4).

Table 2: Enthalpy, H (Kcal/mol), thermal energy, E (Kcal/mol), enthalpy gaps, ΔHs-t (Kcal/mol) and thermal energy gaps, ΔEs-t (Kcal/mol) for the singlet and triplet states of divalent three, five and seven membered rings at B3LYP/6-311++G (d, p) level of theory

Compound	M	H	E	ΔH_{s-t}	ΔE_{s-t}
3- membered ring	Singlet state				
	C	-72382.733	-72383.325	52.0059	52.0059
	Si	-230185.370	-230185.962	77.9769	77.9769
	Ge	-1351846.419	-1351847.012	85.9154	85.9154
	Sn	-3792093.770	-3792094.363	62.8987	62.8987
	Triplet state				
	C	-72330.727	-72331.319	-	-
	Si	-230107.393	-230107.985	-	-
	Ge	-1351760.504	-1351761.096	-	-
	Sn	-3792030.871	-3792031.464	-	-
5-membered ring	Singlet state				
	C	-120944.673	-120945.266	-8.9845	-8.9839
	Si	-278748.675	-278749.268	15.1585	15.1578
	Ge	-1400412.738	-1400413.330	22.6383	22.6383
	Sn	-3840690.762	-3840691.355	10.4861	10.4867
	Triplet state				
	C	-120953.658	-120954.250	-	-
	Si	-278733.517	-278734.110	-	-
	Ge	-1400390.100	-1400390.692	-	-
	Sn	-3840680.276	-3840680.869	-	-
7-membered ring	Singlet state				
	C	-169553.931	-169554.523	20.7539	20.7539
	Si	-327323.286	-327323.879	29.9694	29.9700
	Ge	-1448984.861	-1449009.782	38.1350	62.4644
	Sn	-3889282.001	-3889282.594	24.9939	25.6164
	Triplet state				
	C	-169533.177	-169533.769	-	-
	Si	-327293.317	-327293.909	-	-
	Ge	-1448946.725	-1448947.318	-	-
	Sn	-3889257.007	-3889256.977	-	-

NICS in three membered ring

NICS values for 3-membered rings indicate that NICS(0) and NICS(1) for singlet state and NICS(2) for triplet state follow the order Si> C> Ge> Si. However, NICS(2) for singlet state and NICS(0) for triplet state show different trends. In this case, changes in aromaticity can be ordered as Sn> Ge> Si> C. NICS(1) for triplet state represent the order Si> Sn> Ge> C. This shows that the highest level of aromaticity is achieved (the most negative

NICS is observed) when M is substituted with Si (Table 3).

NICS in five membered ring

A different trend was observed for five and six-membered rings. The orders observed for aromaticity in singlet state in NICS(0) and NICS(1) were C> Si> Sn> Ge and Si> C> Ge> Sn, respectively. The order found for NICS(2) was Sn> Si> Ge> C. However, NICS values found for triplet

Table 3. Nucleic independent chemical shifts (NICS) ppm, were carried out using the gauge invariant atomic orbital (GIAO) for the singlet and triplet states of divalent three, five and seven membered rings at B3LYP/6-311++G (d, p) level of theory

Compound	M	NICS(0)	NICS(1)	NICS(2)
3- membered ring	Singlet state			
	C	-30.5926	-21.7357	-10.4315
	Si	-12.4494	-18.9520	-11.9475
	Ge	-29.7748	-19.7659	-13.9157
	Sn	-80.8433	-32.1239	-17.5721
	Triplet state			
	C	-20.7604	-11.2080	-3.4286
	Si	-31.6946	-16.4606	-1.2241
	Ge	-57.2664	-14.6836	-2.4658
	Sn	-113.5339	-15.3631	-5.0354
5-membered ring	Singlet state			
	C	-45.1691	-26.2162	-1.4794
	Si	-37.0825	-29.3654	-5.4469
	Ge	-30.3250	-24.3309	-3.8170
	Sn	-36.1966	-16.1279	-12.9061
	Triplet state			
	C	-38.4954	-19.8261	-1.4947
	Si	-16.2150	-2.0361	-7.6837
	Ge	-14.9109	-2.0706	-9.5110
	Sn	-37.0216	-14.0482	-11.1830
7-membered ring	Singlet state			
	C	-2.6009	-10.6652	-11.5608
	Si	-5.7278	-14.9630	-13.4699
	Ge	-3.2827	-13.5845	-13.5061
	Sn	-11.0090	-14.7214	-15.0400
	Triplet state			
	C	-69.4983	-50.9039	-20.0842
	Si	-45.8468	-33.9914	-15.1718
	Ge	-33.5077	-28.9980	-11.2562
	Sn	-35.6734	-39.5311	-16.0442

5-membered ring were different from those of singlet state. For NICS(0), aromaticity can be ordered as C> Sn> Si> Ge and for NICS(1), we have C> Sn> Ge> Si. The order found for NICS(2) is Sn>Ge>Si>C. This shows an increase in aromaticity as M is substituted with Sn (Table 3).

NICS in seven membered ring

A different trend was found for 7-membered rings compared to 3- and 5-membered rings. In singlet state, the orders found in aromaticity

for NICS(0) and NICS(1) were Sn> Si> Ge> C and Si> Sn> Ge> C, respectively. In singlet state, for NICS(2) we have Sn> Ge> Si> C indicating variation in aromaticity as M is replaced with other atoms. In triplet state, armoaticity for NICS(0) is in the order C> Si> Sn> Ge. The order found for both NICS(1) and NICS(2) was C> Sn> Si> Ge (Table 3).

NICS compared in different state

Two major factors contribute to NICS values: atomic radius which is a measure of volumes

Table 4: HOMO (eV), LUMO (eV), Chemical hardness, eV (η), Chemical potential, eV (μ), Electrophilicity (ω) and maximum amount of electronic charge transfer (ΔN_{max}), in atomic units, for the singlet and triplet states of divalent three, five and seven membered rings at B3LYP/6-311++G (d, p) level of theory

Compound	M	HOMO	LUMO	μ	η	ω	ΔN_{max}
3- membered	Singlet state						
ring	C	-0.24283	-0.04850	-0.14566	0.19433	0.05459	0.74957
	Si	-0.25528	-0.06546	-0.16037	0.18982	0.06774	0.84485
	Ge	-0.24399	-0.07292	-0.15845	0.17107	0.07338	0.92625
	Sn	-0.22132	-0.06149	-0.14140	0.15983	0.06255	0.88472
	Triplet state						
	C	-0.16814	-0.01756	-0.09285	0.15058	0.02862	0.61661
	Si	-0.15306	-0.06232	-0.10769	0.09074	0.06390	1.18679
	Ge	-0.14876	-0.06922	-0.10899	0.07954	0.07467	1.37025
	Sn	-0.15557	-0.06120	-0.10838	0.09437	0.06224	1.14851
5-membered	Singlet state						
ring	C	-0.23496	-0.12187	-0.17841	0.11309	0.14073	1.57763
	Si	-0.22634	-0.12986	-0.17810	0.09648	0.16438	1.84597
	Ge	-0.23096	-0.12673	-0.17884	0.10423	0.15343	1.71586
	Sn	-0.20576	-0.09135	-0.14855	0.11441	0.09644	1.29844
	Triplet state						
	C	-0.23961	0.01053	-0.11454	0.25014	0.02622	0.45790
	Si	-0.19540	-0.01602	-0.10571	0.17938	0.03114	0.58930
	Ge	-0.18859	-0.02062	-0.10460	0.16797	0.03257	0.62276
	Sn	-0.19405	-0.00799	-0.10102	0.18606	0.02742	0.54294
7-membered	Singlet state						
ring	C	-0.22143	-0.05484	-0.13813	0.16659	0.05727	0.82919
	Si	-0.21177	-0.09296	-0.15236	0.11881	0.09769	1.28242
	Ge	-0.22039	-0.08897	-0.15468	0.13142	0.09102	1.17699
	Sn	-0.18993	-0.09023	-0.14008	0.09970	0.09840	1.40501
	Triplet state						
	C	-0.15579	-0.08108	-0.11843	0.07471	0.09387	1.58526
	Si	-0.15705	-0.08552	-0.12128	0.07153	0.10282	1.69558
	Ge	-0.15275	-0.07772	-0.11523	0.07503	0.08849	1.53585
	Sn	-0.14910	-0.07310	-0.11109	0.07598	0.08120	1.46209
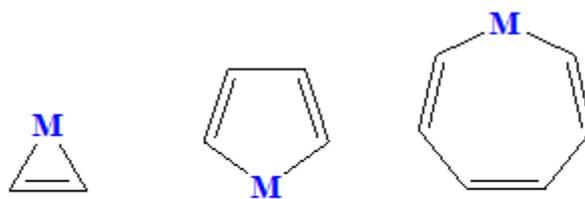
M= C, Si, Ge and Sn

Fig. 1: Show divalent three, five and seven membered ring structures
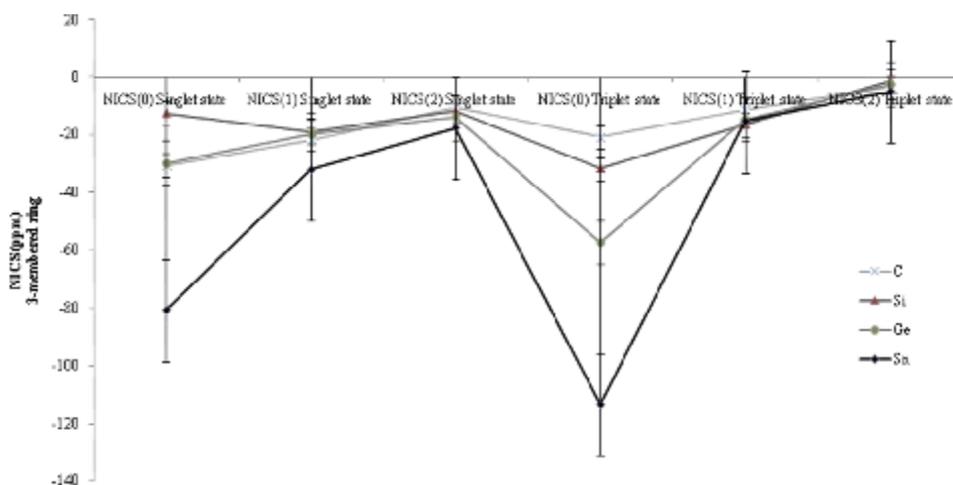
Fig. 2: Plot of NICS(0) ppm, NICS(1) ppm, NICS(2) ppm for divalent 3-membered ring Carbene structure with M= C, Si, Ge and Sn at B3LYP/6-311++G (d, p) level of theory
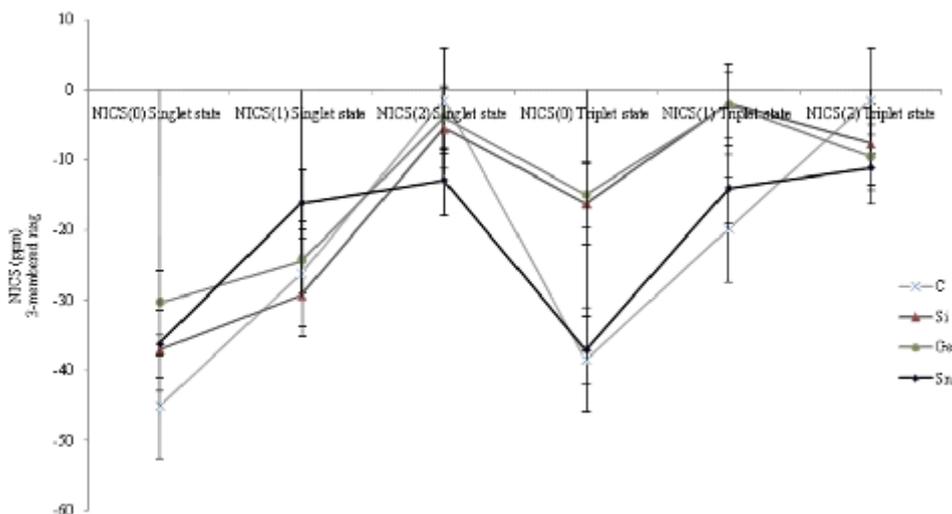
Fig. 3: Plot of NICS(0) ppm, NICS(1) ppm, NICS(2) ppm for divalent 5-membered ring Carbene structure with M= C, Si, Ge and Sn at B3LYP/6-311++G (d, p) level of theory
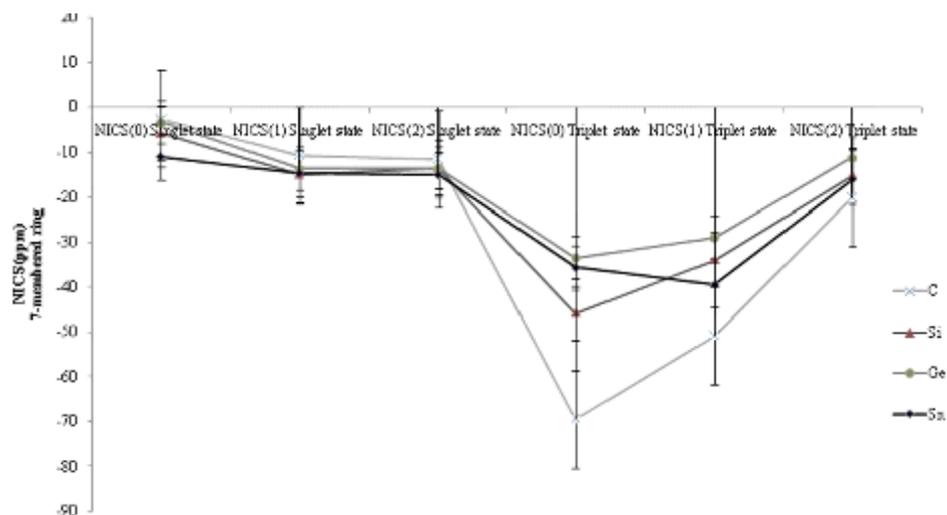
Fig. 4: Plot of NICS(0) ppm, NICS(1) ppm, NICS(2) ppm for divalent 7-membered ring Carbene structure with M= C, Si, Ge and Sn at B3LYP/6-311++G (d, p) level of theory

$\left(\text{M}\right)$ = C , Si , Ge and Sn
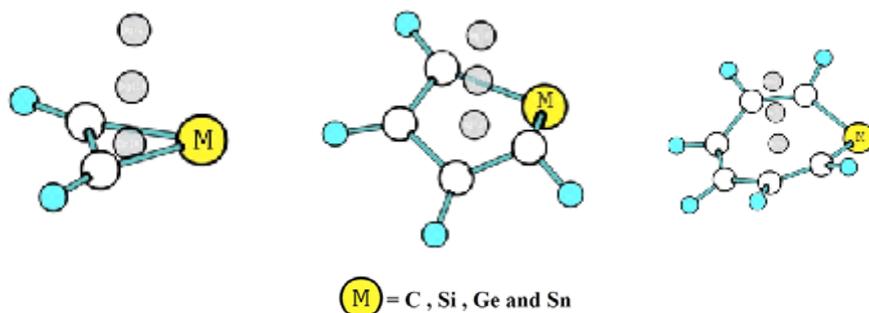
Fig. 5: Definition of points at which the NICS values were calculated
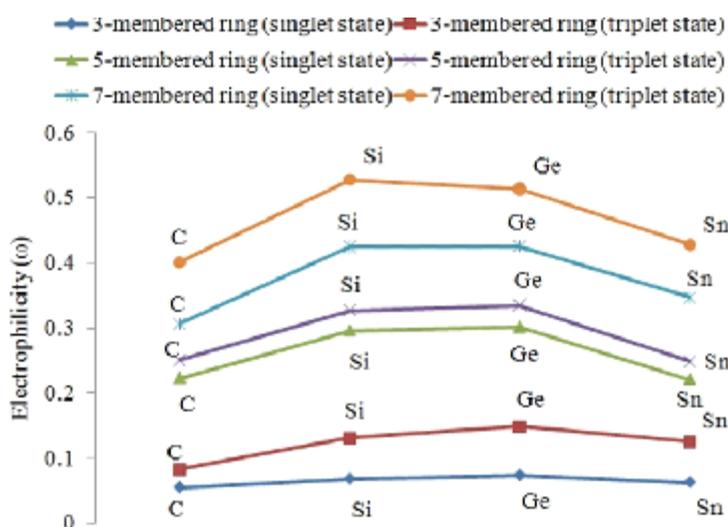
Fig. 6: Compared obtained results for Electrophilicity in various Carbenes structures

of M; and ring size whose small values results in more negative NICS values. In addition, the larger or heavier is M, the more negative will be NICS value (*e.g.* NICS(0) in 3-membered ring when M is substituted with Sn in singlet or triplet state) since a larger shift will be observed at the point where NICS is measured. Comparing NICS values for the three types of ring, the following order was found for negative values of NICS: 3-membered ring> 7-membered ring> 5-membered ring (Fig 5).

Electrophilicity indices

Our findings suggest that ring size influences HOMO-LUMO-related parameters such as Chemical hardness, Chemical potential, Electrophilicity, and the largest amount of charge transferred by electrons. It should be mentioned that different results were found for singlet state compared to triplet state. Chemical hardness and chemical potential vary as electrophilicity changes. For singlet state in 3-membered ring, the increase in Electrophilicity can be ordered as Si> Ge> C> Sn. The order for the triplet state is C> Sn> Si> Ge. For singlet and triplet states in 5-membered ring we have C> Ge> Si> Sn and C> Si> Sn> Ge, respectively (Fig 6). Electrophilicity follows a slightly different order for 7-memebred ring. For singlet state, we have C> Ge> Si> Sn while for triplet state, Si> C> Ge> Sn. An investigation of ascending order of Electrophilicity shows that Electrophilicity decreases as the ring grows in size. In other words, Electrophilicity is larger in 3-membered ring compared to 5- and 7-membered rings (Table 4).

CONCLUSIONS

Quantum mechanics computations using DFT indicated changes in Electrophilicity, energetic levels, and HOMO-LUMO values as we shift from singlet state to triplet state. An increase in $\Delta G_{s\text{-}t}$ improves stability in singlet state and decreases stability in triplet state. NICS values showed that aromaticity in 3-membered ring is higher compared to 5- and 7-membered rings. In addition, ring size influence thermodynamic parameters as well as those parameters associated with HOMO-LUMO levels. Our results also suggest nearly the same levels of aromaticity and the almost the same values of $\Delta G_{s\text{-}t}$ for carbenes with different ring sizes. One may argue that increased aromaticity lowers the level of $\Delta G_{s\text{-}t}$, resulting in improved stability for singlet state.

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